

Sulfur: New Sources and Uses

Publication Date: March 29, 1982 | doi: 10.1021/bk-1982-0183.fw001

Sulfur: New Sources and Uses

Michael E. D. Raymont, EDITOR
*Sulphur Development Institute of
Canada (SUDIC)*

Based on a symposium jointly
sponsored by the Divisions of
Petroleum Chemistry and Industrial
and Engineering Chemistry
at the 181st ACS National Meeting,
Atlanta, Georgia,
April 2-3, 1981.

A C S S Y M P O S I U M S E R I E S **183**

AMERICAN CHEMICAL SOCIETY
WASHINGTON, D.C. 1982

ACS Symposium Series

M. Joan Comstock, *Series Editor*

Advisory Board

David L. Allara	Marvin Margoshes
Robert Baker	Robert Ory
Donald D. Dollberg	Leon Petrakis
Robert E. Feeney	Theodore Provder
Brian M. Harney	Charles N. Satterfield
W. Jeffrey Howe	Dennis Schuetzle
James D. Idol, Jr.	Davis L. Temple, Jr.
Herbert D. Kaesz	Gunter Zweig

FOREWORD

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the Series parallels that of the continuing ADVANCES IN CHEMISTRY SERIES except that in order to save time the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. Papers are reviewed under the supervision of the Editors with the assistance of the Series Advisory Board and are selected to maintain the integrity of the symposia; however, verbatim reproductions of previously published papers are not accepted. Both reviews and reports of research are acceptable since symposia may embrace both types of presentation.

PREFACE

During the late 1960's and 1970's free world production and consumption of sulfur have changed significantly, especially in North America. Because of the very nature of sulfur sources and uses, the future holds the potential for some major shifts in the traditional patterns. In the spring of 1981 a Sulfur Symposium held as part of the 181st Annual ACS Meeting in Atlanta attempted to review the potential for new sulfur production and utilization (traditional production and consumption technology was not addressed), and this volume is based on the papers presented.

On the supply side, sulfur production is now controlled more by the demand for energy through the desulfurization of fuels than by the demand for sulfur per se, and this tendency is increasing. In 1965 involuntary by-product recovered sulfur amounted to less than 20% of total elemental sulfur production in the United States and Canada, but by 1980 over 60% of all elemental sulfur resulted from refinery and natural gas processing operations. Many future hydrocarbon energy sources (coal, deep gas, heavy oil, shale, etc.) contain considerably more sulfur compared with conventional hydrocarbon fuels, and thus their exploitation will add to the ever increasing supply of "by-product" sulfur.

On the demand side, consumption has experienced less noticeable shifting of traditional patterns, but environmental restrictions, new process developments, and world economics have all imposed some alterations on end uses. In addition to these changes, recent political difficulties have adversely affected some of the major world suppliers of sulfur. Clearly, the balance between sulfur supply and demand, which has traditionally been somewhat variable, is now more unstable because the potential exists for major shifts in supply/demand patterns.

Because it is inevitable that new energy sources will have the greatest impact on sulfur supply, the majority of the papers in this symposium address the questions of the potential and problems of sulfur production from fuel desulfurization of deep sour gas, heavy oil, tar sands, coal, and oil shales. The chapters cover a variety of topics from the production, handling and processing of sulfur-bearing process streams to estimates of future sulfur production from new energy sources, and thus provide an insight into the emerging technology of new sulfur production and its supply potential.

Because of predictions and realities of excess sulfur production, a significant amount of research has been devoted towards finding new uses for elemental sulfur. Spearheaded by the U.S. Bureau of Mines and the Sulphur Development Institute of Canada (SUDIC), this research has focused on finding potential large volume uses for sulfur that take advantage of its unique properties resulting in genuinely useful new materials rather than "throw away uses." Principal among these new products are sulfur asphalts and sulfur concretes. Although this brief symposium cannot cover all the advances in these fields, the new use chapters summarize the current state of the art and review recent attempts at commercial developments of these technologies. In this respect, these papers update the laboratory and pilot plant research on new sulfur uses described in two earlier ACS volumes (Advances in Chemistry Series No. 140 and 165).

Finally, I am very grateful to all the authors for their contributions, and to the symposium attendees who demonstrated the strong interest and enthusiasm that exists in the whole field of sulfur chemistry. I hope this volume will be both of use to, and an encouragement to researchers and practitioners in the field.

MICHAEL E. D. RAYMONT
Sulphur Development Institute of Canada (SUDIC)
Calgary, Alberta, Canada

October 5, 1981

New Sulfur Sources in the United States

MICHAEL RIEBER

University of Arizona, College of Mines, Tucson, AZ 85721

The production of domestic sulfur values (elemental recovered sulfur and the sulfur content of acid) will total about 18 million long tons per year by the year 2000. By region (Petroleum Administration for Defense districts), except for the east coast (PAD I), there will be no deficit areas in the U. S. Major contributors are sour natural gas and the refining of heavier, sour, crude oil. Proximate, scenario dependent sources, are electric utilities and coal-based synfuels. Shale oil, domestic tar sands and heavy oil, and unconventional sources of natural gas will be small suppliers. Each of the sulfur sources is examined with respect to scenario, location, and time frame. An estimate range is provided.

Energy demand, the implementation of sulfur oxide pollution controls, and the future commercialization of coal gasification and liquefaction have increased the potential for the development of considerable supplies of sulfur and sulfuric acid as a result of abatement, desulfurization and conversion processes. Lesser potential sources include shale oil, domestic tar sands and heavy oil, and unconventional sources of natural gas. Current supply sources of saleable sulfur values include refineries, sour natural gas processing and smelting operations. To this, Frasch sulfur production must be added.

Recovered sulfur supply predictions depend on explicit assumptions or scenarios concerning the development of specific fuels and the production of sulfide ores. They also depend on a second set of assumptions with respect to sulfur pollution control regulations, the means by which these will be met, and the recursive impact of the controls on the production scenarios. For example, given uncertainties surrounding regenerative flue gas desulfurization (FGD) processes, including the sale of sulfur products and concern over process reliability, utilities have been emphasizing throw-away techniques. As new control standards are implemented the disposal

0097-6156/82/0183-0001\$05.00/0
© 1982 American Chemical Society

problem will grow. The choice between the adoption of a process which produces a saleable output and one which produces a waste product will eventually depend on the relative costs and the expected value of the products. Additionally, while it may be technically feasible to meet smelter SO₂ regulations, it is conceivable that smelters and, possibly, mines will close reducing, rather than increasing, forecasts of acid production as regulations are implemented and/or tightened.

The present paper is based on the author's study (1) funded by the U. S. Bureau of Mines which, however, is not responsible for the views expressed or the conclusions reached. The time element has been subdivided into three discrete points and a period. The points include current output levels, for use as a base line, 1985 and 1990. The period encompasses the decade from 1990. This reflects the increasing unreliability of the estimates as the projection is extended. Because sulfur markets tend to be discrete and sulfur sources tend to be geographically differentiated regional supply projections are required. The definition chosen here is the Petroleum Administration for Defense districts. [These are defined as: I - Connecticut, Delaware, District of Columbia, Florida, Georgia, Maine, Maryland, Massachusetts, New Hampshire, New Jersey, New York, North Carolina, Pennsylvania, Rhode Island, South Carolina, Vermont, Virginia, and West Virginia. II - Illinois, Indiana, Iowa, Kansas, Kentucky, Michigan, Minnesota, Missouri, Nebraska, North Dakota, Ohio, Oklahoma, South Dakota, Tennessee, and Wisconsin. III - Alabama, Arkansas, Louisiana, Mississippi, New Mexico, and Texas. IV - Colorado, Idaho, Montana, Utah, and Wyoming. V - Alaska, Arizona, California, Hawaii, Nevada, Oregon, and Washington.] The justification is that for the next decade at least oil and gas are likely to continue as the primary sources of domestic recovered sulfur. Second, the inclusion of Arizona and Nevada in PAD district V roughly corresponds with the present market for acid production from copper smelters. Third, as the districts are established on the basis of an aggregation of states, data compilation is simplified. And fourth, as the districts have been defined a priori they were not based on present expository requirements.

Existing Sulfur Sources

Frasch Sulfur. Based on an analysis by Manderson (2), if a few limiting assumptions are made, the U. S. Frasch future is easily sketched. (1) No additional mines are opened. (2) Previously closed mines prove too costly to reopen. (3) Increasing costs due either to fuel prices or to increasing water requirements are not sufficient to force any more mine closures. (4) Existing production rates are maintained to the end of mine life. Then, if it is assumed that currently proposed mines are brought into production, output capacity in 1980 is at 6.86 million long tons (MMLT), increasing to 8.63 MMLT by 1985. By 1990, output capacity falls to 5.55 MMLT and to 2.25 MMLT by 1995. There is no output after 1997.

While the new mines increase mid-term supplies, they do not extend industry life. Ceteris paribus, as fuel prices rise, mines with high water ratios are apt to close unless some form of hydrodynamic mining can be introduced (3). If normal depletion curves are used rather than constant production rates, Frasch industry life is extended but at the cost of lower short and mid-term production. Based on data supplied by producers and the Bureau of Mines, production in 1979 was reported at 6.26 MMLT and estimated at 7.2 MMLT for 1980 (4). Current industry capacity, corrected for past mine closures, is estimated at 8.5 MMLT/Y (5).

Output of recovered sulfur and acid, unlike Frasch sulfur, depends almost entirely on the demand for the primary product. Recovered sulfur values therefore provide the basic market supply which serves to limit the market remaining to the discretionary production of Frasch sulfur. The Frasch portion of the industry is seen as passive and reactive. Its competitive implements are inventories, capacity utilization, and mine openings or closure. Its market share may diminish due to increased production of domestic abatement and process sulfur. It may also be reduced as the production of recovered sulfur and/or phosphatic fertilizer in the rest of the world increases, possibly backing out U. S. fertilizer exports but almost certainly backing out U. S., Canadian, and Mexican sulfur exports due to transport costs. The latter two are likely to turn toward the U. S. market. Sulfur imports in 1979 were 2.5 MM metric tons; virtually all were evenly divided between Canada and Mexico (6). As the former is natural gas based, it will be aided by increasing energy costs; it need not be deterred by falling sulfur prices. In the absence of tariffs or embargos, Mexican sulfur is highly competitive. Recent developments in dry sulfur forming (prills, granules, etc.) might make the Tampa market available to Canadian recovered sulfur sources. Ocean charter rates plus Vancouver sulfur prices are unlikely to equal present sulfur prices in Tampa.

The stakes in the Tampa market may be described by observing that in 1977, sulfur shipments into the market were at the rate of 3.4 MMLT/Y, employing 7 tankers, and 17 storage tanks with an aggregate capacity of about 270,000 LT (7). As large shipments of dry bulk sulfur are handled elsewhere in the U. S. (8, 9, 10), the Tampa environmental issue must be regarded as site specific.

The ability of the U. S. Frasch industry to fly-wheel domestic supply and demand in the short-run depends on its current inventories and capacity utilization. In the mid-term, mines may be opened or closed based on perceived long-term market equilibria. Long-term, however, in the absence of a significant successful exploration program, Frasch sulfur is a depleting resource. As the peak-load, rather than base-load, producer its minimum price is that which will cover the costs of the incremental mine. Its actual price will represent supply-demand equilibrium in world markets. To the extent that the Tampa market is protected, somewhat higher delivered prices may be levied. It may be argued that current

prices represent a conglomerate of short-run structural problems rather than a long-run supply-demand imbalance at current prices.

Finally, the Frasch industry, both domestic and Mexican, distributes its U. S. sulfur through an extensive system of liquid sulfur terminals located in major consuming regions. For practical purposes these define the Frasch sulfur market. With the exception of facilities in St. Louis and El Dorado, Arkansas, no terminals are located west of the Mississippi.

Refineries and Sour Natural Gas. Sulfur recovered from refineries and gas processing plants is a by-product. Its production is mandated by process requirements, product specification, and pollution control regulations. Its presence as an input has been a negative factor in the initial investment decision. Costing the sulfur production, while arbitrary as is the case for any joint product, may be useful for tax, income, and anti-air pollution control purposes. As there is no evidence of large scale domestic stockpiling, it need not be assumed that sale price necessarily covers assigned costs. If the primary product is produced, the sulfur will be produced in any event. Costing of recovered sulfur imports may also be useful for Tariff Commission proceedings, but the same principles should apply. It may be noted that the application of such cost analyses to the domestic industry is virtually absent. The competitive issues, even if they existed, could not be used to counter the domestic competition of recovered sulfur to Frasch sulfur. For practical purposes recovered sulfur costing includes transportation and handling and/or processing from vatted storage where the latter is applicable.

In 1978, U. S. recovered sulfur production and shipments were balanced at 4.1 MM metric tons each (11). Year end capacity has been estimated at 6.2 MMLT and 6.4 MMLT for 1980 and 1985, respectively (12, 13). Assignable daily capacity at year end 1978 was 9,132 metric tons for refineries, 5,464 metric tons for natural gas processing plants, and 1,682 metric tons from H_2S and acid gas (14).

Refinery Sulfur Production. By PAD district, approximate annual refinery sulfur production in 1978, assuming a 330 day operating year, was 310,000 LT in district I; 524,000 LT in district II; 993,000 LT in district III; 59,000 LT in district IV; and 856,000 LT in district V (15). Increases in refinery sulfur output will be occasioned by the worldwide shift towards the trading of more high-sulfur, heavier, crudes. In general, this means that the additional sulfur will become available on the west, east, and Gulf coasts where the imported crudes are actually refined. In 1975, the average crude refined in the U. S. was 35.2° API and contained .73% sulfur by weight [S(wt)]. By 1990, it is anticipated that the averages will be 34.75° API and 1.0% S (wt). This includes some small shift to coal-based syncrude (16). The shift to higher sulfur crudes has been worldwide. In the U. S., about 42 percent of

the reserves are low sulfur. As additional sulfur production is a concomitant of both sulfur in the crude oil and the severity of desulfurization, estimates of both are relevant. One such estimate suggests that U. S. high sulfur crude throughput ($> .5\%$ S wt) will be 8.9 million barrels per day (MMBD) by 1990 or 53 percent of the total. In 1976, it was 5 MMBD or 37 percent.

On the refinery side, distillate oil desulfurization will come from vacuum gas-oil desulfurization, catalytic cracker feed pretreatment and straight run hydrotreating. More importantly, residual oil desulfurization is expected to be extended to the entire fraction above 650° F rather than just the 650° F - 1000° F vacuum gas-oil with the rest going to coke or asphalt. Residual oil desulfurization capacity in 1978 was 110,000 barrels per calendar day (bbl/CD) with 130,000 bbl/CD under construction. This was expected to total 600,000 bbl/CD by 1985 and 800,000 bbl/CD by 1990, but the latter could be higher if the nuclear power program is further delayed (17). Given increasing fuel prices, however, it is possible that all of the predicted outputs will in fact be smaller as total energy forecasts are reduced including those of petroleum products.

Much of the sulfur contained in a crude oil remains with the tar, asphalt or coke after refining. As crude prices rise, even this residuum becomes valuable as a feedstock for cracking to make lighter products. This involves deep desulfurization. Whether the coke is burned as a fuel or used for anodes, desulfurization will take place before or after combustion or processing. Sulfur removal from coke plants is a currently feasible process.

Table I presents a refinery sulfur recovery capacity forecast made by the National Petroleum Council (NPC). The top portion of the table represents the initial conditions based on current crude input and refinery product slates; the bottom indicates additional capacity required for each of three, non-additive, scenarios. As the NPC study shows that sulfur production, as a percent of capacity, in 1982 is expected to be 60% in district I, 54% in district II, 71% in district III, 72% in district IV, and 49% in district V (18), the 1982 projections may well be extended to 1985. To 1990, this may be coupled with the light, high sulfur crude input scenario both because this implies the minimum refinery shift and because it reduces crude oil production shifts. Subsequently, the heavy, high sulfur, crude input scenario appears to be the more likely as world reserves of lighter crudes are preferentially depleted. Given current energy programs and domestic depletion, overall refinery crude oil capacity may not rise much over the period.

Natural Gas Processing. In 1978, based on a 330 day operating year, sulfur output from natural gas processing plants was estimated at: 276,000 LT in district I; 30,000 LT in district II; 1.0 MMLT in district III; and 59,000 LT in district IV (15). Projections, however, must be based on the depletion of current reserves, anticipated new additions to reserves, and the probable

TABLE I
ANTICIPATED REFINERY SULFUR RECOVERY CAPACITY

	PAD DISTRICT					Total
	I	II	III	IV	V	
<u>January 1, 1979</u> ⁽¹⁾						
Crude Oil Capacity (MBD)	1457	3163	5855	296	2212	12983
Refineries (No.)	10	30	32	7	19	98
Sulfur Recovery (LT/CD)	1525	2546	4812	186	3464	12533
<u>January 1, 1980</u> ⁽²⁾						
Crude Oil Capacity (MBD)	1451	3333	6194	303	2323	13604
Refineries (No.)	10	31	36	7	22	106
Sulfur Recovery (LT/CD)	1621	2559	5088	204	3524	12996
<u>January 1, 1982</u> ⁽³⁾						
Crude Oil Capacity (MBD)	1489	3564	7052	307	2430	14842
Refineries (No.)	10	33	39	7	24	113
Sulfur Recovery (LT/CD)	1711	3095	5749	204	3594	14353
Additional Sulfur Processing Capacity ⁽⁴⁾ Needed, for Given Scenarios, Beyond Those Committed Prior to January 1, 1982.						
(Scenario)	(LT/CD)					
Light, High Sulfur, Crude ⁽⁵⁾	388	1115	2578	36	410	4527
Heavy, High Sulfur, Crude ⁽⁶⁾	540	1475	3482	54	726	6277
Heavy Fuel Oil ⁽⁷⁾	169	348	581	47	206	1351

Source: National Petroleum Council. "Refinery Flexibility: An Interim Report"; National Petroleum Council: Washington, D. C., December 1979; Volume I.

MBD: thousand barrels per day
LT/CD: long tons per calendar day

- (1) Table C.4.1.1, p. C-25
 (2) Table C.4.1.2, p. C-30
 (3) Table C.4.1.3, p. C-35
 (4) Sulfur plant and tail gas cleanup
 (5) Table 59, p. 131
 (6) Table 60, p. 132
 (7) Table 94, p. 183

sulfur content of the additions. Projections are not made easier by a regulatory history which has served to both reduce exploration and production incentives and to skew past domestic production away from sour gas.

U. S. resources of conventional natural gas (excluding Alaska) have been estimated at 186 trillion cubic feet (TCF) in the probable category and 359 TCF in the possible category (19). As the estimates do not include a price or time frame, only the probable category should be considered. Of the increase in drilling in 1979 (over 1978), 90 percent was in the Overthrust Belt, the outer continental shelf, deep gas areas and the Appalachian Basin (20). This reflects the pattern of gas price deregulation rather than the geographic location of the largest sources of probable reserves. Unconventional sources of natural gas including western tight sands, eastern Devonian shales, coal seam methane and geopressured methane appear to be 10-15 years away from development. Even the range of the estimates of recoverable resources is a factor of 12 at a minimum (21).

Table II presents a distributed, scaled, estimate of future sulfur production from sour natural gas based on Manderson (22).

TABLE II
FORECAST SULFUR PRODUCTION FROM SOUR NATURAL GAS
(000 LT/Y)

<u>PAD District</u>	<u>1984</u>	<u>1990</u>
I	611	821
II	50	68
III	1939	2611
IV	760	3000
<u>Total</u>	<u>3360</u>	<u>6500</u>

Reflection suggests that some of the sulfur allocated to district I might be reapportioned to district III. However, the major increase is found in district IV. This is based on a projection of production from the Overthrust Belt. The evidence for this is currently very scanty. Proved reserves have been estimated at ≤ 4.5 TCF with ultimate resources at 100 TCF but drilling costs are high (23). The H_2S content appears to run from 10 percent to 18 percent (24, 25). One processing plant with a sulfur capacity of 1200 T/d is already planned (26). Eight such plants would fulfill the 1990 estimate. By 1990, however, development of western tight sands and imports of Alaskan and/or Canadian gas could reduce the competitive position of the Belt.

Finally, if current expectations of future sulfur prices are in continued excess of \$100/long ton, the development of very sour natural gas wells ($> 60\%$ H_2S) may be anticipated. The methane content, even if gas prices remain controlled, becomes secondary. Like Frasch sulfur, this production is discretionary. The absence

of such a development may indicate that the sulfur industry expects current price levels to be short-run.

Smelter Acid. If acid is produced involuntarily, as in a smelter operation, it is possible to estimate the cost of acid production in the same manner as that for an elemental sulfur acid plant. To the smelter, however, acid output is simply a mandated concomitant of the process required to produce the metal. Depending on the location of the smelter, the sources of demand, the size of the market, and competition from other producers, the acid sale price may or may not be sufficiently high even to yield a positive net-back, much less a desired rate of return on investment for the acid portion of the operation. This situation does not necessarily lead to closure. Positive or negative, the effect should be registered only in the overall profitability of the entire smelter operation.

Acid can be stored on site, used internally, or sold as merchant acid. Storage facilities have limited capacity. Once the available tankage is filled, additional acid must be moved or disposed of in some manner regardless of price. Failure to do so leads to smelter closure despite opportunities to profitably move the metal. This is sometimes called "fatal acid," referring not to any environmental, hazardous, or other acid characteristic, but merely to the fatal effect on the smelter operation. In the short-run, a combination of the exigencies of air pollution control and increased sulfide bearing ore production can lead to conditions in which some or most smelters must sell acid at a minimal profit or an actual loss. As the local market demand is saturated, sales at increasingly great distances will be sought.

Smelter acid capacity measures are not entirely consistent. Among several possible estimates the two following are given in thousands of short tons of 100% H₂SO₄ per annum for 1978:

PAD District

I	330 ⁽²⁷⁾	519 ⁽²⁸⁾
II	133	1565
III	1111	1030
IV	1144	1070
V	2211	2095
Total	4929	6279

The difference in district II is principally due to the inclusion of Copperhill in column 2.

Obviously, not all smelter acid capacity is utilized and not all SO₂ produced is transformed into acid. For copper, lead, and zinc alone, if it is assumed that only 93.5 percent of the sulfur had been removed, metal production in 1976 implied an acid production of 6 million short tons. Actual acid production was 3.2 million short tons. A doubling of acid output due to abatement

implementation alone may be expected even if metal production remained at the 1976 level. Table III provides estimates of future acid output on a scenario basis. It is implied that sufficient complying smelters remain to produce the metal. The regional distribution is based on current capacity. Given the pace of air pollution control implementation, both the 1985 and 1990 estimates may well be shifted five years into the future. Furthermore, a downward shift in metal production as well as smelter closure is a very real possibility.

Future Sulfur Sources

Electric Utilities. For coal fired electric utilities most, but not all, of the initial conditions to the year 1986 have already been set. Variations will occur but they are unlikely to be significant. The extent of the solidification is based on existing coal supply contracts. The specification of a coal contract to some extent also implies the specification of an air pollution control strategy. Of the 260 units [111,573 megawatts of electricity (MWe)] scheduled to go on-line between 1977 and 1986, 134 (66,210 MWe) are scheduled to enter service between 1977 and 1981. Of these, 72 plants (37,279 MWe) were reported to be using low sulfur coal to meet (the then expected) air pollution control regulations. An additional 61 plants (28,601 MWe) were considering flue gas desulfurization (FGD) while one (330 MWe) was undecided.

Utility sulfur values can be obtained only from regenerative FGD processes. At the end of 1977, thirty FGD systems were in operation in the U. S. Only two utilized a regenerative process; both were demonstration units. The Philadelphia Electric unit recovers sulfur as acid. The Northern Indiana Public Service Unit recovers elemental sulfur. Based on current conditions, there appears to be little likelihood of substantial sulfur or acid production from utilities in the near term. A review of all contracted or planned retrofit FGD systems due to become operational by 1986 indicates that only three utilities will use a regenerable approach. Sulfur output is estimated at 31,590 short tons annually. This tonnage, combined with that reported for existing plants, provides an estimate of total retrofitted regenerable sulfur production of 41,542 short tons per year at a maximum. All are in PAD district I. Two new units are being brought on-stream by Public Service of New Mexico (district III). These should produce about 9000 tons of sulfur per year.

There is no shortage of SO₂ stack gas removal processes. The issues involved, however, range from the economics to the technical feasibility. Both are likely to be more suitable by 1990. From a list of 65 processes (29) ranging from on-stream to developmental, 31 have at least a potentially saleable product. Of these, 11 yield elemental sulfur, 5 produce concentrated acid with 5 more producing weak acid, 6 yield ammonium sulfate, and 4 produce gypsum. The production of sulfur may be the safest course for a

TABLE III
ESTIMATED SMELTER ACID RECOVERY, 1985 and 1990,
FOR SELECTED GROWTH RATES AND 93.5 PERCENT SO₂ RECOVERY

	1985		1990	
<u>Copper</u> (1)				
Growth rate (%/annum)	1.9	.95	1.9	.95
Total output (000 s.t.)	1731	1591	2089	1748
Acid output (000 s.t.)	5884	5361	7101	5942
<u>Lead</u>				
Growth rate (%/annum)	2.0	.00	2.0	.00
Metal output (000 s.t.)	780	653	951	653
Acid output (000 s.t.)	332	278	405	278
<u>Zinc</u>				
Growth rate (%/annum)	2.0	.50	2.0	.50
Metal output (000 s.t.)	596	522	727	549
Acid output (000 s.t.)	938	822	1145	864
Total Acid Output (000 s.t.)	7154	6461	8651	7084
		<u>Acid Distribution</u> (000 short tons)		
<u>PAD District</u>				
I	501	439	611	461
II	1845	1664	2231	1823
III	1101	995	1330	1093
IV	1130	1015	1367	1105
V	2577	2348	3110	2602

Source: Rieber, M.; Okech, B.; Fuller, R. "Sulfur Pollution Control: The Disposal Problem"; U.S. Bureau of Mines (Contract No. J0188144): Washington, D.C., July 1980; Volume 8, "Sulfuric Acid," Table 8.37, p. 8-89.

(1) Assumes that 5 percent of total copper metal production is from oxides.

s.t.: short tons

utility to follow if a ready acid market is not available or cannot be easily developed. Even though most sulfur is converted to acid, the elemental sulfur markets appear to be structurally larger than the acid markets. While this may change over time, utilities are not usually in a position to undertake the risks of a transition in market structure.

Given the age distribution of existing coal fired utilities and the new Environmental Protection Agency (EPA) regulations, FGD will become more important in the future. The choice among systems will depend upon the availability, characteristics and cost of the various coals as well as the relative costs of the candidate FGD processes.

While low-sulfur coals are available both east and west of the Mississippi, they may be expected to increase in price in tandem with competing fuels; specifically natural gas and residual oil. The proposed Mexican and new Canadian natural gas export prices as well as the forecast delivered price for Alaskan gas lead to an expectation of significantly higher future prices. Residual oil prices are tied not only to OPEC price schedules but to any crude oil production restraints and refinery constraints which may develop. With respect to western low sulfur coals, even though the ability to move much larger volumes is not questioned, future transport costs may be significantly higher. The result of such trends, particularly when assessed against the background of the new EPA regulations, may cause a shift to FGD and higher sulfur coals. The latter, with no market outlets other than coal conversion, may be expected to move more closely in tandem with mining costs than with the prices of fuel alternatives.

The production of sulfur values by electric utilities after 1986 is based on projections of electric output by utilities and assumptions related to regenerable flue gas scrubbing. The results should be viewed as speculative. The U. S. Department of Energy (DOE) has modeled five energy scenarios for the period 1977 through 1995; only three appear plausible given the rapid rise of energy prices.

Based on the DOE high fuel cost (\$37.30/bbl of crude oil in 1990) mid-level supply and demand scenario, by assuming a range of coal sulfur content and a percentage use of regenerable FGD (at 90% scrubbing efficiency), an estimate of potentially recovered sulfur can be made. This is presented in the upper portion of Table IV. Regionalization, shown in the lower portion, is based on a simple trend line-least squares analysis of electrical generating capacity for 1960-1977. For practical purposes only 5% of all FGD units are assumed to be regenerable.

Given the mechanistic approach to the scenario, the lower end of the output range seems most likely. Given the amount of currently burned non-compliance coal, it is unlikely that even an average 90 percent scrubbing level will be reached by 1985. A five year forward time shift is probable. While implementation of the Power Plant and Industrial Fuel Act (1978) may hasten the

switch to coal, increased fuel costs may reduce all energy consumption. Even a 3.5%/annum growth rate for electric power is probably high. Fluidized bed technology could lead to lower sulfur output for any scenario. Finally, co-generation could, by 1985/1990, lead to a reduction in utility production of 65-82 billion kilowatt hours (30).

TABLE IV
ELECTRIC UTILITIES: POTENTIAL SULFUR PRODUCTION

Scenario	Total Output (10 ⁶ long tons)		
	1985	1990	1995
5% Regeneration (1.9% S Coal)	0.7	0.9	1.0
5% Regeneration (2.5% S Coal)	1.0	1.2	1.3
10% Regeneration (1.9% S Coal)	1.4	1.7	2.6
10% Regeneration (2.5% S Coal)	1.9	2.2	2.7
5% Regeneration (1.9-2.5% S Coal) PAD District	Regional Output (10 ³ long tons)		
I	438-598	527-714	616-839
II	196-268	241-330	286-384
III	-----	nil	-----
IV	9-18	9-18	9-18
V	36-54	45-62	54-80

Synfuels, In Situ Coal Gasification, Heavy Oil and Heavy Crude Oil. Sulfur values may be produced from each of the fossil based synthetic fuels. However, forecasting sulfur output from these sources is subject to a number of intangibles. At best, the results are projective. With the exception of heavy crude oil, none of the processes or fuel sources are commercially developed in the U. S. Some have been run commercially elsewhere, usually under considerably different economic conditions and/or constraints.

Basic to the entire exercise is the issue of how much alternative fuel development can be reasonably expected over the next twenty years. Given the previous synfuel program parameters, sulfur output then depends on both the characteristics of the original fuel source and the specific method of processing. These also serve to determine the location of the sulfur output.

Assuming that environmental, ecological and other problems can be met and subsumed under costs, all of the candidate sources,

except coal conversion, are fuel supply site specific. Numerous locations for coal conversion are possible. However, while water usage is unlikely to be other than a site specific factor for individual plants, it may be a limiting factor on a programmatic basis particularly in semi-arid western regions. The problem arises because coal, ranging from 3.5-7 percent H₂, has a 16:1 carbon to hydrogen ratio. Transport fuels contain 12-14 percent H₂. Fuel oils, at 9-11 percent H₂, have a 6:1 carbon to hydrogen ratio while the ratio for methane or syngas is 4:1. The extra hydrogen comes from water. DOE estimates that 5-25 MMgal/day/100,000 bbl/day plant will be required (31). Alternative estimates are 20,000 acre feet/year/100,000 bbl/day plant and 15 MM gallons per 75,000 tons/day of coal input. These are simply orders of magnitude. Specific estimates depend not only on the products but on the processes.

Western coal conversion development appears to be favored because of relatively low mining costs, process reactivity of the subbituminous coals and lignite, and the avoidance of rail coal transport. Product transportation implies that the outputs are synthetic liquids and high Btu gas. Both extract a high water penalty. If a low or medium Btu gas is produced, mine mouth power generation with extra high voltage transmission (765 KVAC or ±600 KVDC) is required. This also applies to the output from in situ coal gasification. Water requirements for large scale electric utilities are high.

Eastern coal conversion development may come to be favored because of market proximity, water availability, and coal sources which, because of their high sulfur content, are currently unusable and, hence, largely decoupled from other energy prices. Proximity reduces transport costs and allows an increased use of low and medium Btu syngas processes. Reactivity and swelling problems may be overcome by technology.

Shale Oil. Optimistic shale oil production estimates are (32): 75 - 125,000 bbl/d by 1985; 375 - 625,000 bbl/d by 1992-93; and 1,000,000 bbl/d by 2000. The Carter administration energy program required 400,000 b/d of shale oil by 1990. A conservative estimate is 500,000 b/d by 2000.

If it is assumed that existing projects develop as planned, by 1987 between 182,000 b/d and 282,000 b/d of shale oil will be available. By 1990 the estimate ranges between 391,000 and 491,000 b/d. This allows for neither problems nor development slippage. It also assumes no new entrants. Finally, the estimate excludes those firms which have not finalized their plans even to the extent of proposing a facility size. Some may come on-stream after 1990. All of the developments and most of the sulfur produced will be located in PAD district IV.

How much sulfur will actually be produced depends on the shale oil production assumed, the amount of contained sulfur and the method of disposal. It is assumed here that shale oil output will

be 100,000 b/d by 1985, 350,000 b/d by 1990 and 500,000 b/d by 1995. An early study (33) assumed, for by-product credit purposes, the production of 100 tons/day of sulfur for each 100,000 b/d of shale oil production. On a calendar day basis this equals 36,500 T/Y by 1985, 127,750 T/Y by 1990 and 182,500 T/Y by 1995. The estimate agrees with the analysis of Green River shales of 19.2-20.5° API containing .6-.67% S (wt) (34). It is possible that not all of the sulfur contained in the shale is produced. At least one study indicates that in a retort operation, 82.5 percent of the sulfur contained in the as-mined shale feed is retained in the spent shale (35).

It is concluded that as a producer of sulfur, the shale oil program will have a negligible impact under any foreseeable conditions.

Coal-Based Synfuels. Given the time frame from feasibility studies to commercial operation, coal-based synthetics are unlikely to make a meaningful contribution in this decade. Their effective output may be delayed until the mid-1990's even under a Carter administration energy program. With respect to high Btu syngas, existing proposals and plans appear to support the position that near-term development will depend on proven technology; essentially Lurgi. Liquefaction is likely to be direct (Exxon Donor Solvent and Solvent Refined Coal) rather than indirect (Fischer-Tropsch). However, as the latter can be added to Lurgi gasification, this position is not strongly held.

A search of the recent literature indicates identifiable plans for 19 high Btu coal gasification, 10 medium and low Btu gas, and 15 liquefaction projects. These range from laboratory scale, through seeking funds for feasibility studies, to the construction of commercial scale demonstration plants. The implied coal input in Table V is based on extrapolations to commercial size of those projects which are sufficiently advanced to provide data on input and/or output, site, and time frame. Other projects may be included later; but they could not make a contribution before the mid-1990's.

Sulfur production from coal conversion processes owes far more to the sulfur content of the coal than to either process or location. Based on an examination of the sulfur production potential of several coal conversion processes over a range of coals, when coal sulfur content (MF basis) is plotted against sulfur produced, of 32 observations all but 6 fall tightly along a linear trend. Fischer-Tropsch produces slightly more sulfur for a given coal sulfur content while the Synthoil process apparently produces much more. Of the remaining 4 exceptions, 3 are slightly below the trend (COED, Hydrodesulfurization, and EDS) but COGAS produces far less sulfur for a given sulfur content in the coal.

If it is assumed that the high sulfur coals average 3.5% S (wt) while the low sulfur coals average 0.7% S (wt), the sulfur production estimates in Table V may be derived. Process examination

suggests that not all of the contained sulfur is produced, some remains with unconverted coal; some is lost. Finally, it must be acknowledged that the estimates are quite speculative.

TABLE V
POTENTIAL SULFUR FROM COAL-BASED SYNTHETICS

	1985	1990	1990-2000
<u>PAD District</u>		<u>Implied Coal Input (tons/day)</u>	
I	620 H	9,000 H	25,600 H
II	10,600 H 13,600 L	89,850 H 67,600 L	163,800 H 131,600 L
III	250 H	28,000 H 15,000 L	42,700 H 15,000 L
IV	--	32,600 L	119,200 L
V	1,000 L	10,000 L	37,000 L
		<u>Estimated Sulfur Output (10³ long tons/year)</u>	
I	4	65	184
II	93	730	1,342
III	2	220	546
IV	--	41	149
V	1	12	46

H = high sulfur coal

L = low sulfur coal

In Situ Coal Gasification. In situ coal gasification is a process which DOE believes will be ready commercially by the mid to late 1980's (36). As in any combustion process, the contained sulfur is changed to SO₂. While some will be absorbed in the char and some in the surrounding material, a portion of the SO₂ will be recovered with the low or medium Btu gas. It is likely that the output of SO₂ will be greater with medium than with low Btu in situ gasification because of the use of oxygen rather than air. Given the current stage of development, little contribution to the supply of sulfur is seen from this source before 1990. As most of the pilot studies are being set up in the West and as most of the coals are low sulfur, total sulfur output is unlikely to be significant even in the 1990's. The order of magnitude is estimated to be about the same as that of shale oil.

Heavy Oil and Tar Sands. Heavy oil and the tar sands in the U. S. must be categorized as a resource rather than a reserve as

the techniques needed for development are not yet in place and current economics are not favorable. Compared to the rest of the world, U. S. resources are not great.

Given the apparent lack of current industrial interest in U. S. tar sands and heavy oil as well as the developmental time horizons suggested by the Canadian experience, sulfur output from this source appears unlikely through the year 2000.

Heavy Crude Oils. Heavy crude oils are produced in California. Production problems have been related to air pollution from the generation of steam used for flooding and refining the heavy, high sulfur, crude. Additional development may, however, be expected following the decontrol of prices on crudes up to 20° API and the exemption of crudes of 16° API and under from the windfall profits tax. It is expected that output additions will be 65,000 b/d in 1981 and 130,000 b/d by 1983. The goal is to double output from 250,000 b/d to 500,000 b/d by 1985 and to 750,000 b/d by 1990 (37). Untreated California heavy crude contains 3.56 pounds of sulfur per barrel of crude oil. After treatment (Gulf HDS) the material contains 0.998 pounds of sulfur per barrel. Of the 2.56 pound difference, it is assumed that 75 percent is produced. This suggests that, assuming the Carter administration goals were met, 1985 and 1990 sulfur output would be 150,000 LT/Y and 225,000 LT/Y, respectively, for a 350-day refinery operation year. Output in the decade of the 1990's is unlikely to be much higher. Total reserves would not be able to support a very much increased output. A portion of this is subsumed in the district V refinery estimates, above.

Conclusion

The simple sum of the preceding estimates, subject to the time shifts and scenarios suggested in the text, is presented in Table VI. It is emphasized that the estimates represent capacity rather than output and that the low end of each range is the most probable. If the estimates are approximately correct, only PAD district I will continue to be a net inter-regional importer of sulfur. In other regions, sulfur may be vatted or returned to the ground. Prices are unlikely to remain sufficiently high for a sulfur credit to be usefully applied to process costing. Smelter acid will be particularly vulnerable to the increase in competitive supplies. Frasch sulfur will hardly be missed.

On a qualitative basis, the estimates of recovered sulfur from refinery operations appear to be the most secure. Except for district IV, which depends heavily on the ultimate productivity of the Overthrust Belt, estimates of sulfur production from sour natural gas also seem reliable. The heavy crude oil sulfur output estimate is reasonably firm. Oil shale, tar sands, heavy oil and in situ coal combustion will produce little sulfur even under optimistic scenarios. The smelter acid projection is weak. Metal output may

not increase and smelters may close rather than comply with the new regulations. If the Overthrust Belt production forecast is correct, the smelter acid position will be worsened. The electric utility forecast may be high unless electric demand increases from current levels. Finally, sulfur from coal conversion is highly scenario dependent. Total synfuels forecast may be too high in the absence of government supported programs. Even with a correctly forecast total, a shift from western to eastern coals will reduce western sulfur output (district IV) somewhat while increasing eastern sulfur output (districts I, II, III) considerably.

TABLE VI
PROJECTED SULFUR VALUE CAPACITY
(10^3 long tons/year)

PAD District	1985	1990	1990-2000
I	1508-1546	2218-2396	2250-2481
II	1888-2132	3032-3159	3801-4014
III	5164-5193	6213-6245	6727-6799
IV	1184-1241	3502-3621	3636-3874
V	2109-2174	2223-2247	2398-2577
Total Recovered	11853-12286	17188-17668	18812-19745
Frasch Sulfur (District III)	6330-8630	4550-5550	2250

In view of the domestic estimates, imports are almost redundant. It appears likely, however, that by 1985-1990 Canada will have about one million additional short tons of acid available for export. At least some would be available in PAD districts I and II. Furthermore, sulfur production from sour natural gas and tar sands is likely to increase. As transport problems are mitigated and formed sulfur gains acceptance, Canadian output will become available to districts I, II, and IV. Excluding the existing stockpile, the estimate for tar sands and heavy oil is 1.3-1.9 MMLT/Y in the 1990's. An estimate of 5 MMLT/Y of sulfur from Canadian sour natural gas processing in the mid 1980's is probably low.

Mexican Frasch sulfur output, like our own, will decline over the next 15 years. However, an estimate of Mexican recovered sulfur from oil and associated natural gas is 2-4 MMLT/Y by 1985 and 4-8 MMLT/Y by 1990 (38). The obvious market is district I. The product will be molten, will have the cost advantage of any form of recovered sulfur, and, given the Jones Act which restricts intra-coastal shipping to U. S. flag vessels, will have a transport cost advantage over U. S. Gulf Coast shipments.

Literature Cited

1. Rieber, Michael. "Sulfur Pollution Control: The Disposal Problem"; U.S. Bureau of Mines (Contract No. J0188144): Washington, DC, 1981; Volumes 1-10.
2. Manderson Associates. "Phosphates, Phosphate Rock, Sulfur, Sulfuric Acid, Uranium: Their Emerging Interaction and Outlook During the Coming Decade (1980-1990)"; Manderson Associates, Inc.: Winter Park, Florida, September 1979; Volume II, Table IV-3, p 130.
3. Anonymous. Sulphur. 1978, 136, 68.
4. U.S. Bureau of Mines. "Minerals and Materials"; Washington, DC, February 1980; p 51.
5. Mayhew, L. D. Industrial Minerals. 1978, 134, 41.
6. U.S. Bureau of Mines. "Frasch and Recovered Sulfur in August 1980," Mineral Industry Surveys; Bureau of Mines: Washington, DC, 10 October 1980.
7. Lundgren, D. A.; Durham, M. D.; and Genoble, A. L. "Analysis of Proposed Dust Control Program and Predicted Ambient Air Impact for Agrico Chemical Company's Big Bend Sulfur Nugget Terminal"; Environmental Engineering Consultants: Gainesville, Florida, February 1978.
8. Freeport Sulphur Company. "Solid Versus Molten Sulphur-- Handling, Storage and Processing"; Freeport Minerals, Inc.: New York City, N.Y., 11 March 1977.
9. Staffa, R. I. "Letter" [to Ad Hoc Committee on Latest Reasonably Available Control Technology for Dockside Sulfur Unloading Facilities, Department of Environmental Affairs, State of Florida]; Environmental Affairs, U.S. Sulphur Operations, Texasgulf, Inc.: Stamford, Conn., 3 February 1978.
10. Anderson, J. Colin. Sulphur. 1979, 140, 29-31.
11. U.S. Bureau of Mines. "Sulfur in 1979," Mineral Industry Surveys; Bureau of Mines: Washington, DC, 26 March 1980; Table 5, p 8.
12. McCalsin, John C., Ed.; "Worldwide Sulfur Production (Petroleum Derived)"; International Petroleum Encyclopedia; Petroleum Publishing Co.: Tulsa, Oklahoma, 1978; Vol. 11, p 393-96.
13. Anonymous. Oil and Gas J. 1979, 77 (19), 142-144.
14. McCalsin, John C., Ed.; "Worldwide Sulfur Production (Petroleum Derived)"; International Petroleum Encyclopedia; Petroleum Publishing Co.: Tulsa, Oklahoma, 1979; Vol. 12, Preprint.
15. McCalsin, John C., Ed.; "Worldwide Sulfur Production (Petroleum Derived)"; International Petroleum Encyclopedia; Petroleum Publishing Co.: Tulsa, Oklahoma, 1978; Vol. 11, p 393-96.
16. Anonymous. Oil and Gas J. 1980, 78 (17), 66-67.
17. Posey, Lloyd G.; Kelley, Peter E.; Cobb, Calvin B. Oil and Gas J. 1978, 76 (43), 133.
18. National Petroleum Council. "Refinery Flexibility: An Interim Report"; National Petroleum Council: Washington, DC, December 1979; Vol. II, Tables C.6.1.1-C.6.1.3, pp C-196, C-199, C-202.

19. Anonymous. Oil and Gas J. 1979, 77 (15), 82-83.
20. Anonymous. Oil and Gas J. 1980, 78 (19), 77.
21. Rosenberg, Robert B.; Sharer, John C. Oil and Gas J. 1980, 78 (17) 145, Table 3.
22. Manderson Associates. "Phosphates, Phosphate Rock, Sulfur, Sulfuric Acid, Uranium: Their Emerging Interaction and Outlook During the Coming Decade (1980-1990)"; Manderson Associates, Inc.: Winter Park, Florida, September 1979; Volume II, Table IV-5, p 141.
23. Anonymous. Oil and Gas J. 1980, 78 (19), 79.
24. Anonymous. Oil and Gas J. 1979, 77 (12), 62-63.
25. Anonymous. Oil and Gas J. 1980, 78 (9), 35.
26. Anonymous. Oil and Gas J. 1980, 78 (2), 48.
27. Anonymous. Sulphur. 1979, 144, 30.
28. Manderson Associates. "Phosphates, Phosphate Rock, Sulfur, Sulfuric Acid, Uranium: Their Emerging Interaction and Outlook During the Coming Decade (1980-1990)"; Manderson Associates, Inc.: Winter Park, Florida, September 1979; Volume II, Table IV-7, p 148.
29. Goar, R. Gene. Oil and Gas J. 1979, 77 (4), 58-61.
30. General Accounting Office. "Report to the Congress: Industrial Cogeneration--What It Is, How It Works, Its Potential"; General Accounting Office: Washington, DC, 29 April 1980; EMD-80-7, Table III-7, p 111.
31. Bhatia, Gauri. Coal Age. 1979, 84 (8), 113.
32. Wilson, Howard M. Oil and Gas J. 1979, 77 (25), 49-52.
33. National Petroleum Council. "U.S. Energy Outlook: Oil Shale Availability"; National Petroleum Council: Washington, DC, 1973; p 16-17.
34. Frost, C. M.; Cottingham, P. L. "Hydrogenating Shale Oil at Low Space Velocity"; U.S. Bureau of Mines: Washington, DC, 1973; RI 7738, p 4.
35. Harak, H. E.; Dockter, L.; Carpenter, H. C. "Some Results from the Operation of a 150-Ton Oil Shale Retort"; U.S. Bureau of Mines: Washington, DC, January 1971; TPR-30; Table 1, p 10, Table 2, p 13.
36. Sullivan, Allanna M. Coal Age. 1979, 84 (4), 84-89.
37. Anonymous. Oil and Gas J. 1979, 77 (35), 38-39.
38. Rieber, M.; Okech, B. "Sulfur Pollution Control: The Disposal Problem"; U.S. Bureau of Mines (Contract No. J0188144): Washington, DC, December 1980; Volume 9, "Secondary Impacts of Rest of World Production of Sulfur, Sulfur Values, and Fertilizer," pp 9-80--9-94.

RECEIVED October 5, 1981.

Sulfur Recovery from New Energy Sources

D. K. FLEMING

Institute of Gas Technology, Chicago, IL 60616

This paper is presented as an overview of the technical aspects of the sulfur question in synfuels production. In general, the disposition of sulfur species in synfuels processes is a complex function of -

- Feedstock type - and the chemical forms of sulfur in the specific feedstock utilized
- Primary feedstock processing
- Synfuels product upgrading systems employed.

Sulfur recovery to a useful by-product can range from very low to very high fractions of the total sulfur in the feed, depending upon the combinations of the above factors in a specific synfuels facility.

The discussion examines the disposition of sulfur, presents available sulfur removal and recovery techniques, and outlines possible problems that might be encountered in the transfer of proved sulfur technology to these new energy processes.

This paper is designed as a technical overview of the sulfur question in synfuels production. It is not intended as a detailed literature review; rather, the discussion is a compilation of engineering experience in the field. In the context of the sulfur symposium, the paper is directed at those who are interested in sulfur itself and not, for example, in the environmental implications of sulfur.

In general, the feedstocks considered for the synfuels industry contain small but significant quantities of sulfur. Indeed, one of the main driving forces behind the development of the synfuels industry is the conversion of sulfur-laden fuel into one that is low in sulfur content.

0097-6156/82/0183-0021\$05.00/0
© 1982 American Chemical Society

The chemical processing techniques considered for synfuels flowsheet for the removal and recovery of sulfur are similar to those employed in other industries - notably natural gas sweetening, petroleum hydrodesulfurization, and coke oven gas treatment - but with certain significant differences attributable to the operating conditions encountered in synfuels processing.

It is also appropriate in this introduction to address the question of the quantity of sulfur to be expected as a by-product from the synfuels industry. Although the fraction of sulfur in the feedstock is low, the quantities of feedstock required to support a full synfuels industry are immense. Although scenarios differ, as do time frames, the most common size projected for the total synfuels industry is two million barrels/day of fuel-oil equivalent (BPDFOE)¹. Such an industry would require about 50 energy refineries, each producing 250 billion Btu/day of clean energy product. Each of the facilities is a massive undertaking. A coal refinery of this size will consume the full output of three of the largest underground coal mines. An oil shale plant will require three times the feedstock of a coal refinery - even more if lower grade, Eastern shale is considered. The capital requirements are huge (but not when considered relative to our imported fuel bill). The manpower required to design, construct, operate, and provide feedstock to these energy refineries will also be significant. The investment of these resources will be necessary to provide energy that is in a preferred form and that can be consumed in an environmentally satisfactory manner.

The 2 million BPDFOE industry will produce a by-product of 5 to 10 million tons/year of sulfur; the exact production within this range is dependent upon the eventual mix of feedstocks and technology that is employed. If high-sulfur Eastern coal were the predominant feedstock for these refineries, even more by-product sulfur will be produced, but much less would be realized from oil shale refineries. A small, but still significant influence upon the total sulfur production will be the environmental regulations that are promulgated. Of course, environmentally, sulfur has a bad name - a name that is possibly undeserved. Considering the historical odor and SO_x problems that have been associated with sulfur and coal, however, the future environmental regulations on the synfuels industry will probably require a high recovery of sulfur.

A single energy refinery would require about 20,000 tons/day of high-sulfur Eastern coal, producing about 600 long tons/day of elemental sulfur by-product. For the purposes of this paper, the future price of sulfur has been projected to be about \$100/LT, with a floor provided by the energy cost to produce discretionary sulfur. At this sale price, the sulfur by-product credit is about \$0.25/million Btu of energy produced. This credit, for 2 million

BPDFOE production, is \$0.5 to \$1 billion annually. Therefore, the sulfur question in synfuels production has significant economic importance.

Sulfur in Feedstock - Occurrence

In attempting to assess the disposition of sulfur in the overall synfuels system, one must first examine the characteristics of the sulfur in the feedstock. Then, the feedstock is examined for sulfur "getter" materials. With evaluation of the operating parameters of the primary energy conversion reaction system, the fate of sulfur in the feedstock can be projected.

The sulfur in the general energy conversion facility feedstock may be classified as organic and inorganic sulfur. The organic sulfur is bound to the carbonaceous material in the feed; the inorganic sulfur is generally associated with the ash fraction of the feed. This distinction is convenient in assessment of the feedstock because it affords a qualitative measure of the fate of sulfur during processing. During processing, however, sulfur can transfer between inorganic and organically bound species.²

Each of the major classifications of sulfur types may be further subdivided. The inorganically bound sulfur is conventionally subdivided among pyrite, sulfate, and sulfide types of sulphur³. Again, sulfur can transfer among these types, as well as back and forth to organically bound sulfur or escape from the solid as a gas.

The pyrite sulfur is generally considered to be sulfur associated with iron pyrite, FeS_2 . In most cases only the second sulfur of the pyrite molecule can be considered to be in this class. This sulfur can be expelled from iron pyrite with moderate heating (approximately 500°C) to form iron sulfide, FeS , and elemental sulfur condensate in the cooler vapor space above the sample.

Iron sulfide (FeS), on the other hand, is much more difficult to decompose. Even at 800° to 850°C , FeS is relatively stable in reducing atmospheres, depending upon the relative concentrations of H_2S , H_2O , and H_2 in the reacting gas⁴. When one assesses the thermodynamics of this system, together with the reaction conditions in most synfuel processes, it will be found that iron sulfide is relatively stable until high temperatures are reached.

The third form of inorganic sulfur - the sulfate variety - is relatively unimportant in energy conversion. Fresh coal contains very little sulfate; its presence is usually indicative of a weathered (oxidized) feedstock. Additionally, sulfate may be formed to a minor degree from other types of sulfur by moderate heating of the feedstock, by reaction with the bound oxygen in that feed. This effect can even occur under a hydrogen atmosphere².

The organically bound sulfur can also be generally divided into three types. However, before considering the organically bound sulfur, we must recognize the basic difference in energy refinery feedstocks. Western oil shales and tar sands are primarily paraffinic in nature, but coal is primarily aromatic. The Eastern oil shales appear to have been formed from both animal and vegetable matter, because both aromatic and paraffinic species are derived from the processing. The degree of aromaticity of the feedstock is important because it appears to control the extent of sulfur bonding into the more complex forms of coke that are derived from these materials.

The three general forms of organic sulfur are characterized by the temperatures at which they are released from the feedstock under hydrogen treatment³. A very loosely bonded form of sulfur is released at temperatures that are lower than the range at which the iron pyrite decomposes. Generally this sulfur form exists as "-SH" groups on the organic structure. This is the predominant form of organic sulfur in paraffinic feeds but is not so common in aromatic structures (perhaps 25% to 40% of the organic sulfur).

The second form of organic sulfur is released at temperatures greater than that of pyrite decomposition, but less than iron sulfide decomposition. In general, this sulfur can be considered as being part of the "volatile matter" of the carbon feedstock that is released as the "oils" are driven out of the system. Typically, these materials are thiophenic in nature, but they may be released as hydrogen sulfide as the aromatic structure is broken. Most of the organic sulfur probably exists in this form, although it may convert to the third organic type in processing or conventional analysis.

The third form of organic sulfur is more tightly bound into the carbon lattice of the coal char. Apparently, when coal polymerizes, or chars, some of the sulfur is organically trapped with that coal char. Tests have indicated that approximately 30% of the original sulfur content of the coal (whether it was originally organic or inorganic sulfur) may be trapped in the charring process and not released by extensive hydrotreatment at 800°C⁵. This sulfur is, however, gasified when the char is reacted at still higher temperatures.

With the above background on the apparent occurrence of sulfur in the carbonaceous feedstocks, one can obtain a qualitative estimate of its fate during treatment, depending upon the residence time, temperature, and hydrogen partial pressure.

Fate of Sulfur in Feedstock - Mineral Matter Characteristics

The mineral matter constituents within the feedstock can have

an important effect upon the fate of sulfur during processing. The affinity of sulfur for iron has previously been discussed. The other primary material that is both commonly present and has a high affinity for sulfur is calcium. Both iron and calcium may be considered to be sulfur "getters", with a higher affinity for sulfur than coal. The sulfides of calcium are quite stable in the environments of energy conversion processes. In fact, in an earlier program a process was developed for the hydrotreating of coal in the presence of iron or calcium to desulfurize the coal, converting the coal-sulfur into iron or calcium sulfide from which the sulfur could be recovered. Approximately 90% of the sulfur in the coal could be removed by this technique⁵.

The stability of the inorganic sulfides appears to be a major factor in the disposition of trace metals in the feed. As examples, lead, tin, cadmium and nickel can be largely recovered as the sulfides in most energy conversion processes, although many forms of these materials are volatile⁶.

Fate of Sulfur in Energy Conversion - Processing Conditions

The entire spectrum of energy conversion processes may be considered as part of a general, three-dimensional system of time, temperature, and hydrogen partial pressure.* The most common type of system employs a single reaction stage, contacting the feed with reacting gas to produce the desired product. Several staged processes exist (e.g. COGAS and HYGAS): in these cases, each stage should be evaluated and the impacts of integration should be assessed. In countercurrent, fixed-bed processes, a continuum of varying conditions exists. These systems can be evaluated similarly to the staged systems. For either the single-stage, multi-stage, or countercurrent systems, the sum of the total system is arranged to yield a high conversion of the feedstock to the desired product species.

For example, single-stage liquefaction processes normally operate at relatively low temperatures and high hydrogen partial pressures (as sometimes influenced by hydrogen donor solvents or catalysts) with sufficient residence time to yield the desired conversion. Extremely-high-temperature (1500⁰C) gasification processes require very short residence times to effect conversion, but more moderate temperatures (1000⁰C) require longer residence times.

Pyrolysis processes simply cook the feedstock in an essentially inert atmosphere at relatively low temperatures (500⁰ to 700⁰C); hydrolysis operates under similar conditions, but in a reducing atmosphere.

* Although apparently obvious, this concept is not generally recognized. Rather, the conventional approach is to consider each synfuel process as a separate and distinct entity.

When one considers a single-stage system, the operating temperature is usually sufficient that the primary sulfur species present in the off-gas are hydrogen sulfide and carbonyl sulfide; these will be present in the ratio determined by the H_2/CO content of the contacting gas. In multistage systems and in some liquefaction processes, one must consider the "devolatilization" of the feedstock. Usually the temperature during devolatilization is not high, so the reactions to H_2S and COS are kinetic-limited. Thus, the off-gas will probably also contain carbon disulfide, mercaptans, organic sulfides, and thiophenes. The relative quantities of these materials that are present from devolatilization, of course, are functions of the time, temperature, reacting gas composition, and contacting mode. These species are most apparent in the simplest of coal conversion processes - such as coke production; their presence decreases in more advanced processes.

Fate of Sulfur Compounds - Product Upgrading

The primary purpose of the energy conversion facility is the production of liquid or gaseous fuels; most of the sulfur will be removed from these products. Liquid fuel streams will be hydrodesulfurized to meet combustion standards, with the sulfur transferred to the gas phase.** In the case of oil shale, extensive hydrotreatment will be required to remove the refractory nitrogen compounds from the oil. With this degree of treatment, the sulfur will also be removed.

If the product is a low- or medium-Btu gas, produced for direct combustion, the stream will probably be desulfurized for environmental reasons. In this instance, approximately 95% sulfur removal is typical of a reasonable level of purification - better than direct combustion of the coal by a factor of two, yet not requiring an excessive energy penalty. If the gaseous product is a synthesis gas, as in the production of methane, methanol, or Fischer-Tropsch liquids, extreme desulfurization is required to protect the sulfur-sensitive downstream catalysts.

In addition to the primary product and by-product streams, sulfur will be present in other streams in the facility. For example, water that is condensed from the product will contain some dissolved sulfur compounds, as will the stack from the boiler house that is required to provide steam for the system. Dissolved sulfur gases will normally be stripped from foul water to the gas streams, but some fixed sulfur (e.g. thiocyanate) may not be attacked until biological oxidation or other water treatment. The sulfur compounds present in the boiler house stack might be recovered to salable products, depending on the flue gas desulfuri-

** In some instances, where the liquid stream is a small by-product it may not be desulfurized onsite. Rather, that material might be sold as feedstock to a petroleum refinery.

zation system utilized. Note that sulfur and many of its common compounds (unlike nitrogen, also present in energy refineries) are relatively well studied and characterized chemicals. With thermodynamic data on the many possible sulfur forms (thiosulfates, thiocyanates, polysulfides, etc.), the fate of sulfur can be adequately projected.

Sulfur Removal from Gas Streams

As outlined above, most of the sulfur released from the feed will eventually appear in the gas phase. The primary sulfur problem is synfuels production, therefore, is gas-phase desulfurization.

This portion of the discussion is limited to a general overview. Significant literature exists on this subject^{7,8}, however, most gas purification processes have not been extensively tested on coal- or oil shale-derived gases; the engineering transfer of technology from other systems entails a measure of risk.

The two primary approaches to removal of sulfurous compounds from process gas streams are 1) the direct-oxidation processes and 2) the acid-gas removal systems^{9,10}. In the direct-oxidation processes, hydrogen sulfide is selectively removed from the process gas, and the sulfur is recovered in its elemental form. The acid-gas removal processes, as a group, remove acidic components (H_2S , CO_2 , HCN , etc.) and regenerate these species into a separate side stream.

In general, the direct-oxidation processes employ a redox couple that has sufficient oxidation potential to convert H_2S into elemental sulfur but insufficient potential to oxidize sulfur to higher states. Examples of materials that have this redox potential are vanadium compounds, arsenic compounds, iron compounds, and certain organic species. Typically, the redox materials, dissolved in a hot potassium carbonate solution with the species in its oxidized form, contacts the H_2S -laden gas and the H_2S dissolves as the hydrosulfide. This sulfur reacts with the redox couple, forming elemental sulfur and the reduced state of the couple. Air-blowing of the solution reoxidizes the couple and removes the elemental sulfur from solution as a product froth.

Direct-oxidation processes can conveniently remove H_2S from the process gas to levels of 100 ppm. At significantly greater cost, levels of perhaps 10 ppm can be achieved. The systems are characterized by relatively low sulfur-carrying capacities and, therefore, high liquor recirculation rates. They are not generally applicable to gas streams with high partial pressures of carbon dioxide; the carbon dioxide also dissolves in the solution, causing a pinch in the column and a reduction of sulfur purification capability.

The direct-oxidation systems are specific to hydrogen sulfide; other sulfur species are apparently not attacked. Solution degradation problems may be caused by thiosulfate formation as well as thiocyanate formation (if HCN is present in the gas to be treated). Solution regeneration techniques have been developed to attempt to minimize the impact of these effects. The systems must be operated with caution, in some cases, the solutions contain species that are considered toxic or environmentally hazardous. Some of the commercial processes comprising this group include Stretford, Takahex, Giammarco-Vetrocoke, Ferrox and others.

The acid-gas removal systems remove hydrogen sulfide, as well as other acid gases, from the process stream and regenerate them as a separate side stream. In the application of acid-gas removal processes, one must consider the downstream recovery process. The direct oxidation processes, discussed above, are applicable for this duty; usually, however, a Claus plant is a less costly approach. The conventional Claus reaction, however, requires H₂S concentrations that are higher than 15%; over 30% is preferred for smooth operation of the system¹¹. In a typical energy refinery, the quantity of sulfur in the total acid gas may be in the range of 1% to 5%. This range of H₂S concentration is satisfactory for a direct-oxidation process. Usually, however, the combination of a Claus sulfur plant with a "selective" acid-gas removal system is an economically preferred alternative¹². A selective acid-gas system is designed to remove hydrogen sulfide from the gas at a greater rate than carbon dioxide. Hence, the sulfur in the gas can be recovered at a concentration that is satisfactory for Claus plant operation.

The three general classifications of acid-gas removal processes are 1) amines, 2) activated hot potassium carbonate, and 3) physical solvents. These systems each have preferred operating ranges, as generally controlled by the acid-gas partial pressure, have different energy requirements, and offer different degrees of selectivity.

The amine-based acid-gas removal systems have a high affinity for acidic species and are operable when the partial pressure of the acid gases is relatively low. This high chemical affinity, however, means that significant energy is required to break the amine-acid bond for regeneration of the acid gases. This high energy demand generally dictates the selection of an alternative acid-gas removal system unless the system must operate at low pressure. Although common in oil refineries, this type of system may not find significant application in synfuels facilities where the acid gas partial pressure is usually high.

Amines are occasionally used in combination with other systems for secondary purification. For example, an alternative pro-

cess may be used for the more economical bulk removal of the acid gases, but an amine scrubber is used for improved cleanup when the partial pressure of the acid gases is low. Primary amines do not exhibit significant selectivity for H₂S over CO₂; moderate selectivity is obtainable in some secondary and tertiary amines. Some of the common amine-based processes (abbreviated as per custom) include MEA, DEA, DGA, MDEA, TEA, and DIPA⁸.

The activated hot potassium carbonate systems are generally applied when the partial pressure of acid gases is above approximately 15 psig¹³. For these systems, the acidic constituent must first dissolve in the solution and then react with the basic solution. A moderate degree of selectivity can be achieved by taking advantage of the relatively rapid kinetics (not equilibrium) of H₂S dissolution compared with CO₂ dissolution. Energy demands for regeneration of the hot carbonate systems are less than for the amine-based processes, but still high compared with the physical solvent processes. Some of the process names associated with hot carbonate systems include Benfield, Catacarb, and Alkazid.

The physical solvent-based acid-gas removal systems do not rely upon the acidic properties of the acid gas. Rather, the polar acid gases have a much greater solubility in many oils and solvents, compared with fuel gas species.

These solubilities are functions of temperature and, of course, pressure. Thus, these systems operate by dissolving the acid gases in the solvents at high pressure and relatively low temperature. The acid gases can be regenerated by temperature and/or pressure swing. Generally, a pressure swing is utilized to further minimize the already low thermal energy requirements of the system. However, significant mechanical energy may be required for solution pumping (at high operating pressures), refrigeration (at low operating temperatures), or flash gas recompression (if a high degree of selectivity is required).

In general, the physical solvent-based processes appear to have economic advantages when the partial pressure of acid gas is greater than approximately 200 psig¹². By making use of the difference in solubility between hydrogen sulfide and carbon dioxide, a significant degree of selectivity can be achieved. This selectivity is usually improved at lower temperatures and with greater flash gas recycle (which changes the relative concentration of H₂S and CO₂ in the scrubber feed). Some of the process names associated with the physical solvent systems include Rectisol, Selexol, Purisol, and Sulfolane.

In many synfuel refinery flowsheets, the acid-gas partial pressure is borderline between obvious preference for hot carbonate and physical solvent-based acid-gas removal systems. In these

cases, a careful process trade-off study, on a plant-specific basis, is required. For example, low-cost power favors a physical-solvent system, but a surplus of low-pressure steam from the process favors a hot carbonate acid-gas removal process.

Some acid-gas removal systems include mixed solvents - usually an amine in a physical solvent. This approach modifies the relative characteristics of the physical solvent by the amine and provides many of the advantages of each. Generally, only a moderate degree of selectivity can be achieved, but the total system appears to be improved. Typical in this area are the Sulfinol and Amisol processes.

Sulfur Recovery Systems

The direct-oxidation processes for recovery of sulfur from raw gases are also applicable on acid-gas streams. Usually, a direct oxidation process would be applied when a nonselective acid-gas removal system had been employed and the sulfur concentration in the acid gas is relatively low. At higher H₂S concentrations, as achieved through selective acid-gas removal, the conventional Claus process appears to be more economic.

The reason that a conventional plant requires higher sulfur levels in the feed gas may be found in the heat balance of the system. In a conventional Claus plant, where the entire gas stream is reacted with stoichiometric oxygen to drive the hydrogen sulfide to elemental sulfur, the first reaction stage is an H₂S-air flame, and high sulfur concentrations are required so that the flame temperatures are high enough to be stable¹¹. In a split-flow process, one-third of the H₂S-containing stream is reacted with sufficient oxygen to react the H₂S to SO₂. The resulting SO₂ is reacted with the remaining H₂S of the original sulfur-plant feed to form elemental sulfur. With this approach, the H₂S concentrations may be somewhat lower - down to 15% - and still maintain a stable flame in the combustion section¹¹.

For leaner sulfur streams, several techniques have been suggested to provide the heat balance. Among them are 1) use of oxygen rather than air for combustion¹⁴, 2) addition of hydrocarbon or other fuel species to the sulfur burner section to provide heat, 3) recycle of product sulfur to the burner section to provide heat¹¹, and 4) preheat of inlet acid gas and air¹⁵. Recently, discussions have appeared in the technical literature on the satisfactory operation of sulfur plants at feed-concentration down to 1% to 5% sulfur, utilizing preheat of the inlet area. For that matter, according to other licensors, this approach was practiced 25 years ago. It is known that sufficient heat is produced in the H₂S/O₂ reaction, if properly recuperated, to operate catalytically with this low sulfur concentration in the acid gas.

The Union Oil selective sulfur oxidation catalyst¹⁶ is the basis for many modified sulfur plant designs announced in recent years^{17,18}. This system may be ideal for a synfuels facility because of the low H₂S/CO₂ ratio of synfuel raw-gas streams. If a physical solvent is employed for acid-gas removal, some hydrocarbon will be lost to the acid-gas stream. With the selective sulfur oxidation catalyst, this fuel is not oxidized, rather it is available for tail-gas reduction over cobalt-molybdenum, prior to final treatment.

The primary problem with the systems that have been developed to utilize lower feed sulfur concentrations is the reduced efficiency of sulfur recovery. This effect is not so apparent in lost sulfur revenues as it is in the increased size and cost of the downstream tail-gas treating unit required to minimize the sulfur emissions from the overall sulfur-treatment section.

Sulfur-Plant Tail-Gas Treating

A number of approaches are possible to minimize the sulfur content in the tail gas from the sulfur plant, and several processes have been developed for each of these approaches^{9,10}. A complete discussion of tail-gas treatment is beyond the scope of this document. The processes available have a wide range of recovery efficiencies; some of them result in a nearly sulfur-free tail gas. In general, the cost of the processing increases with the degree of purity achieved, and, more importantly, those processes that do achieve higher purity in the final tail gas generally have excessive energy demands. In most cases, the additional sulfur recovered in the tail-gas treating processes is insufficient to pay for the capital requirement of the tail-gas treating process, let alone the operating costs in terms of energy. For that matter, on a total system basis, some of these processes may not be environmentally cost-effective.

Systems Analysis

The overall problem, from sulfur in a raw gas through sulfur recovery and tail gas treating, has historically been addressed by a case study approach. In this approach, each plant section is optimized, based upon predetermined subsystem interfaces. A preferred approach, rather, is to evaluate the entire system analytically, allowing the interfaces between the subprocesses to float, to determine the overall cost-effective approach. In this technique, compromises are taken in each of the unit processes so that the total system operates more effectively.

A further question arises on the need for the exceptionally high purity tail-gas treating processes. The energy demands of these systems are excessive, compared with less efficient systems.

Indeed, more pollutants may be emitted in the production of energy to replace the energy used for tail-gas treatment, than are recovered by the more efficient tail-gas treating processes.

Potential Problems

One of the primary problems to be encountered in energy conversion facilities will be the variability of the feedstock. A coal or oil shale facility will probably see greater variability, day-by-day, than experienced in planned changes in oil refinery crude runs. Even with extensive blending in the feed stockpile, the variation in feed characteristics will be significant.

The feedstock variation will impact on the characteristics of the raw-gas. Added to the effect of the feedstock variation is the cyclic impact of loading of lockhoppers, full of fresh feedstock, into the reactor. Thus, the downstream purification system can be expected to be faced with a wide and constantly changing range of concentrations of minor species.

Nowhere is this effect more important than in the sulfur plant. In the sulfur recovery section, the air flow to the Claus reactor must be carefully proportioned to the sulfur flow in the feed; even slight variations cause significant penalty in the sulfur plant efficiency and increased load on the tail-gas treating unit¹⁵.

The sulfur plant of the energy refinery, as contrasted to other sulfur plant applications, will have a high concentration of carbon dioxide. This CO₂ will have a significant impact, both chemically and thermally, on the sulfur plant operation and downstream tail-gas treating. Energy demands and/or sulfur emissions may be adversely affected, relative to known operations.

The sulfur plant will also be impacted by minor constituents in the raw gas. Depending upon the primary conversion system utilized, the raw gas may contain significant quantities of cyanides, ammonia, oils, and light hydrocarbons. Sulfur may be present in the forms of carbonyl sulfide, carbon disulfide, mercaptans, thiophenes, or other species. Design engineers should be aware of these species and their variability, in order to provide sufficient protection in the overall system.

Excess oils and hydrocarbons in the sulfur plant feed can readily darken the sulfur, minimizing its sales value¹⁵. Ammonia can cause fouling of the Claus catalyst beds¹⁵. Cyanides have a tendency to polymerize, causing significant problems with the formation of Prussian blue. Organic forms of sulfur are not so readily reacted in low-temperature Claus beds and may cause problems in achieving the desired sulfur plant efficiency. Addi-

tionally, some of these organic forms of sulfur are not readily recoverable in certain types of tail-gas treating processes.

Another area of concern that has not received adequate attention is the possible contamination of the sulfur products. Feedstocks to these refineries will contain a full spectrum of the elements of the periodic table. Theoretical analysis indicates that certain of these materials may undergo chemical reactions and end up in the sulfur plant feed. Theoretically, we can expect a significant contamination by arsenic, selenium, tellurium, and perhaps mercury⁶.

New Developments

The major factor affecting sulfur in the synfuels industry is the growing tendency to design for sulfuric acid manufacture, rather than elemental sulfur production. From a technical viewpoint, many of the problems inherent with the sulfur plant can be overcome by proper design of a sulfuric acid plant. On an economic basis, the value of sulfuric acid, per unit of sulfur, is significantly higher. Thus, the overall plant economics appear favorable with sulfuric-acid production. For a plant located in the Illinois coal basin, the market for sulfuric acid appears strong. Thus, we can anticipate seeing more process designs that include sulfuric acid production, rather than elemental sulfur manufacture. However, unlike elemental sulfur, sulfuric acid cannot be inventoried and long distance transportation can be economically unviable.

An area of research that is receiving increased attention is the removal of sulfur from process gas streams at elevated temperature. This approach has significant efficiency-impact upon the overall energy conversion system, particularly if the product is a medium-Btu gas that is to be fired onsite (for example, into combined-cycle power generation). Several laboratories are working on systems for this operation. In most cases, the sulfur is recovered from the system as sulfur dioxide, which would probably be upgraded to sulfuric acid. AT IGT a system is being developed that removes the sulfur from the gas at elevated temperature, but the sulfur is discharged from the process in elemental form.

Efforts to develop modified Claus processes that will operate with low concentrations of sulfur in the feed gas have been previously mentioned. A similar system is being laboratory tested at IGT which does not require precise, instantaneous control of the oxygen/sulfur feed ratio.

In the acid-gas removal area, process engineers continue to work on systems that have lower energy demands and produce cleaner

gas. In the direct oxidation processes, developers are striving toward increased sulfur-carrying capacity for the solution and regeneration techniques to minimize system costs. Improved COS hydrolysis systems are being developed to convert COS into H₂S, which is more readily recovered. Additional work of course is required at all of these areas, to further improve plant economics. Also, as discussed earlier, proper evaluation of the sulfur problem from a total systems basis, is required. Additional work should focus upon energy demands of tail-gas treatment processes and the need, or desirability, of employing high energy consumption for minimal improvements in sulfur recovery.

References Cited

1. International Gas Technology Highlights IX No. 16 (1979) July 30.
2. Fleming, D.K. and Smith, R.D., "Pilot Plant Study of Conversion of Coal to Low Sulfur Fuel", Chicago: The Inst. Gas Technology, EPA-600/2-77-206 October 1977.
3. Vestal, M.L. and Johnston, W.H., "Desulfurization Kinetics of Ten Bituminous Coals", Report No. SRIC 69-10. Baltimore: Scientific Research Instruments Corp., 1969.
4. Rosenquist, T., "A Thermodynamic Study of the Iron, Cobalt, and Nickel Sulfides", J. Iron Steel Inst. London 176, 37-57 (1954) January.
5. Fleming, D.K., Smith, R.D., "Evaluation of the Flash Desulfurization Process for Coal Cleaning", EPA-600/7-79-016 Chicago: Institute Gas Technology, January 1979.
6. Anderson, G.L., Hill, A.H. and Fleming, D.K., "Predictions of the Disposition of Select Trace Constituents in Coal Gasification Processes", Paper presented at Environmental Aspects of Fuel Conversion Technology Symposium, Hollywood, Florida, April 17-20, 1979.
7. Kohl A. and Riesenfeld, F., Gas Purification, 3rd Ed. Houston: Gulf Publishing Co., 1979.
8. Maddox, R.N., "Gas-Liquid Sweetening", 2nd Edition, Campbell Petroleum Series, Norman, Oklahoma (1974).
9. Fleming, D.K. and Primack, H.S., "Purification Processes for Coal Gasification", Paper presented at the American Institute of Chemical Engineers, 81st National Meeting, Kansas City, Mo., April 11-14, 1976.

10. Hyne, J.B., "Methods for Desulfurization of Effluent Gas Streams", *Oil & Gas Journal*, August 28 (1972), 64-67.
11. Beavon D.K. and Leeper J.E., "Sulfur Recovery from Very Lean Hydrogen Sulfide", 27th Canadian Chem. Eng. Conf., Calgary, Alberta, Oct. 1977.
12. Christensen, K.G. and Stupin, W.J., "Comparison of Acid Gas Removal Processes", Final Report No. FE-2240-49, prepared for DOE and GRI under Contract No. EX-76-C-01-2240 C.F. Braun & Co., Alhambra, Calif.: April 1978.
13. Benson, H.E. and Parrish, R.W., "HiPure Process Removes CO₂/H₂S", Hydrocarbon Process. 53, 81-82 (1974) April.
14. Anon, "The TRW S-100 Process", TRW Systems Ltd., Redondo Beach Calif., (1971).
15. Grancher P., "Recent Advances in Claus Techniques for Sulfur Recovery from Acid Gases", 27th Canadian Chem. Eng. Conf., Calgary, Alberta, Oct. 1977.
16. Hass, R.H. (assigned to Union Oil Company of California), "Catalytic Incineration of Hydrogen Sulfide from Gas Streams", U.S. Patent 4,171,347 (1977) April 15.
17. Beavon, D.K., Hass, R.H. and Muke, B., "High Recovery, Lower Emission Promised for Claus-Plant Tail Gas", *Oil & Gas Journal*, (1979) March 12.
18. Hass, R.H., et al., II, 76-80 "Process Meets Sulfur Recovery Needs", Hydrocarbon Process. 60, 104-107 (1981) May.

RECEIVED October 5, 1981.

Recent Developments in Sulfur Production from Hydrogen Sulfide-Containing Gases

J. B. HYNE

Alberta Sulphur Research Ltd. and University of Calgary, Department of Chemistry,
2500 University Drive N.W., Calgary, Alberta, Canada T2N 1N4

Since the 1950's there has been a remarkable growth in sulfur production from the hydrogen sulfide of natural and refinery gases. Once a minor source of world brimstone, sour gas now makes a very significant contribution to world sulfur production.

The early pioneering work on sour gas production and conversion to sulfur has been followed in the last ten years by some remarkable developments in both recovery and processing. Deep, hot, high pressure sour gas deposits, previously avoided as technologically unworkable, can now be produced using modern metallurgy and anticorrosion techniques. Improved methods for separating the acid gases (H_2S , CO_2) from the hydrocarbon component using kinetic rather than equilibrium control of sweetening solution loading have been developed. The efficiency of the Claus Process, long the means of conversion of H_2S to sulfur, has been increased through improvements in reaction furnace, catalyst bed and computerized feed composition control leading to recovery efficiencies in excess of 98%. Recent development of a Claus Process under pressure may yield further important improvements. Add on tail gas clean-up processes have further reduced plant effluent in response to environmental protection requirements.

The sulfur product itself has also been the subject of recent research and development with improvements in handling, storage and transportation of both liquid and new types of formed, solid sulfur.

0097-6156/82/0183-0037\$05.00/0
© 1982 American Chemical Society

Recovered sulfur has grown steadily in importance as a world source of brimstone since the mid 1950's. Between 1965 and 1977 recovered sulfur's share of world supply grew from 18% to 30% (1) and continues to grow in relation to Frasch mined and other forms of native elemental sulfur. All of this has meant a rapid growth in the number of sulfur recovery facilities and new developments in the various techniques and processes associated with the industry.

It is the purpose of this paper to review some of these developments relating to the production of sulfur from hydrogen sulfide containing gases. These gases can be natural or man made; the former being found as sour natural gas deposits around the world, the latter the result of hydrodesulfurization of sulfur-containing crude oil in modern refinery practice. Although these higher sulfur containing crudes (>0.5%) have increased in volume in recent years (from 36% to 46% of U.S. supply between 1973 and 1978 (2)) the total tonnage of sulfur recovered from oil is less than that from sour natural gas. Canada alone provided some 45% of world production of recovered sulfur in 1976 virtually all from sour natural gas. Thus the emphasis in this review will be on recovery of sulfur from sour natural gas sources. Apart from the initial discussion of development of these sources, however, the balance of the review applies equally to sulfur recovered from man made gases.

The sour natural gas sulfur recovery industry covers virtually the entire gamut of chemistry. From the sour gas reservoir to the Claus plant end product problems are encountered in thermodynamics, kinetics, corrosion, catalysis, redox, rheology and the environment - plus all the rest! In reviewing recent developments in such a wide ranging field it is only possible to select examples. It is hoped, however, that these highlights will serve to illustrate the dynamism of the industry in recent years and the progress it has made in developing a new source of one of the world's most basic and essential elements in an environmentally acceptable manner.

The four major sections of the review cover developments in new sour gas Sources, improvements in Production techniques associated with the separation and conversion of H_2S to elemental sulfur, aspects of the Environmental impact and its minimization and, finally, new developments in the forming and handling of the sulfur Product itself.

Sources

The first major source of recovered sulfur from H_2S containing natural gas was the Lacq field in southern France developed by SNPA in the mid 1950's. This 15% H_2S containing gas stream was the forerunner of many subsequent sour gas developments around the world. In the early days of sour gas production the major product sought after was the methane; hydrogen sulfide and

the sulfur derived from it was very much a by product, not infrequently referred to as a waste product!

The intervening years to 1981 have seen several world market sulfur demand cycles which have effected the rate of acceptance of these new sulfur sources but slowly the recovered sulfur product has taken its place alongside other world sulfur sources such as Frasch mined and pyrites. In very recent times there have even been moves to re-open very sour gas wells as sulfur wells as world demand for this key commodity has grown and prices have crossed \$100/tonne FOB the plant gate.

H₂S Rich Deposits. Some examples of H₂S rich natural gas wells around the world are listed in Table 1. While some of these sources are relatively well established (e.g. France, Canada, West Germany) many new high H₂S gas deposits are now being developed. In the USSR the Orenburg sour gas fields have been in production for some years but the new central Asian deposits at Astrakhan are only now being brought on stream. Deep drilling into the sediments of the Mississippi basin in the southern USA is uncovering hot, high pressure, high H₂S containing gases that present some new challenges in metallurgy and phase behaviour. Most recently of all the Chinese have discovered and are now considering the development of a relatively shallow (7,000') and very cool (25°C) sour gas reservoir at Zhaolanzhuang south of Peking which may contain levels of H₂S of up to 90%. Because of the low reservoir temperature and pressure changes during production some interesting phase behaviour problems may be encountered.

Table I
Some H₂S Rich Sour Gas Fields

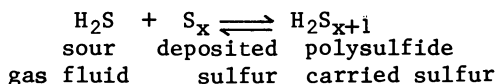
<u>Location</u>	<u>% H₂S</u>
France (Lacq)	16.0
W. Germany (Varnhorn)	22.4
Canada (Harmattan)	53.5
Canada (Bearberry)	90.0
(Panther River)	70 - 80
U.S.A. (Mississippi)	25 - 45
(Smackover)	
USSR (Astrakhan)	22.5
China (Zhaolanzhuang)	60 - 90

These new developments of high H₂S natural gas come at a time when the world sulfur market is particularly bouyant, sufficiently

so to encourage re-examination of some older high H₂S deposits previously not considered economic because of depressed sulfur prices. In this category are some Western Canadian fields such as Bearberry, Panther River and Hunter Valley all in deeply buried foothills formations with relatively high temperatures and pressures. Some of the technical problems associated with the development of such high H₂S containing reservoirs will be discussed below.

Recovered sulfur sources in Middle East countries have also been developed recently. Most important of these is the Saudi Arabian gas recovery program at Berri, Shedgum and Uthmaniyah which will initially add some 4,000 tons/d to recovered sulfur production. This additional 1.5 million tons/annum of recovered sulfur will further enhance the growing dominance of recovered sulfur in the total world market picture.

Sulfur Deposition. The development of high H₂S containing natural gas resources has not been without its problems and a few of these will be touched on here. High H₂S containing gases under pressure are an excellent "solvent" for elemental sulfur which is often found in association with sour natural gas reservoirs. The so called solubility of sulfur in such fluids has been the subject of studies by authors such as Kennedy and Wieland (3) and Brunner and Woll (4). Field studies (5,6,7) have shown that as the pressure and temperature of the sour gas fluid changes during the trip from bottom hole to well head the sulfur carrying power of the fluid decreases and sulfur deposition can occur in the tubulars. Although physical solution of the sulfur in the high pressure fluid phase contributes to the solvent carrying capability it is now generally accepted that hydrogen polysulfide formation and decomposition plays a major role in the deposition phenomenon (8). Thus as pressure and temperature change the position of the polysulfide equilibrium moves

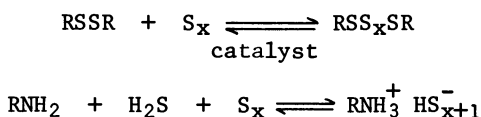


either picking up or depositing the elemental sulfur. If temperatures are above the melting point of the sulfur, plugging will not occur but below 120°C solid sulfur may well be deposited. While the most likely location of such deposition is in the production tubulars conditions of pressure and temperature can be encountered where the sulfur is deposited in the formation around bottom hole. When this occurs formation damage can result and producibility can be effected.

Another feature of the polysulfide equilibrium is that the forward and reverse reactions are not instantaneous. Thus the flowing system can be in meta-stable equilibrium because of the

inability of the chemical equilibrium to track the pressure and temperature changes occurring in the flowing sour gas fluid. Prediction of location of sulfur deposition thus becomes a complex matter involving H₂S content, sulfur content, pressure, temperature and flow rates.

Solvent Systems. The problem of sulfur deposition in sour gas producing wells has resulted in the development of new solvent systems for treating plugged wells or for continuous circulation to prevent deposition. The hazards of using carbon disulfide as a sulfur solvent have resulted in the development of techniques based on either disulfide liquids (e.g. Mercox) or amines both of which are capable of combining chemically with the deposited sulfur and carrying it to the surface (8).



The mechanisms for these chemical solvent processes are now quite well understood. Corrosion problems downhole have been encountered in the ionic amine system (9) but the disulfide oil solvent appears to be without such complications and can carry up to 60% w/w of sulfur. Handling the material requires some insensitivity to malorodous fluids!

Corrosion. The development of deep, hot, high pressure sour gas reservoirs has brought with it a suite of new problems in the materials area. Sulfide stress cracking, hydrogen embrittlement and general corrosion problems have been well recognized in the sour gas industry for many years (10), but these and related material failure problems are significantly amplified when temperatures rise to near 200°C pressures to 16,000+ psi and H₂S content to 30% or higher. The situation can be further complicated if connate brine and carbon dioxide are also present in the production fluid (11). The chloride ion is believed to be involved in pitting corrosion which can result in failure of tubulars by puncture of the pipe wall (12, 13).

Much recent work has been carried out on the development of special alloy materials capable of withstanding the hostile environment found in deep, hot high pressure sour gas wells. Asphahani has recently surveyed (14) progress to date in the field with particular reference to the CO₂/H₂S/Cl⁻ environment. The inadequacy of typical 410 type stainless steels in this environment has led to a search for more resistant alloy materials and high iron, nickel base alloys such as Incoloy 825 (30 Fe, 42 Ni, 22 Cr, 3 Mo, 2 Cu) and Hastelloy G (20 Fe, 49.5 Ni, 22 Cr, 7 Mo, 1.5 Cu) appear to offer best performances. They show a

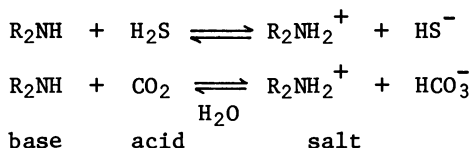
general resistance to corrosive attack and to chloride/sulfide stress cracking at elevated temperatures. The presence of CO₂ can also be tolerated. The Hastelloy G appears to resist localized pitting corrosion better than the Incoloy 825.

Although the use of inhibitors can mitigate corrosion to some extent in such hostile environments (15) designing systems with appropriate phase behaviour under bottom hole conditions is difficult. To date oil based inhibitor carrier systems have been employed but these require large volumes of fluid circulation and it is often difficult to maintain a continuous oil wet surface on the tubulars. A water-inhibitor system would overcome many of these problems since the sour gas fluid is already saturated with water in the reservoir. Such a system, however, remains to be designed.

Until such an inhibitor system is developed the use of the so called "exotic" alloys for downhole tubulars in the new deep sour gas plays will be required. Exxon's 21,000' D.B. McDonald Smackover wildcat in Mississippi (16) with expected bottom hole conditions of 400°F and 23,000 psi and H₂S between 25% and 45% will have an internal tubing string of Hastelloy C-276 with a yield strength of over 150,000 psi. This string will carry continuously circulating corrosion inhibitor to protect the other tubulars. At an estimated \$42 million total drilling, completion and testing costs for such developments it is just as well that the gas will bring \$3+ per MCF and the recovered sulfur \$100+ per ton!

Production

Selective Absorption in the Sweetening Process. In recent years removal of the acid gas (H₂S, CO₂) components from a gas stream has increasingly been by absorption in a solvent system containing amines. While non-reactive solvent sweetening processes are in use, the ability of the basic amine to react chemically with the acid gas to yield water soluble salts has favored the chemical sweetening system. Thus



The equilibria are readily reversed by heating and the salt loaded aqueous amine solutions can be made to release the carried H₂S and CO₂ after separation from the hydrocarbon gas being sweetened.

Normal practice has been to allow the amine sweetening solution to approach equilibrium loading levels in the gas/solution contactor. While various amine solutions show different

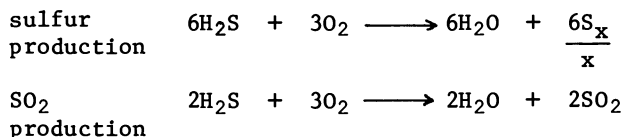
equilibrium affinities for CO₂ and H₂S the equilibrium selectivity is not great. Recent work (17, 18) however, has shown that if the differential rate of the H₂S and CO₂ reactions with amines are utilized much greater selectivity of absorption can be achieved. Thus high loadings and short contact times between gas and solvent favor the selective non-equilibrium chemisorption of H₂S over CO₂. It has been shown that selectivity as high as 27 to 1 for H₂S over CO₂ can be obtained in methyldiethanolamine solutions (MDEA).

This non-equilibrium loading of the sweetening solution can be coupled with new instrumentation for continuous monitoring of the H₂S loading level in the amine using sulfide ion selective electrodes. This can significantly improve the efficiency of both the absorption and regeneration steps in the sweetening process and reduce the amount of CO₂ in the acid gas feed to the front end furnace of the sulfur plant. As will be seen later this improves the combustion characteristics in the furnace and reduces the amount of COS appearing in the Claus plant tail gas stream.

The Front End Reaction Furnace. An essential component of any sulfur plant based on the chemistry of the H₂S/SO₂ redox reaction is the reaction furnace. Here a portion of the feed H₂S is oxidized by combustion with air to yield the SO₂ which will act as oxidant in the downstream catalyst units. While the general overall thermodynamics of the combustion process in the front end furnace have long been appreciated there have been some important recent developments in our understanding of some of the more sophisticated aspects of the combustion chemistry. These, in turn, have led to higher sulfur conversions in this initial high temperature region of the sulfur plant and lower loading of the downstream catalyst beds. Overall conversions have thus been improved and the amount of unrecovered sulfur going to atmosphere in the incinerated tail gas has been further reduced.

These and other improvements have resulted largely from a better understanding of the combustion process. The homogeneity of the gas mixture being burned has been improved by better design of acid gas (H₂S, CO₂) injection nozzles and, in some instances the introduction of internal furnace structures (checkered walls) to assist in mixing of the air and acid gas feeds.

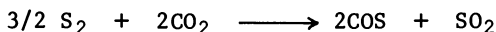
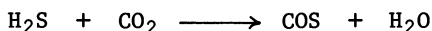
While the overall chemistry of the combustion process was well understood viz.,



the rate controlling steps involving a variety of intermediate species were not known at the high furnace temperatures employed (19). Rate data were available for many of these processes at

25°C but extrapolation to 1,000°C or higher was not possible. This is an interesting illustration of the gap between the conditions chosen for the basic research studies and those of the plant operation. Recent research (20) has helped bridge this gap by further investigation of reaction rates at elevated temperatures. The work of SNPA (SNEA) in particular (21) has resulted in a much better understanding of the relationship between residence time, temperature and extent of reaction within the furnace.

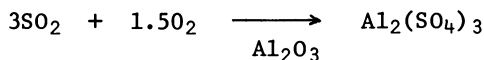
The production of COS in the front end reaction furnace presents special problems since sulfur in this form may be difficult to remove in the downstream catalytic beds under conditions that are optimal for the Claus redox reaction between H₂S and SO₂. COS (and CS₂) were known to be generated from hydrocarbon impurities carried over in the acid gas feed thus the efficiency of the up-stream sweetening process became an important factor. The reaction of CO₂, a common constituent of the acid gas feed, with H₂S and/or sulfur under furnace temperature conditions has also been shown to be an important source of COS.



Thus minimizing the CO₂ content of the acid gas feed, as for example by the selective absorption of CO₂ and H₂S discussed previously, takes on added significance.

Furnace temperatures have also been shown to be important in controlling the formation of COS. While COS has little effect on the downstream Claus catalyst efficiency its presence in the gas stream leads to higher loading of the reductive tail gas clean-up processes (e.g. SCOT, BSR, see environment) or to higher SO₂ emissions in the stack gas. The recent developments regarding the control of its formation in the front end furnace are thus a significant contribution to the improvement of environmental quality control.

Adequate control of the chemistry in the front end furnace can significantly effect the lifetime and efficiency of the downstream catalyst beds in a sulfur plant. Inadequate removal of C₆+ hydrocarbons from the acid gas feed can result in catalyst fouling by polymeric materials formed under furnace conditions. Toluenes, ethylbenzenes and xylenes have been shown to be particularly troublesome in this regard. Oxygen breakthrough into the catalyst beds can also shorten the effective lifetime of the Alumina catalyst by sulfation i.e.



Thus the control of the ratio of air to acid gas being fed to the

front end furnace becomes a crucial parameter. Significant advances have been made in front end furnace feed ratio control through the use of on-line gas chromatography with automatic feed back to the ratio controller (22). Further recent improvements involve the use of on-line spectrophotometric detectors (UV, IR) which reduce maintenance and speed up response times (23, 24). In this manner the precise stoichiometry required for optimizing sulfur recovery in the Claus converters can be maintained.

Recent improvements in the operation of the front end reaction furnace have not only increased sulfur recovery at this stage in the plant but have reduced the production of undesirable by-products which, ultimately, leads to a reduction in the environmental impact of the processes.

The Claus Catalytic Converters. These units represent the heart of any sulfur recovery plant. While the bulk of the sulfur yield may be obtained in the front end reaction furnace the high overall recovery levels demanded by environmental regulations are largely dependent on the efficiency of the Claus catalytic converters.

Recent developments in Claus converter efficiency can be divided into two categories; improvements in process operating technique and improvements in catalyst management.

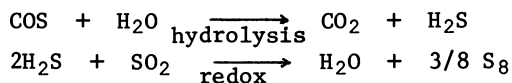
Paskall (25) has recently reviewed the various modifications to the Claus process that result in optimum sulfur recovery efficiency. Overall plant conversion efficiencies in the range of 97% were considered to be the upper limit at the beginning of the 1970's (26). While this is a very respectable conversion efficiency for an industrial process the unrecovered 3% in a 2,000 tonne/d sulfur plant represents 60 tonnes/d of sulfur lost, mainly to atmosphere as 120 tonnes/d of SO₂. Modifications to the four stage Claus converter train however, can raise overall conversions to over 98.5% thus halving the sulfur loss to the plant tail gas. This either reduces environmental impact or the load on tail gas desulfurization units that will be discussed later.

Among the most effective of the modifications to Claus operating procedure is accurate temperature control of the catalyst beds. Gamson and Elkins (27) in the early 1950's showed that equilibrium sulfur conversion efficiencies in the catalytic redox reaction rise dramatically as operating temperatures are lowered toward the dewpoint of sulfur. While some highly efficient sub-dewpoint Claus type processes are now in use the bulk of sulfur production from H₂S still requires that the converters be operated above the dewpoint. Careful control of converter bed temperature has, however, contributed to improved efficiencies. This has in large part resulted from better instrumentation of the Claus train and effective information feed back systems.

A major component of the 3% sulfur loss in earlier multi-stage Claus plants was entrained sulfur mist in the process gas stream. Precise control of interstage sulfur condenser tempera-

tures to ensure that the product liquid sulfur temperature is as low as possible without freezing has reduced sulfur vapor pressure and the amount of entrained sulfur mist. While it is often difficult to persuade operators to work with liquid sulfur at temperatures as little as 5 - 10°C above the freezing point, especially under quick chill winter conditions, the benefits in terms of reduced sulfur mist entrainment are quite noticeable in further reducing the already small sulfur loss. Interestingly, the control of liquid sulfur product temperature near the freezing point has become an important factor in maximizing the quality of the spherically formed sulfur products now being favored around the world (see Product section).

Elsewhere in this review we have commented on the problem of COS production as a result of high temperature reactions occurring in the front end furnace. Sulfur in this form is not subject to conversion to elemental sulfur in the catalytic redox Claus reaction and thus appears as COS in the tail gas where it is incinerated to SO₂ thus adding to losses to the environment. The COS and any CS₂ can be hydrolyzed to H₂S which can then be converted by the redox Claus reaction.



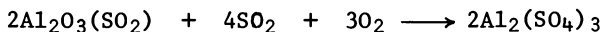
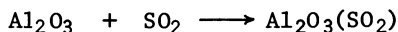
The hydrolysis reaction however, requires higher temperatures (650°F) than the optimum for the Claus redox. Nonetheless it has been clearly demonstrated in plant studies during the 1970's that running the first converter bed at this higher COS hydrolysis temperature and sacrificing some Claus redox efficiency that can be recovered in later beds does result in an improved overall sulfur recovery efficiency especially in four stage Claus converter systems.

During the 1970's there was considerable research activity in the further investigation and improvement of the Claus catalyst, its use and regeneration (21, 28-31). A better understanding of the nature of the active site in the alumina catalyst and its interaction with SO₂ and H₂S has resulted in recommendations for improved operating procedures and catalyst regeneration techniques.

Although there still remains some "art" in the production of high activity catalysts, surface area, pore size and other factors relevant to the accessibility of the reactant gases to the catalytic sites are clearly of primary importance. Thus any deposition of product or by-product within the catalyst pore structure is undesirable. In recent years the relationship between impure Claus feed containing hydrocarbons and catalyst lifetime has been well demonstrated (32). Carbon or hydrocarbon polymer deposition on the catalyst usually results in blocking access of the reactant gases to the internal catalytic sites. Product sulfur depos-

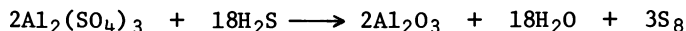
ition within the pore structure can also occur even at temperatures significantly above the dewpoint due, in part, to the capillary forces involved. Past practice has been to remove these deactivating deposits by so called "regenerative burn-off" where temperatures in excess of 600°C can be reached in the catalyst. It has been clearly demonstrated that extensive and irreversible damage to the catalyst can occur during such procedures and they have been largely replaced by the "heat soak" technique. In this procedure the inlet temperature to the catalyst bed is held at some 15 - 20°C above normal for several hours and it is generally effective in removing intrapore retained sulfur.

A major deactivating mechanism has been shown to be the sulfation of the active hydroxyl or oxide ion sites by chemical reaction with the chemisorbed SO₂ (29, 30).



It should be noted that the sulfation reaction requires the presence of oxygen. This serves to highlight the importance of air/acid gas ratio control in the front end furnace feed and the prevention of oxygen breakthrough into the catalyst beds. This can be of particular importance when oxygen enriched air feed is used in the front end reaction furnace (31).

Regeneration of the sulfated catalyst can be accomplished under reducing conditions as opposed to the previously practiced "regenerative burn-off" which is an oxidative process and probably generates sulfate on the catalyst. The reducing conditions required can be generated by going off stoichiometric ratio of the H₂S/SO₂ being fed to the catalyst and raising the temperature above normal Claus conditions (33). This generates a reducing, excess H₂S atmosphere which reverses the sulfation reaction.



Although the Claus catalytic conversion is a highly efficient process as presently employed in sulfur recovery plants the continuing efforts to reduce sulfur emissions to atmosphere demand that the last possible ounce of efficiency be squeezed from the process. Whether further small but critical improvements in the already high sulfur recovery efficiency can be achieved by more fine tuning of the converters and their catalyst charge remains to be seen. What cannot be accomplished in the catalytic converters will be achieved in the tail gas desulfurization processes.

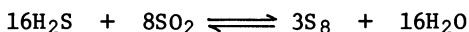
The Richard Process - A Claus Alternative? The Claus reaction process is by far the most common for recovering elemental sulfur from hydrogen sulfide. This heterogeneous gas phase catalysis over alumina of the redox reaction between H₂S and SO₂,

**American Chemical
Society Library
1155 16th St., N.W.
Washington, D.C. 20036**

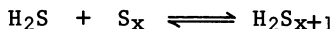
however, has a number of problems, some of which have been noted above. Although solutions to these problems are being found research effort has also been directed toward developing quite different reaction conditions for the redox reaction. One such development is the so called Richard Process (34) announced in 1980.

In this new process the $\text{H}_2\text{S}/\text{SO}_2$ reaction is carried out in liquid sulfur at pressures in excess of five atmospheres. Typical Claus catalysts are still employed but temperatures are lower (below the dewpoint of sulfur) and thus the redox reaction occurs in the liquid sulfur phase at the surface of the catalyst. Vapor losses due to sulfur mist entrainment are reduced and interstage condensers in the tradition Claus train are not required thus avoiding wasteful heat transfer problems. The authors claim that overall sulfur recoveries in excess of 99% are possible without the use of tail gas clean up units.

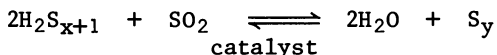
We believe that the key feature in this new process may be the presence of the liquid sulfur phase itself. Wiewiorowski (35) in 1969 showed that the redox reaction of H_2S with SO_2 proceeded smoothly in liquid sulfur in the presence of a base catalyst. One of the major thermodynamic barriers to the production of sulfur (S_8) at Claus reaction temperatures from molecules of H_2S and SO_2 is that the product molecule contains eight sulfur atoms and reagents only one each. Thus there is a considerable entropy barrier in building an S_8 molecule from the monothio-reagents. There is some evidence to suggest that the polythio S_8 chain is built up gradually on the surface of the catalyst via the intermediacy of hydrogen polysulfides (H_2S_x). When $x > 8$ the S_8 ring can break out from the H_2S_x . Thus there is no need for the entropically unfavorable simultaneous aggregation of all reactant species in a particular configuration as would be required by the minimum stoichiometrically balanced equation.



When the reaction medium is liquid sulfur, as in the Richard Process, the H_2S reactant can readily form hydrogen polysulfide e.g.



which can then undergo catalyzed redox reaction with SO_2 to form water and a new, larger sulfur molecule.

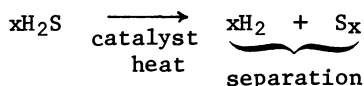


The presence of the liquid sulfur phase in the Richard process may favor the formation of the product liquid sulfur by aiding the formation of the intermediate hydrogen polysulfide building block. The success of a 5LTD demonstration plant may well determine whether future sulfur recovery from H_2S feed continues to be by

heterogeneous gas phase redox reaction or liquid phase in sulfur under pressure.

Direct Thermal Decomposition of H₂S. Sulfur recovered from the hydrogen sulfide removed from either natural or refinery gas streams is a useful and now valuable by-product. The hydrogen of the H₂S, however, has traditionally been converted to water yielding useful energy and an environmentally acceptable end product - water. The demand for hydrogen by the petrochemical and petroleum processing industries, however, continues to increase especially as hydrosulfurization of heavier crudes becomes more commonplace. Recovery of both hydrogen and sulfur from H₂S has thus been the subject of renewed investigation in recent years.

Work on the thermal decomposition of H₂S has been reported by several workers (36, 37, 38). The key to an effective economic process would appear to lie in finding an effective catalyst for the decomposition at readily accessible temperatures and a means for separating the products from each other at reaction temperature.



Kotera et al (37) have patented a technique that requires condensing out the product sulfur after each decomposition cycle. This involves significant temperature swings in the process. Raymont (36) has shown that hydrogen polysulfides may be important intermediates in the mechanism just as they appear to be in the redox reaction of the Claus process. Chivers et al (38) have explored the efficacy of a number of transition metal sulfides as catalysts and the prospects for fine tuning this all important catalytic role look promising.

While these recent developments have not as yet been fully commercialized the possibilities for producing two valuable chemical commodities rather than one from H₂S extracted from gas streams are encouraging.

Environment

The fact that sulfur recovery processes do not achieve 100% efficiency means that there is the potential for loss to the environment in the vicinity of the plant. Over the last decade there have been very significant improvements in the sulfur recovery efficiency of typical Claus processes but these have often been matched by increasingly restrictive regulations regarding maximum permissible emission of sulfur to the atmosphere. This has been especially true in densely populated urban areas with unusual meteorological conditions (e.g. the Los Angeles Basin) but even in rural settings concern regarding the long term

effects of acid rain have further heightened sensitivity to industrial sulfur emissions.

Sulfur values emitted to the atmosphere from a sulfur recovery plant are primarily in the form of sulfur dioxide. This results from the combustion of all plant tail gases in an incinerator before venting to atmosphere. Thus unconverted H_2S , CS_2 , COS and unrecovered sulfur vapor in the tail gas are largely oxidized to the common sulfur effluent SO_2 . Sulfur dioxide is also the form in which the sulfur content of many hydrocarbon fuels finally reach atmosphere after combustion. Technologies for the removal of SO_2 from flue gases have therefore received a great deal of attention during recent years (39) but more in regard to fuel combustion effluent desulfurization than in connection with sulfur recovery plants.

Recent developments in desulfurizing the effluents from sulfur plants have concentrated on the plant tail gas before incineration. This avoids the further dilution of the effluent stream with nitrogen from air used as the oxidant and many of the sulfur values are still in a reduced or at least unoxidized state.

High Efficiency Claus Reactions. One of the earliest commercial processes for tail gas desulfurization was the Sulfreen Process developed by Lurgi and SNPA and first introduced in 1970 (40) as a retrofit to SNPA's two stage Claus unit in Lacq, France. The first North American unit was installed at Aquitaine Canada's Ram River plant in Alberta (41). The Sulfreen units raised the overall sulfur recovery in these two-stage Claus units to over 98% comparable to the well tuned 4-stage Claus converter trains discussed previously. The principle upon which the Sulfreen units are based is the high equilibrium conversion possible in the Claus redox reaction at temperatures below the dewpoint of sulfur. Catalyst used is now alumina although earlier versions of the process employed activated carbon. Because of operation below the sulfur dewpoint the catalyst becomes loaded with sulfur from the redox reaction between the low concentration H_2S and SO_2 in the tail gas and reactors are sequentially taken out of service for heat soak regeneration to remove sulfur. Sulfur concentration levels of 2,000 ppm (0.2%) at the stack mouth are possible using the Sulfreen process.

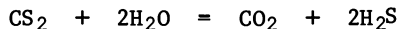
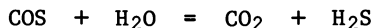
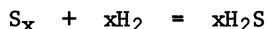
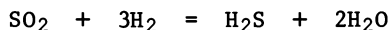
Using essentially the same sub-dewpoint Claus reaction principle the Cold Bed Absorption (CBA) process of Amoco (42) achieves the same level of tail gas desulfurization. The low temperature high efficiency swing converters can be in line rather than as a tail gas clean up add on unit.

These developments and similar tail gas desulfurization processes based on the Claus such as the Bumines Citrate (43) IFP (44) and Clean Air (45) processes are simply methods for forcing the Claus redox reaction of the upstream converter units further to completion. Thus they increase sulfur recovery from H_2S and

SO₂ components of the process gas stream. None, however, directly attack the problem of removal of other sulfur values in the gas such as CS₂, COS and entrained sulfur mist. These sulfur components can easily exceed 1% of the total sulfur feed and failure to remove them from the process stream can frustrate any attempt to achieve 99%+ recovery even when the Claus reactants, H₂S and SO₂, have been reduced to low ppm levels.

Reductive Tail Gas Treatments. It was largely as a result of the effort to achieve better than 99% recovery that the reductive tail gas desulfurization processes (46) were developed in the 1970's. The two main methods are the Beavon Sulfur Removal (BSR) (47) and the Shell Claus Off-Gas Treatment (SCOT) (48) processes. Both of these processes are now widely used as tail gas desulfurization units on sulfur recovery plants and can readily achieve point source emission levels below 250 ppm and below 100 ppm if necessary to meet regulatory standards.

The first step in these highly efficient reductive tail gas processes is the reduction or hydrolysis of all sulfur values to H₂S i.e.



The reactions are catalyzed by cobalt-molybdate and utilize existing H₂ in the process gas stream that is formed by thermal cracking in the front end furnace, or make up hydrogen from water shift, methane reforming or the like. The conversion of all entrained sulfur values to H₂S is highly efficient. In the BSR process the hydrogen sulfide is then treated by the Stretford Process (49) which involves oxidation to elemental sulfur using aerobic oxygen in a series of complex steps involving anthroquinone disulfonic acid and vanadate ion redox couples. Although the solution oxidation process is a complex one there is virtually no limit to the degree of sulfur removal attainable. In the SCOT process the hydrogen sulfide from the reduction step is absorbed and concentrated in a traditional alkanolamine scrubbing process, regenerated by heat and returned to the Claus acid gas feed stream.

More recently the BSR process has been modified by coupling to the Selectox step (50). This replaces the complex Stretford by directly oxidizing some of the produced H₂S to SO₂ at low temperature over the new proprietary Selectox-32 catalyst. The SO₂ and H₂S then react to form sulfur in the traditional Claus redox reaction. While overall conversions by the BSR/Selectox are somewhat less than that possible with the BSR (Stretford), values of 99.8% are claimed.

The recovered sulfur industry exists primarily as a result of the necessity of removing sulfur values from hydrocarbon fuels before combustion so that sulfur emissions to atmosphere are reduced. In the case of sour gas, the principal source of recovered sulfur, the product that results from recovery of the sulfur is clean-burning, non-polluting methane. In the case of refineries handling high sulfur crude the product is low sulfur gasoline and oils. Thus every ton of sulfur recovered is a ton that is not added to the atmosphere. The recovery process itself however, is also the subject of optimization and recent developments in recovery efficiency have further ensured that the environmental impact in the immediate vicinity of these desulfurization facilities will be minimized.

Product

Recovered elemental sulfur is one of the purest bulk commodities available on the market today. Typical analyses quoted for bulk shipments are 99.95% purity with ash, carbon and other contaminant levels in the 10 - 100 ppm range. This is a remarkably pure bulk commodity for a 5¢/lb price. What then remains to be developed by way of improvement of product quality?

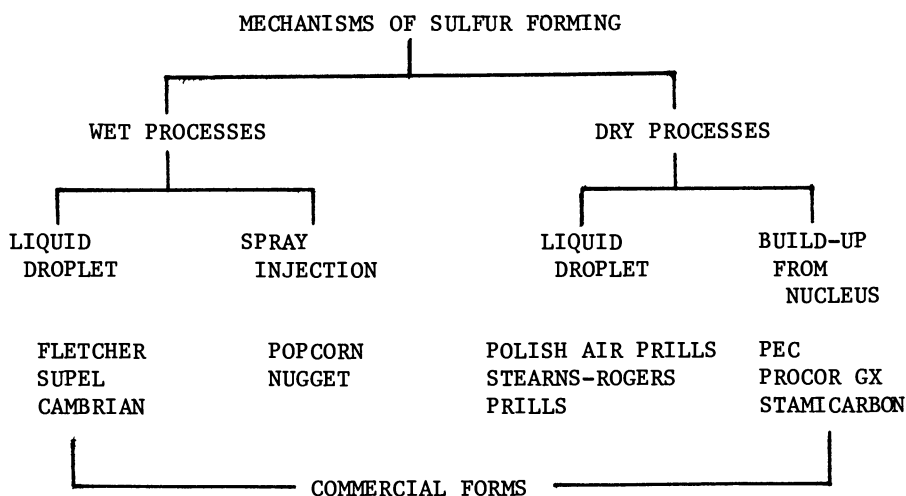
While a significant portion of the elemental sulfur moving in world trade is handled, shipped and stored in the liquid form, the bulk of the export shipments, especially from Canada, Poland and soon from Saudi Arabia, move in the solidified state. The last decade has seen some important changes in the form of the solidified sulfur partly to improve handling characteristic but, more importantly, to minimize environmental impact.

Slated Sulfur. Until the late 1960's solid elemental sulfur was recovered from stockpile blocks by excavation (front end loaders, bull dozers, etc.) and shipped in the resulting "crushed bulk" form. In open railroad gondola cars and exposed stockpiles at transfer points, the dust associated with the crushed bulk form was generally regarded as environmentally undesirable. By the late 1960's or early 1970's, the slated form of solid sulfur had been widely adopted throughout the world for the storage and transportation of the element and resulted in significant improvements in environmental impact. Formed by cooling and solidifying a thin sheet of liquid on a water cooled moving belt the fresh slate did indeed have a resistance to breakdown that resulted in reduced dust formation, but after ageing the essentially two dimensional solid form was still quite a friable material.

New Forms. Even at the time of introduction of slate it was recognized that the best geometric form for friable solid sulfur was a spherical particle enclosing maximum volume in minimum surface area and with least opportunity for fulcrum effects to increase rupture forces. A number of methods for forming liquid

sulfur into solid spherical or pseudo spherical particles were devised and during the 1970's extensive testing and evaluation of these forms was carried out (51). The Canadian industry also established "premium product" specifications which attempted to identify minimum values for certain critical properties of the formed material. These included friability as measured by standardized tumbling tests, angle of repose (storage factor), flowability, uniformity, water retention and the like. By the late 1970's the many entries in the sulfur forming field had been reduced to a few prime candidates. Some of these together with the general features of the process by which they are made are noted in Table II.

Table II



The new sulfur forming processes can be classified into two primary categories - wet processes using water as the cooling medium for the liquid sulfur and dry processes in which air is the heat sink into which the liquid sulfur heat flows during solidification. Although the wet processes are inherently simpler and less capital intensive the product retains considerable amounts of water which makes it less attractive to customers and introduces some corrosion problems. The wet product can, of course, be dried but the additional costs involved make large scale drying a less attractive proposition.

Premium Products. By the late 1970's two dry process forms, Polish Air Prills and Procor GX granules were emerging as the front runners in the premium product stakes. Although air is the common heat sink in both of these processes the mechanism of

formation is very different. The Polish Prill (52) developed in the late 1960's at the Polish sulfur mining center of Tarnobrzeg, is a modified air prilling technique similar to those developed for urea and other fertilizer materials. A spray of liquid droplets flows downward counter current to an upward flow of cooling air solidifying the droplets into spherical particles. Because the solidification occurs from the outside inward and because solid sulfur has a smaller specific volume than liquid the solidifying sphere tends to collapse inward on itself and a small hole often develops leading into a more crystalline (slow inner cooling) hollow centre. Provided the outer shell is well formed and amorphous the small (1.5 - 3.5 mm diameter) prill has excellent resistance to rupture. The key feature of the prilling process is the avoidance of supercooling of the liquid droplet during its decent through the prilling tower. This is achieved by ensuring that the upward flowing air contains nucleating sulfur dust which impacts on the liquid sulfur droplets and initiates solidification.

The Procor granulating process (53) operates on the principle of sequential build up of layers of sulfur on to a seed nucleus. A rotating granulating drum with the axis at a slight angle carries the growing particles several times through a spray of liquid sulfur as the particles move down the inclined axis of the drum. Each application of liquid sulfur increases the size of the granule until the desired diameter is achieved. Crucial to the quality of the resulting granule is the bonding between successive layers of the sulfur. This requires accurate control of temperature and time interval between applications to ensure that each subsequent liquid sulfur application has sufficient heat content to fuse effectively on to the precursor surface. If this is not achieved the product has onion skin properties and fractures by spalling.

Both processes are now in use in Canada as well as elsewhere in the world. European and South African sales have been negotiated for Procor GX and the Polish Air Prill has been selected for installation in Saudi Arabia. The products represent a very significant improvement in dust suppression in the handling, storage and transportation of solid elemental sulfur and while the processes require careful fine tuning and operational monitoring they are clearly another contribution to the improvement of the environmental impact of the recovered sulfur industry.

Conclusion

The recovered sulfur industry has come of age in the last two decades and is now a major world source of this essential element. Much progress has been made in the improvement of various process steps, particularly those related to overall recovery efficiency. These improvements continue to reduce undesirable process losses to atmosphere and the environmental impact of the industry. As

society's continued demand for hydrocarbon fuels forces greater utilization of higher sulfur containing sources the sulfur recovery industry will grow in both size and importance but the industry will continue to try to meet the dual goals of energy sufficiency and environmental protection.

Literature Cited

1. Newton, B.F., Hydrocarbon Processing, 1978, Jan., 1981-184.
2. Oil & Gas J. Newsletter, 1978, Mar.
3. Kennedy, H.T., Wieland, D.R., Petrol. Trans. AIME, 1960, 219, 166.
4. Brunner, E., Woll, W., BASF.AG. WAA D-6700, 1977, Ludwigshafen, W. Germany.
5. Hyne, J.B., Oil & Gas J., 1968, Nov., 107-133.
6. Kur, C.H., J. Pet. Tech., 1972, 1142.
7. Lubben, H., Proc. World Pet. Congress, 1975, 389-399.
8. Hyne, J.B., Derald, G.D., World Oil, 1980, Oct., 111-120.
9. Lyle, F.F., Lechler, S., Brandt, J., Blount, F.E., Snavely, S.E., Materials Performance, 1978, 17 (1), 24.
10. Adams, N., Oil & Gas J., 1980, Mar. 3, 55-62.
11. Mehdizakeh, P., McGlasson, R.L., Landers, J.E., Corrosion, 1966, 22, 325-334.
12. Bernhardsson, S.O., Oredsson, J., Tynell, M., Corrosion/80 (NACE), 1980, Mar. 3-7, Chicago, Paper #14.
13. Herbsleb, G., Corrosion/80 (NACE), Mar. 3-7, Chicago, Paper #13.
14. Asphahani, A.I., Corrosion/80 (NACE), Mar. 3-7, Chicago, Paper #12.
15. Place, M., Soc. Pet. Eng., Sept. 1979, 54th Annual Tech. Conf., Las Vegas SPE 8310.
16. Leonard, J., World Oil, Dec. 1980, 109-112.
17. Vidaurri, F.C., Kahre, L.C., Hydrocarbon Processing, Nov. 1977, 333-337.
18. Goar, B.G., Oil & Gas J., May 5 1980, 240-242.
19. Hyne, J.B. Gas Proc./Can., Mar. April. 1972, 12-16.
20. Kerr, R.K., Berlie, E.M., Energy Proc./Can., 1977, 69 (5), 42-46.
21. Grancher, P., Hydrocarbon Processing, Sept. 1978, 258-262.
22. Hamilton, T., Mathes, A., Little, M., Strong, C., Oilweek, Jan. 1976, 39-40.
23. Beamish, M., Oilweek, 1978, 28, 28-40.
24. Saltzman, R.S., Hune, E.B., ISA Transactions, 1973, 12, 103-107.
25. Paskall, H.B., Capability of Modified Claus Process, Dept. of Energy and Nat. Resources, Alberta Report, published by Western Research and Development, March 1979.
26. Chalmers, W.W., Becker, H.W., Rankine, R.P., Pacific N.W. Air Pollution Assoc. Mtg., Calgary, Nov. 1971, Paper 71-AP-8

27. Gamson, B.W., Elkins, R.H., Chem. Eng. Progress, 1953, 49, 213-215.
28. Pearson, M.J., Hydrocarbon Processing, Feb. 1973, 81-85.
29. Dalla Lana, K.G., Energy Proc./Can., Mar. Apr. 1978, 34-38.
30. Graulier, M., Papee, D., Energy Proc. Can., Mar.-Apr. 1974.
31. Gray, M.R., Svrcek, W.Y., Gas Conditioning Conference, University of Oklahoma, Norman, Oklahoma, March 2-4, 1981.
32. Norman, W.S., Gas Conditioning Conference, March 1976, Norman, Oklahoma.
33. Goar, B.G., Hydrocarbon Proc., July 1974, 129-132.
34. Jagodzinski, R.F., Kerr, R.K., paper Can. Soc. Chem. Eng. Conf., Sept. 1980, Edmonton, Alberta.
35. Wiewiorowski, R.K., U.S. Patent #3,447,903, 1969.
36. Raymont, M.E.D., Hydrocarbon Proc. 54, 1975, 139 and Ph.D. Thesis, Univ. of Calgary, 1974.
37. Kotera, Y., Int. J. Hydrogen Energy, 1976, 1, 219 and U.S. Patent 3,962,409, 1976.
38. Chivers, T., Hyne, J.B., Lau, C., Int. J. Hydrogen Energy, 1980, 5, 499-506.
39. Hyne, J.B., Oil & Gas J., Aug. 1972, 64-67.
40. Guyot, G., Martin, J.E., Paper Can. Nat. Gas Proc. Assoc. Mtg., June 1971, Edmonton, Alberta.
41. Morin, M.M., Philardeau, Y.M., Energy Proc./Can., 1977 69, (5), 30-40.
42. Goddin, C.S., Hunt, E.B., Palm, J.W., Hydrocarbon Proc., 1974, 53, (10), 122-124.
43. Madenberg, R.S., Seese, T.A., Chem. Eng., July 14, 1980 and Chem. Eng. News, June 14, 1971.
44. U.S. Patent, 3,598,529, Aug. 10, 1971.
45. Thomas, G.L., Plum, E., Paper 71st National AIChE Mtg., Feb. 1972 20-23.
46. Semrau, K., Advances in Chem., Series #139, 1975, 1-21.
47. Beavon, D.K., Fleck, Advances in Chem., Series #139, 1975, 93-99.
48. Swaim, D.C., Advances in Chem. Series #139, 1975, 111-119.
49. Beavon, D.K., Ellwood, P., Chem. Eng., July 1964, 128.
50. Beavon, D.K., Hass, R.H., Muke, B., Oil & Gas J., Mar. 12, 1979, 76-80.
51. Hyne, J.B., Hydrocarbon Proc., Apr. 1977, 125-128.
52. Leszczynska, H., Sulphur #132, Mar. Apr., 1976, 44-46.
53. Procor Sulphur Services Division, Procor GX Process Description, 5622 Burleigh Cres., S.E., Calgary, Alberta.

RECEIVED October 5, 1981.

Claus Processing of Novel Acid Gas Streams

DAVID K. BEAVON

The Ralph M. Parsons Company, Pasadena, CA 91124

BERNARD KOUZEL and JOHN W. WARD

Union Oil Company of California, Brea, CA 92621

Plants to produce low-sulfur fuels from coal, oil shale, tar sands or heavy oil frequently are conceived to use the Claus process to produce byproduct sulfur. Often the plant concept imposes unacceptable technical burdens on the Claus section. This paper points out some of the problems, and some solutions. In particular, the paper discusses a Claus type process recently developed with special application to coal and oil gasification plants. The new Selectox process can achieve ninety-five percent conversion of hydrogen sulfide even though the initial H_2S concentration is below the level previously feasible for Claus processing. The effects of various minor components of Claus feed are discussed.

Plants to process alternate sources of energy will make low-sulfur fuels from high-sulfur feeds such as coal, oil shale, tar sands, or heavy oil. Elemental sulfur will be a normal byproduct. Nearly all processing schemes first produce H_2S from the sulfur compounds in the raw material, and then convert H_2S to elemental sulfur. Usually this conversion step is labelled "Claus Process".

Currently there is great interest in alternate fuels manufacture, and plant configuration studies are published by the dozen. Such configurations usually include a "Claus process" box; all too often the material fed into the box could not be handled by any known Claus-type process. This paper is meant to point out some of the problems needing recognition, and some of the solutions. One solution is a new process suited to some coal gasifiers.

Out of several alternate energy sources, coal has been chosen for discussion in order to simplify what can be a very complex subject. Coal gasification, in particular, involves most of the prominent problems.

0097-6156/82/0183-0057\$05.00/0

© 1982 American Chemical Society

In a coal gasification plant, the "Claus" unit is nearly the last in a chain of process steps, and the foregoing steps can have a major effect on the Claus in a number of ways. Most of this paper will be examining the kind of Claus feed, but at the outset we should note that a Claus plant is sensitive to variations in feed rate, and that relatively minor ups and downs in upstream units will tend to amplify into wild fluctuations in the Claus plant. Accordingly our Claus-type plant should be inherently stable, if possible, able to ride through large changes in feed rate as well as composition.

This paper will take note of a number of troublesome components of Claus feed, including olefins, CO₂, ammonia, cyanide, and COS. Proper management of these components usually requires thoughtful selection of preparatory process steps as well as the Claus step itself.

Gasifier Products

Although there are at least a dozen kinds of coal gasifiers, for our purposes we will divide them into two types: high-temperature entrained, and low-temperature pyrolizers. Gases from the high-temperature units contain essentially no hydrocarbons except a trace of methane. In contrast, the pyrolizers produce a range of hydrocarbons including light olefins and aromatics, which tend to follow hydrogen sulfide into Claus plant feed, with undesirable consequences.

The gas from either type of gasifier contains H₂, CO, and CO₂. About 95 percent of the sulfur is present as H₂S, and the balance as COS. Other minor components include NH₃ and HCN. Carbon and ash are always present, and pyrolizers also produce oils, tars and water-soluble organics. Small quantities of oxygen, SO₂, and nitrogen oxides also may be present.

Usually the gas is water-quenched to remove solids and tars. Ammonia, HCN, H₂S dissolve in the water and high CO-content gas at high pressure may produce some formic acid. Purification of quench water contributes secondary Claus feeds, as will be seen.

Direct Desulfurization of Gas

Since both H₂S and CO₂ are acidic, they tend to come out together as mixed "acid gas" when the gas is washed to extract H₂S. Various other compounds, including COS, may be extracted at the same time. Extraction of acid gas may not be needed if the treated gas is to be used only as fuel; it may be sufficient to treat the raw gas by the Stretford process, converting H₂S directly to sulfur. Such treatment removes virtually all H₂S but leaves COS in the fuel gas, which may be unacceptable if air pollution regulations require more than about 95 percent removal of total sulfur.

The Stretford process has the defect of converting a small part of the input H₂S to thiosulfate, leading eventually to a

purge of solution from the unit. The Unisulf process, similar to Stretford, has been developed to avoid thiosulfate formation and essentially eliminate purge; it is offered by Union Science and Technology Division of Union Oil Company of California.

Applying the Stretford or Unisulf processes usually means there is no need for a Claus process. These processes are especially suited to small applications where complete removal of H_2S is sufficient and removal of COS is not needed.

Acid Gas Removal Followed By Claus

When the gasified coal is to be used for synthesis of methane, methanol, or hydrogen, part or all of it is subjected to the water-gas shift reaction, converting CO and water to CO_2 and H_2 . Sulfur must be removed completely. The acid gases H_2S and CO_2 are first extracted from the gas before or after the shift conversion; these acid gases may be processed in a second step in a Claus unit. The acid gas composition depends on each part of the sequence preceding the Claus unit.

The major acid gas component is CO_2 , which is dead weight in a Claus plant but usually makes up 80 percent to 95 percent of the acid gas, while most of the remainder is H_2S . Relatively more CO_2 is produced from lower sulfur coals, or higher temperature gasifiers, or by shifting before acid gas extraction.

Since pyrolyzing gasifiers yield olefins and aromatics in the raw gas, these compounds tend also to occur in the acid gas stream. Physical solvent processes for acid gas extraction, such as cold methanol wash, especially tend to take hydrocarbons into the acid gas stream; water solutions have less tendency to do so.

High CO_2 Acid Gas

The proportion of CO_2 to H_2S in Claus feed is a major factor in Claus design. If the H_2S concentration is at all times 40 percent or higher, the flame in the thermal reactor is hot enough to be self-sustaining; complex organics can be converted completely to simple gases such as COS. Tars are not formed to foul the catalyst and make dark sulfur. But with more CO_2 in the feed, the flame temperature is inadequate to destroy complex organics, tars are formed, and the fire is in danger of going out.

To circumvent such problems, up to two-thirds of the acid gas has been removed from the flame and sent directly to the catalytic reactor, the so-called "long bypass" scheme. This strategy has worked with mixed success in natural gas plants, where hydrocarbons in the acid gas are C_1 - C_3 paraffins, chiefly methane, and no olefins. Such a configuration has been put forward for use in coal gasification plants. In the writer's opinion it is unworkable if the bypassed acid gas contains even traces of olefins or aromatics; these compounds react with SO_2 to form tarry products which foul the catalyst and discolor the product sulfur.

Thus the combination of olefins (in trace quantities) with a high concentration of CO_2 in the acid gas may make a Claus-type process unusable. The path of least resistance may be to use the Stretford or Unisulf process, which tolerate both CO_2 and olefins.

Enrichment of Acid Gas

An alternate path is two-stage extraction of acid gas, the first stage to separate virtually all the H_2S in 40% concentration to feed to straight-through Claus. The second stage separates CO_2 lean enough in H_2S to permit incineration; some examples applicable to treating sour natural gas have been published (1). Usually two distinct acid gas removal plants are needed, back-to-back; these may or may not use the same extraction solvent. To meet U.S. pollution standards with the vented CO_2 may require so much co-absorption of CO_2 with H_2S that attainment of 40% H_2S concentration in the first treating step is very costly or impossible. In any case, acid gas enrichment is an expensive business.

Practical Process Combinations

Figure 1 illustrates the practical combinations of known processes. With low CO_2 acid gas, and only methane as impurity, the conventional Claus process may be used if the reaction furnace is designed to assure complete conversion of hydrocarbons to simple compounds such as COS and H_2S .

In another case, when the acid gas is very rich in CO_2 (i.e. 90 percent or higher) and contains olefins, the author knows no suitable process other than Stretford or Unisulf. An example is Rectisol offgas downstream of a Lurgi gasifier; the Stretford process has been used, although with some problems.

As illustrated in Figure 1, there is another kind of acid gas which promises to be important industrially, i.e. high CO_2 with methane the only hydrocarbon. Such acid gas will be extracted from coal gasified in a high-temperature entrained process. Olefins are not present to form tarry matter blocking catalyst and contaminating sulfur; but the normal Claus process cannot be used because H_2S is too lean to support combustion. It is the judgement of the authors that the borderline for applying the conventional Claus process is an ill-defined area between 30 and 40 percent H_2S , in which one needs to consider the stability of all upstream operations, the range of possible coal feeds, the size of plants involved, and so forth.

A bypass type Claus plant, with fired preheating of acid gas and air, has been advocated by some for use in coal conversion plants, for acid gases containing 20 percent H_2S or less. The authors think this an unwise choice for synfuels plants, even though it can be a good choice for other purposes. Several preheat-bypass Claus plants (of nominal capacity about 1,000 tons

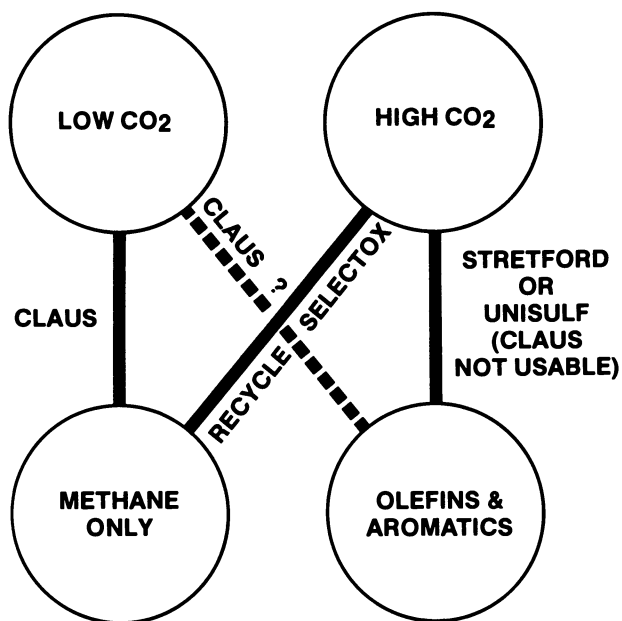


Figure 1. Sulfur processes for separated acid gas.

Publication Date: March 29, 1982 | doi: 10.1021/bk-1982-0183.ch004

daily) have been started recently, processing 20 percent H_2S in CO_2 . These plants perform very well, because of advantages which will not be shared by a synfuels Claus plant; their acid gas has very uniform composition, and may be diverted to flare without serious penalty in case of upset; very cheap high-quality fuel gas is used to fire the preheaters; a complete standby Claus plant is provided; should plant efficiency decline, no serious penalty would be exacted. Pleased as we are with the performance of these plants, we consider them unsuitable for synfuels installations.

Selectox Process

On the other hand, there is a newly-developed process we consider especially suited to handling acid gas containing up to 99 percent CO_2 but free of olefins; this is the Selectox process, which was described to the October, 1980 joint meeting of the American and Mexican Institutes of Chemical Engineers. This is derived from the BSR/Selectox process which has now been working for three years converting 1 to 2 percent H_2S in a Claus tail gas process. Figure 2 is a photograph of the plant of Wintershall, A.G. at Lingen, West Germany, described previously(2).

Selectox catalyst was developed to oxidize H_2S to sulfur and SO_2 in the presence of hydrogen, paraffin hydrocarbons or ammonia. The latter compounds are effectively inert at temperatures which allow complete oxidation of H_2S . Figure 3 shows the direct oxidation section of the Lingen plant. About 80 percent recovery of sulfur is achieved, even though the initial concentration of H_2S is only 1 to 2 percent.

The same catalyst can be applied to higher concentrations of H_2S . All the heat of reaction of H_2S to form sulfur or SO_2 is released in the Selectox reactor; in the configuration of Figure 3 the outlet temperature approaches the maximum we think desirable with a 5 percent concentration of H_2S in the feed gas.

With more than 5 percent H_2S , the configuration of Figure 4 is used to provide temperature control. Spent gas is recycled through the Selectox reactor to keep its temperature in a desirable range. One or more single-pass Claus reactors may follow the Selectox reactor, using Selectox or alumina catalyst.

It is convenient that the normal temperature leaving the recycle blower coincides with the desired Selectox reactor inlet temperature. Thus the recycle acts as a thermal flywheel, keeping the Selectox reactor in condition to convert H_2S even though its fresh feed may be temporarily slowed or made too lean. We expect the process to be very stable. Union and Parsons are confident of the new process, based on experience at Lingen and extensive pilot unit work, and we expect that design of the first commercial plant will be underway by the time this paper is presented.

The Selectox catalyst suffers activity loss when non-paraffin

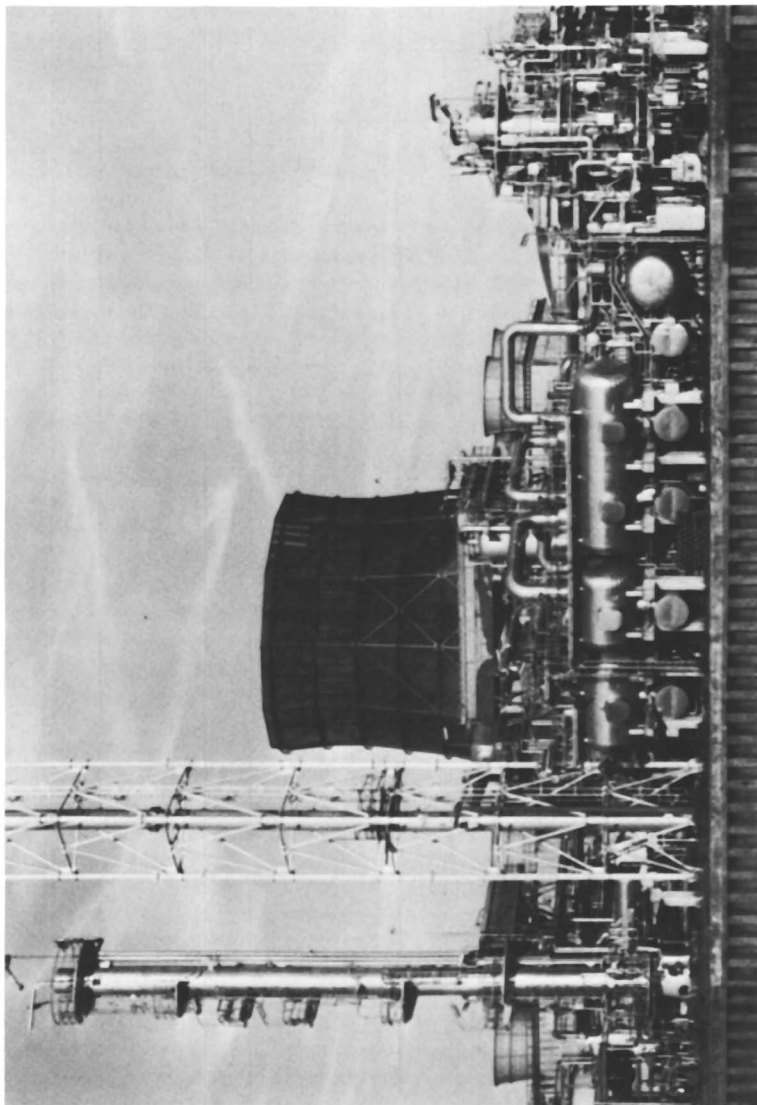


Figure 2. Claus plant with BSR/Selectox tail gas treatment.

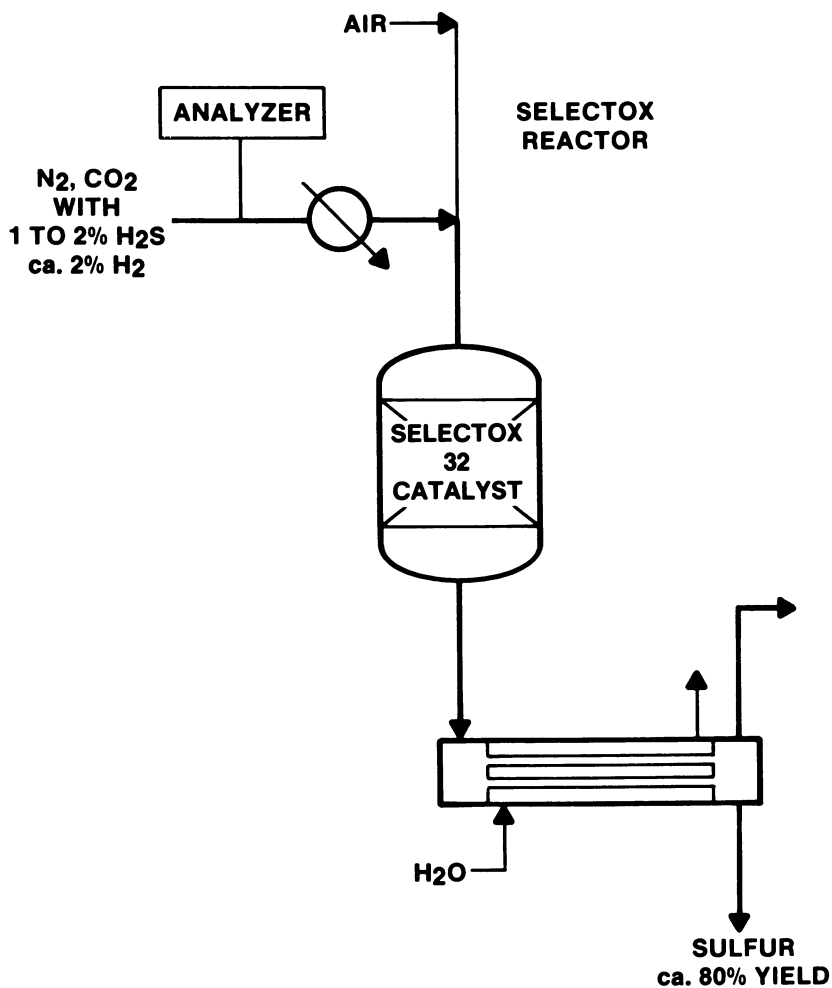


Figure 3. Direct oxidation section of BSR/Selectox plant.

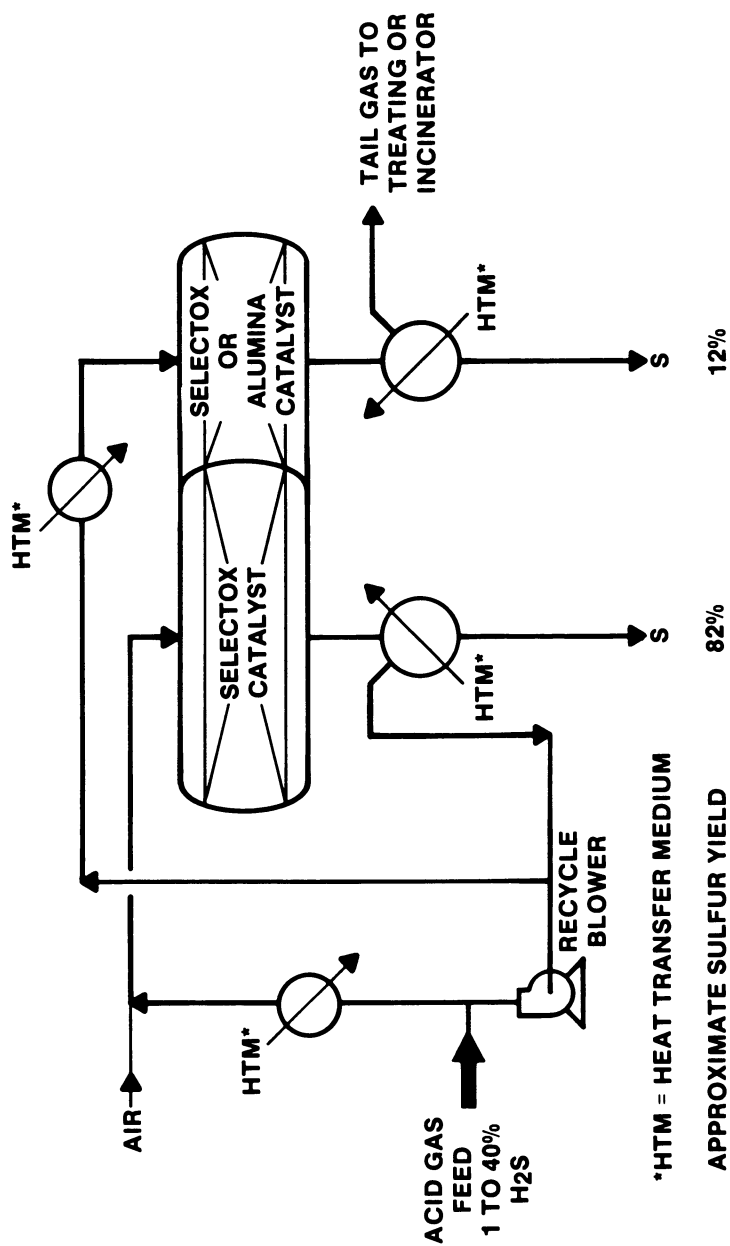


Figure 4. Two-stage Selectox process with recycle.

hydrocarbons are included in the feed; removing the contaminants allows activity to return to normal, at least in some cases. Inclusion of olefins in the feed is not recommended, hence the process probably does not fit downstream of a pyrolyzing type coal gasifier.

The overall sulfur recovery achievable by the recycle Selectox process increases with higher H_2S concentration and with the number of catalytic stages used. We may expect 94 to 95 percent recovery from 10 percent H_2S feed with three catalytic stages; 96 to 97 percent recovery should be had from 20 percent H_2S feed.

Carbonyl Sulfide

COS usually constitutes about 5 percent of total sulfur in the gasified coal. Passing over the complex problem of extracting COS from the gas, its conversion to sulfur in the Claus unit requires some attention. It is best hydrolyzed to H_2S , then converted to sulfur. Alumina Claus catalyst is effective for hydrolysis at above $650^{\circ}F$, and promoted catalysts are said to be effective at still lower temperatures.

Gases Stripped From Process Water

Ammonia evolved in coal gasification usually is washed out with water, taking with it H_2S , CO_2 , and HCN . Phenols and basic nitrogen compounds are also present if a pyrolyzing gasifier is used. Such water usually is purified by steam stripping, which liberates a vapor mixture of NH_3 , H_2S , CO_2 with some HCN . Usable ammonia may be separated by fractional distillation (the WWT process) or by differential absorption (the Phosam process); in these cases a rich H_2S is prepared for Claus processing.

In most similar activities in petroleum refineries, the vapors from stripping "sour water" are processed in a Claus plant. With care in design and operation of the stripper, the vapors typically consist of equal volumes of H_2S , NH_3 and H_2O . Such a mixture can support high-temperature reducing flame in which NH_3 is destroyed.

Virtually complete destruction of NH_3 is required; otherwise ammonium sulfate forms in downstream equipment, blocking condenser tubes and sulfur piping. If the NH_3 is oxidized to form appreciable amounts of nitrogen oxides, SO_3 also forms and contributes to blocking as well as causing deactivation of Claus catalyst by sulfation. Therefore, the ammonia destruction step is best carried out within a narrow range of conditions(3). Any cyanide in the vapors is also destroyed under the conditions recommended.

Hot gases from the ammonia destruction step contain nitrogen, a trace of residual NH_3 , as well as H_2 , H_2S , SO_2 and sulfur vapor. With proper design these gases can be fed into a Claus type process to make sulfur. If the latter process uses Selectox catalyst,

any SO_3 formed by excess air in the NH_3 destruction step will do minimal harm, as Selectox catalyst is immune to sulfation.

Vapors from stripping process condensate may contain phenols and oil matter. With proper design these compounds can be oxidized completely to CO_2 and CO . Incomplete oxidation leads to formation of tars which can block Claus catalyst beds.

Claus Tail Gas Processing

Since the Selectox process is capable of well over 90 percent sulfur recovery, the authors recommend a careful cost-benefit study to see if Claus tail gas processing should be required with such plants. It might well be found that--say--95 percent capture of sulfur in the coal conversion plant is acceptable.

If sulfur capture must be greater than 95 percent, then treatment of Claus or Selectox tail gas will be required.

To meet refinery-style recoveries, there are few choices available. The tail gas must be hydrogenated, with resulting H_2S recovered in one of several ways. The Beavon Sulfur Removal Process(4) achieves almost total sulfur recovery, using the Stretford process; it is energy-efficient because incineration of the tail gas is not needed. The BSR/MDEA process, which uses methyldiethanolamine to extract H_2S from hydrogenated tail gas, becomes more expensive with low-strength acid gas, and incineration of large quantities of effluent CO_2 becomes costly. The BSR/Selectox tail gas process is a possibility if less stringent requirements are set.

Conclusion

Plants to produce low-sulfur fuels from coal, oil shale, tar sands or heavy oil frequently are conceived to use the Claus process to produce byproduct sulfur. Using coal gasification as an example, it is seen that the conventional Claus process is not well suited to the usual problem of processing H_2S at a concentration of 20% or lower. A new process, recycle Selectox, is very suitable to process H_2S in concentrations up to 40%, provided the acid gas is free of olefins; up to 95% recovery is possible, even with very dilute feed.

Ammonia, H_2S , HCN , phenols and oily matter commonly are stripped from process water and then are processed in by partial oxidation under carefully chosen conditions to produce a gas suitable for further Claus processing.

Environmental regulations may force the "Claus" sulfur recovery to exceed 99%, requiring tail gas treatment. High CO_2 in the original Claus feed, hence in the Claus tail gas, works strongly against the tail gas processes which use amine solution to extract H_2S , and subsequently require incineration of residual H_2S in a large volume of CO_2 .

Literature Cited

1. Goar, B. Gene, "Selective Gas Treating Produces Better Claus Feeds"; Oil and Gas Journal May 5, 1980, 78.
2. Beavon, D. K.; Hass, R. H.; Mike, B., "High Recovery, Low Emissions Promised for Claus-Plant Tail Gas"; Oil and Gas Journal March 12, 1979, 77 (11).
3. U. S. Patent 3,970,743.
4. Beavon, D. K.; Fleck, R. N., "Beavon Sulfur Removal Process for Claus Plant Tail Gas"; Sulfur Removal and Recovery from Industrial Processes 1975, Advances in Chemistry 239.

RECEIVED October 5, 1981.

Sulfur Recovery from Oil Sands

A. W. HYNDMAN, J. K. LIU, and D. W. DENNEY

Syncrude Canada Limited, PO Box 5790,
Postal Station L, Edmonton, Alberta, Canada T6C 4G3

Syncrude Canada Limited has been producing synthetic crude oil from the Athabasca oil sand deposit since 1978. In place reserves of this deposit are estimated at $118 \times 10^9 \text{ m}^3$. Oil sands in this deposit have bitumen saturation up to 18 w/w% and average 10-12%. The bitumen is a heavy oil, API gravity 8.3, characterized by high sulphur, 3.5-5.0 w/w%. Chemical and physical modifications during recovery produce a synthetic crude with API gravity in the 30-35 range with less than 2000 wppm sulphur.

At design capacity, 20,500 m^3 /day of synthetic crude, Syncrude's Upgrading facilities will process 28,000 tonnes of bitumen containing 1375 tonnes sulphur. The sour water and sour gas streams are treated individually to produce H_2S rich streams as sulphur recovery unit feed. More than 96% of sulphur entering the recovery unit is recovered as elemental sulphur which is in a molten state for shipment. Recovered sulphur as a by-product represents less than 1% of synthetic crude value.

Coke burner off-gas and sulphur recovery unit tail gas are incinerated in CO boilers to convert all forms of sulphur to SO_2 before emission. Syn-crude's Upgrading is designed so that no more than 292 tonnes SO_2 /day leave the 180 m stack ensuring ground level concentrations prescribed by Alberta Clean Air Regulations are not exceeded. This represents a minimum 89.4% containment of incoming sulphur feed. Regulation compliance is recorded by stack monitors, five continuous and forty static ground level stations. Minute readings from the stack monitors and continuous ground level monitors are transmitted to the Data Acquisition Centre. Violations must be documented and reported to Alberta Environment within 72 hours. Monthly and yearly summaries must also be filed.

0097-6156/82/0183-0069\$05.00/0

© 1982 American Chemical Society

In addition to conventional crude oil and natural gas, the Province of Alberta, Canada, possesses substantial deposits of oil sands. The location of these deposits are indicated in Figure 1. These major deposits are estimated to contain 158 Gm^3 (967 GBBL) of bitumen. The Athabasca deposit is the world's largest deposit covering an area roughly the size of Belgium and contains 118 Gm^3 . The other major deposit is Cold Lake with estimated reserves of 26.2 Gm^3 .

Of these deposits, the Athabasca deposit has received the most attention from scientists and commercial developers since it is the largest and fortunately also has the shallowest overburden thus permitting surface mining. Again, because of the shallow overburden, the Athabasca oil sands deposit is the only deposit in the world to have attracted large-scale commercial development. Smaller developments have taken place in Venezuela, Trinidad, Albania, Rumania and in the U.S.S.R.

The Athabasca deposit is the site of two operational facilities: Suncor, Inc. with a daily production of 8600 m^3 of synthetic crude and Syncrude Canada Limited with a design production of $20,500 \text{ m}^3$ per day of synthetic crude. Plans have been made for the Alsands Project which would have a design capacity of $22,220 \text{ m}^3/\text{day}$ of synthetic crude. Other oil sand plants are in preliminary planning stages.

The geological stratification of the Athabasca deposit is presented in Figure 2. As with most rivers in this region of Western Canada, the Athabasca River has gouged a deep river valley, exposing the oil sands deposits along its banks. On warm days the bitumen oozes from the river banks and eventually works its way to the water line. Native Indians used this bitumen, mixed with spruce gum, to patch their canoes.

The first white man to see the Athabasca oil sands was fur trader Peter Pond in 1778. In 1889 the chronicler of the government sponsored Laird expedition wrote: "That this region is stored with a substance of great economic value is beyond all doubt, and, it will, I believe, prove to be one of the wonders of Western Canada."

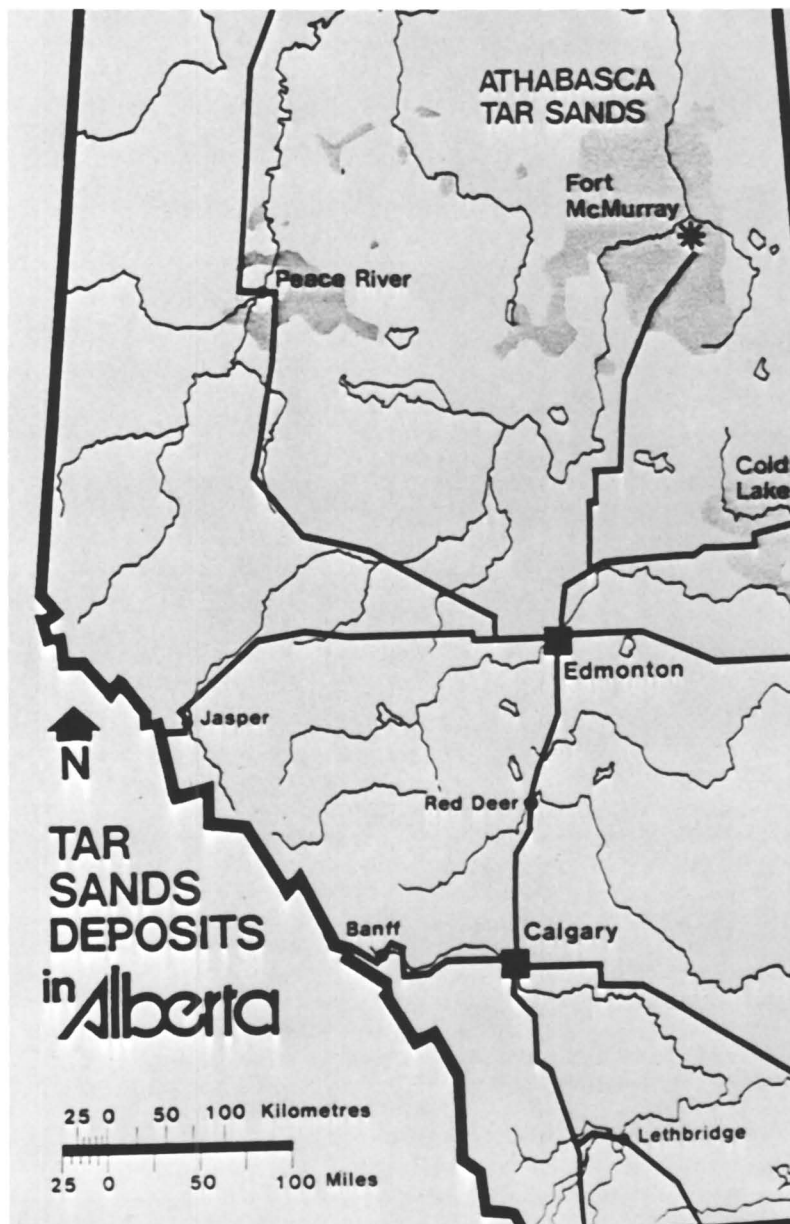


Figure 1. Location of Alberta oil sands deposits.

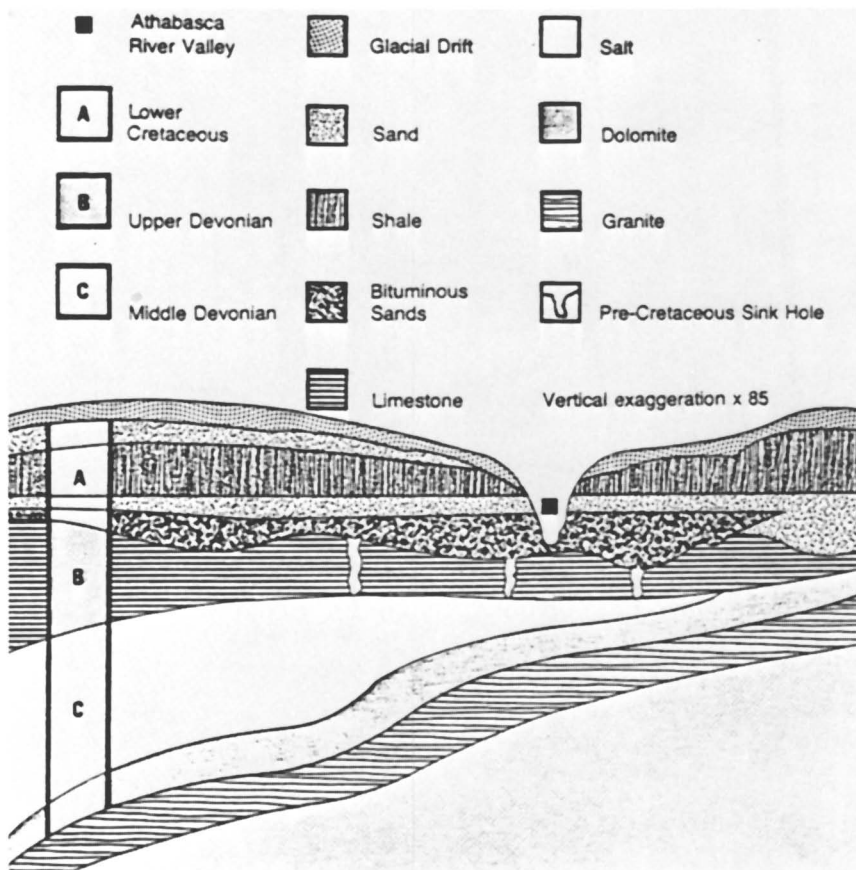


Figure 2. Geological stratification of Athabasca region.

The Athabasca deposit is relatively rich with bitumen saturation up to 18% by weight. The bitumen in its raw state has an API gravity of 8.3^o and is characterized by low hydrogen to carbon ratios, 1.5, and high sulphur content, 4.0-5.5 w/w%. Chemical and physical modifications employed during recovery and upgrading operations yield a synthetic crude with API gravity in the range 30-35^o with less than 2,000 wppm sulphur. Elemental sulphur is produced as a by-product of synthetic crude production and as with the other large source in Alberta-production from sour natural gas treating-it is produced at a rate not influenced by demand for sulphur.

Sulphur Distribution

The Syncrude operation employs surface mining techniques. Oil sand is removed from the deposit using draglines and placed in windrows where it is reclaimed and transferred to conveyor belts by bucketwheel reclaimers. The oil sand is transported from the mine area, via the 17.7 km of conveyor belts, to the Extraction facility. The mine has an annual capacity to move 83.7 million tonnes of oil sand containing 8.6 million tonnes of bitumen with approximately 0.4 million tonnes of contained sulphur.

Bitumen is recovered using a caustic assisted hot water flotation process and diluted with naphtha to facilitate the removal of residual solids and water. Diluent naphtha is removed by distillation prior to feeding bitumen to the Upgrading facilities.

The primary objective in the Upgrading process is to convert the heavy oil into a lower boiling product with low sulphur and nitrogen content. Sulphur is a by-product of this process. Figure 3 presents a schematic of Syncrude's Upgrading and will be used to describe the disposition of sulphur and its recovery at various stages in the process.

Bitumen feed to the fluid cokers contains approximately 4.9% sulphur. During coking, the sulphur is redistributed into sour gas, sour water, coke and hydrocarbon streams. Figure 3 indicates a circulating coke stream between the coker and coke burner.

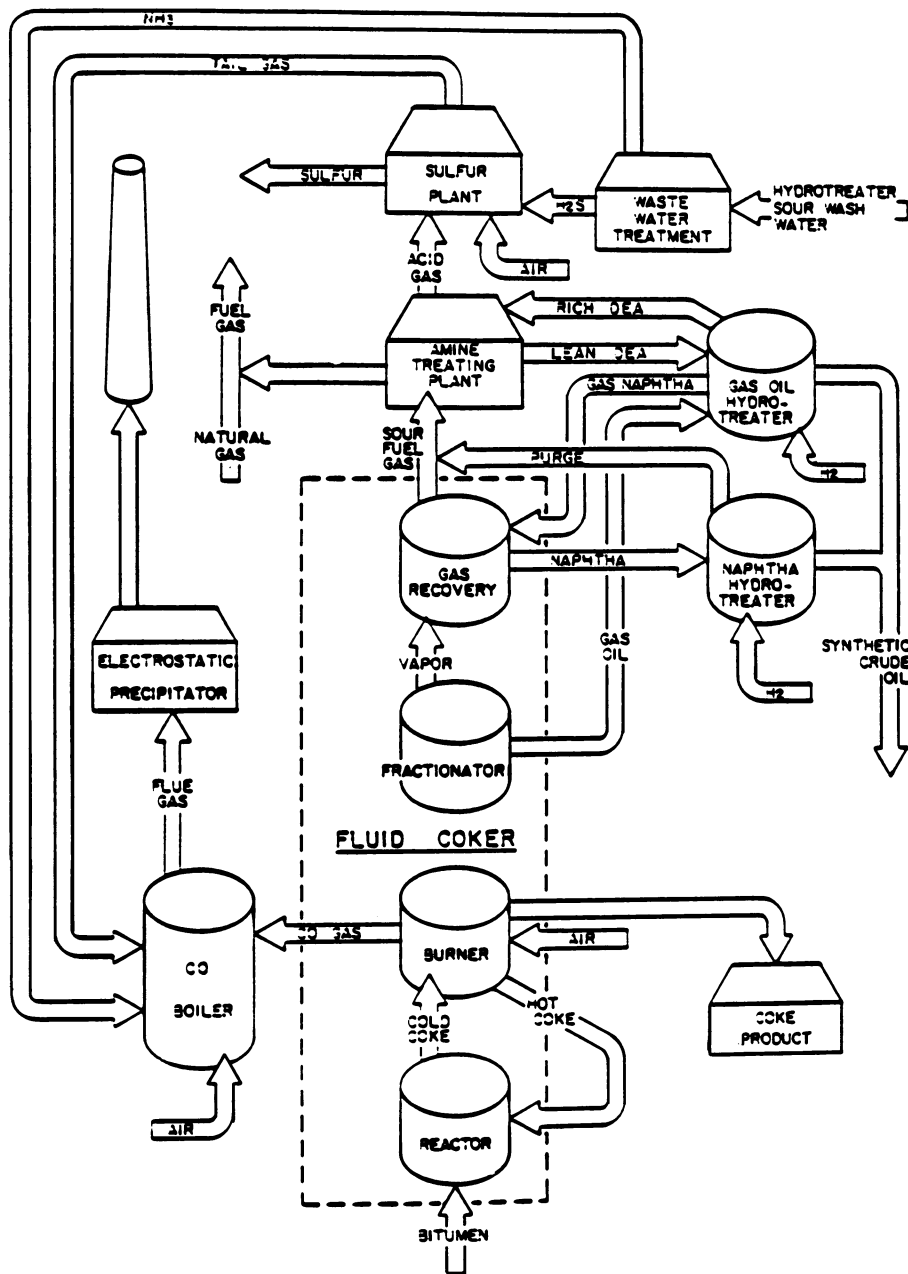


Figure 3. Simplified bitumen upgrading schematic.

Off-gas from the coke burner (CO-Gas) contains nitrogen, sulphur dioxide (SO_2), hydrogen sulphide (H_2S), carbon monoxide (CO), carbon dioxide (CO_2), water vapour and other trace contaminants. The CO-Gas is directed to the CO Boiler for incineration where sulphur compounds are converted to SO_2 . The Boiler flue gas is passed through electrostatic precipitators for particulate control and then emission to atmosphere. The CO Boiler also serves as the Sulphur Plant tail gas incinerator. Maximum sulphur emissions are 146 tonnes/day or 10.6% of sulphur contained in bitumen feed to the cokers.

Figure 3 also indicates coke product from the coke burner. The fluid cokers are net coke producers and the product coke is sulphur-rich analyzing at 6.9% sulphur. This product accounts for roughly 253 tonnes sulphur/day or 18.4% of input sulphur. Presently this coke is being contained on site but investigations are being conducted into on-site or off-site use with acceptable sulphur recovery. Possibilities are fluid bed combustion for steam generation, boiler fuel with flue gas scrubbing, hydrogen production from partial oxidation or utilization as a fuel in the cement industry.

Sulphur also leaves the coking stage in three hydrocarbon product streams: gas oil analyzing at approximately 3.5% S; naphtha analyzing at approximately 1.7% S and sour fuel gas analyzing at approximately 6.2% S. Sulphur is removed from the liquid products during hydro-treating. H_2S is recovered from the sour fuel gas and the hydrotreater gas streams by conventional (DEA) treating. The equivalent sulphur, removed as H_2S from these streams in the Amine Plant is 1007 tonnes or 73.2% of input sulphur.

Syncrude's Sulphur Recovery Units are two parallel trains of the conventional Claus plant consisting of thermal conversion and three catalytic reactors in series. Air is supplied to the furnace to oxidize sufficient H_2S to SO_2 such that an $\text{H}_2\text{S}:\text{SO}_2$ ratio of 2.1:1 is effected (1). The sulphur recovery efficiency is designed for approximately 95% (2); however, experience to date, at near design capacity, has indicated 98% H_2S conversions and 97% sulphur recoveries (1).

Continuous tail gas analyzers provide information on flow rates and $H_2S:SO_2$ ratios which is used to control operation. As indicated previously, the tail gases are routed to the CO Boiler for incineration before emission to atmosphere via the main stack.

Elemental sulphur from the final condensers flows to the sulphur pit where it is available in a molten state for shipment by truck transport or transfer to a storage block. Sulphur which is removed from site travels south to the Edmonton area. A significant portion is used for fertilizer production.

Figure 4 presents a sulphur disposition diagram based on design case with 4.9% sulphur in the bitumen feed to the fluid cokers. The data indicate 18.4% to product coke, 69.6% recovered elemental sulphur, 10.6% SO_2 emissions and 1.4% in the synthetic crude oil.

Increased recovery of sulphur from processing of bitumen is possible with new technology such as Flexicoking or Hydrocracking.

Flexicoking integrates coke gasification with fluid coking. Product coke is converted to low heat content fuel gas reducing net coke production. Sulphur dioxide emissions are comparatively low.

Hydrocracking has the potential for significantly increasing net synthetic crude yields from bitumen, from approximately 85 LV% to perhaps 90 LV% or more.

It is interesting to note the reduction in permissible and planned SO_2 emissions of the two commercial ventures, Suncor, Inc. and Syncrude Canada Limited and the proposed Alsands Project. These data are presented in Figure 5 as well as the target SO_2 emission level proposed by Alberta Environment. Data are in Long Tons $SO_2/1000$ barrels of synthetic crude product. The proposed Alsands rate is approaching the target level of Alberta Environment but implementation of new technology will be required to meet these objectives in the future.

Along with processing changes to achieve higher synthetic crude yields, the employment of future technology will result in greater quantities of sulphur production.

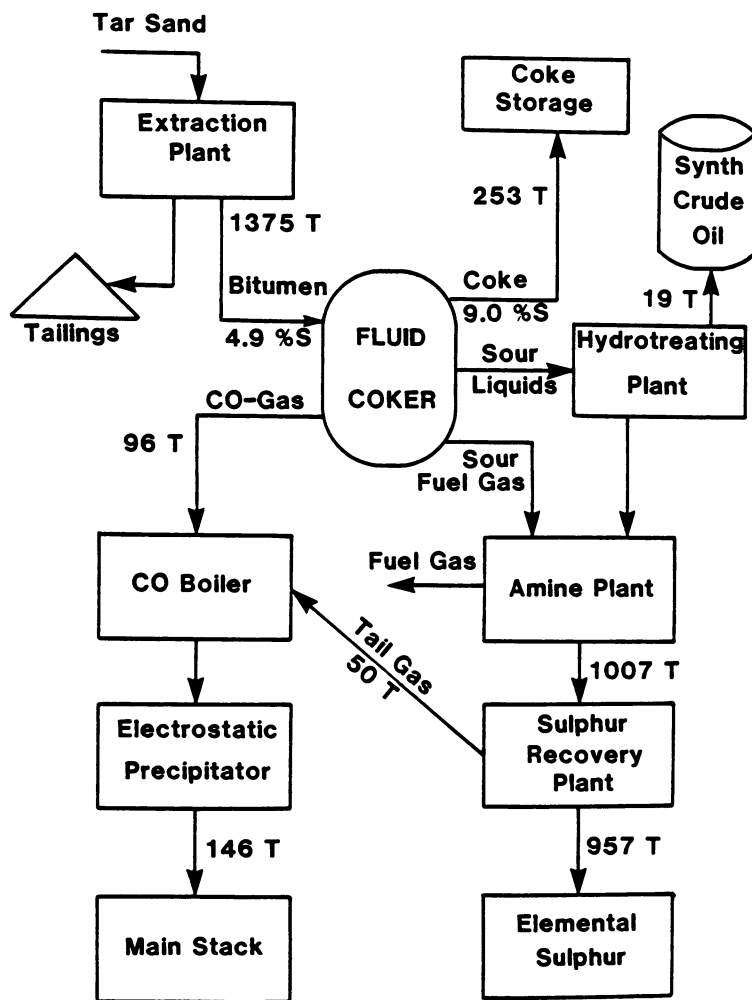


Figure 4. Syncrude's sulfur balance (numbers are in tonnes equivalent sulfur per day).

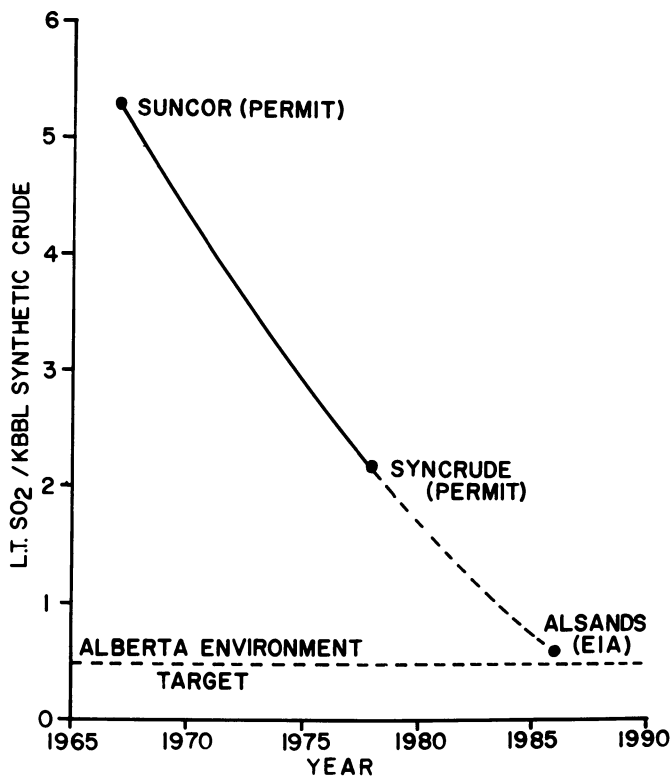


Figure 5. Comparison of licensed and proposed SO₂ emissions for the Athabasca region.

Table I indicates a comparison of synthetic crude yields and product sulphur using various processing schemes. Should synthetic crude production rise to 500,000 barrels/day from the Athabasca region in the Nineties, by-product sulphur could exceed 1.5 million tonnes annually. In comparison, Canadian sulphur sales for 1979 were reported at 6.3 million tonnes (3).

Table I
Comparison of Bitumen Upgrading Processes

<u>Process</u>	<u>Fluid Coking</u>	<u>Flexicoking</u>	<u>LC Fining</u>
LV% (SCO/BIT) (1)	85	85	89
% S Recovery (2)	69.6	95.6	92
% S Emission (3)	10.6	2.2	1.4

1 - Net liquid volume yield on net bitumen feed

2 - Elemental sulphur by-product

3 - SO₂ emission equivalent

Emission Monitoring

As noted in Figure 4, maximum SO₂ emissions represent 146 tonnes equivalent sulphur as the daily rate. Besides taking measures to restrict atmospheric sulphur emissions, the main stack was designed and constructed in accordance with Alberta Environment regulations which set a maximum half-hour average ground level concentration of 150 µg/m³ (approximately 0.06 ppm). This level was set to allow for additional oil sands plants in this area. A computational procedure supplied by Alberta Environment determined a stack height of 183 m would meet these requirements.

The permissible ambient concentrations of SO₂ and H₂S are indicated in Table II. To monitor ambient concentrations, Syncrude established an extensive network of monitoring stations (4).

Five continuous ambient air monitoring stations are indicated in Figure 6. At one minute intervals data on these parameters are transmitted by radio telemetry or land line to a minicomputer in the Operations Laboratory. Data manipulation is performed by the minicomputer and all data are transmitted to a large computer in Edmonton on a daily basis. In addition to these five stations, the monitoring network contains 40 static ("Candle") stations. The location of these stations are also given in Figure 6. The static stations have been in operation since May, 1977, one year before start-up, and provide monthly information on total sulphation and hydrogen sulphide. All data collected from the network are summarized in a prescribed format and submitted to Alberta Environment on a monthly and yearly basis.

Syncrude Canada Limited operates its oil sand extraction facilities to maximize recovery of resources while maintaining compliance with government regulations.

Table II

Permissible Ambient ConcentrationsSulphur Dioxide

<u>Measure</u>	<u>$\mu\text{g}/\text{m}^3$</u>	<u>ppm</u>
Annual Arithmetic Mean	30	0.01
24 Hour Average	150	0.06
1 Hour Average	450	0.17
$\frac{1}{2}$ Hour Average	525	0.2

Hydrogen Sulphide

<u>Measure</u>	<u>$\mu\text{g}/\text{m}^3$</u>	<u>ppm</u>
24 Hour Average	4	0.003
1 Hour Average	14	0.009
$\frac{1}{2}$ Hour Average	17	0.011

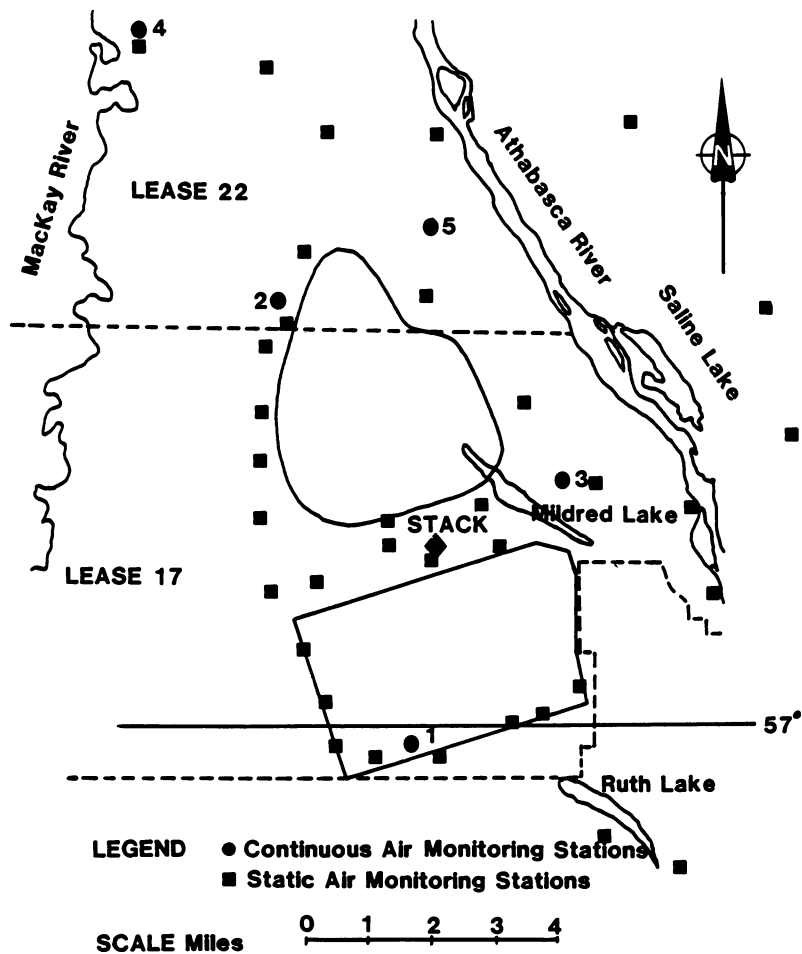


Figure 6. Syncrude's ambient air quality network (not all Candle stations are indicated).

Publication Date: March 29, 1982 | doi: 10.1021/bk-1982-0183.ch005

Sulphur by-product represents less than 1% of the corresponding synthetic crude value but it is an in-place resource to be recovered.

One of the challenges for future generations of oil sand recovery plants will be the development of more efficient technologies increasing yields of synthetic crude and recoveries of sulphur while reducing sulphur emissions.

Literature Cited

1. Vink, K. "From Black Sand to Yellow Sulphur." Paper presented at 7th Canadian Symposium on Catalysis, Edmonton, Alberta, October 19-22, 1980.
2. Syncrude Canada Limited. "Environmental Impact Assessment, Addendum to the 1973 Report, Volume B - Bio-Physical Aspects." October, 1978.
3. "Spring Review and Forecast 1981." Oilweek, April 27, 1981, p. 56.
4. Kumar, Ashok. Environ. Sci. Tech. 1979, 13, 650-654.

RECEIVED October 5, 1981.

The Potential Impact of Synthetic Fuels on the Sulfur Industry

DAVID GRAY, MARTIN B. NEUWORTH, ABDEL EL SAWY,
and GLEN TOMLINSON

The MITRE Corporation, McLean, VA 22101

S. I. FREEDMAN

U.S. Department of Energy, Washington, D C 20545

The importance of sulfur as an industrial chemical is discussed and forecasts of projected sulfur demand in the U.S. are given. Three processes for conversion of coal and oil shale to synthetic fuels are examined in some detail to show how the sulfur in the original feedstock material is recovered as elemental by-product sulfur. Three synthetic fuel scenarios are examined and their potential impact on sulfur availability with current and projected markets to the year 2000 are examined.

Sulfur is a very important industrial chemical. Current consumption ranks sulfur with the top five inorganic and organic chemicals produced in the U.S. The U.S. is the largest producer and consumer of sulfur in the world. The U.S. position in sulfur production resulted from the development of the Frasch process toward the end of the 19th century for mining the large sulfur deposits associated with salt domes in Texas and Louisiana.

Crude oil represents the largest non-Frasch sulfur resource and this source has received added stimulus from the passage of air pollution control laws and increased refining of heavier, high sulfur crudes. Sulfur recovered from sour natural gas contributes a third source of by-product sulfur.

The projected synthetic fuels program involving conversion of coal and shale may have a profound effect on available supplies of sulfur and supply patterns. Desulfurization of intermediate process streams to hydrogen sulfide will be required to meet environmental standards. Conversion of intermediate hydrogen sulfide to elemental sulfur will be carried out as in the case of crude oil desulfurization. Elemental sulfur represents the preferred sulfur

0097-6156/82/0183-0083\$05.00/0
© 1982 American Chemical Society

form for storage, transport and compatibility with environmental regulations. The production of elemental sulfur in the course of synthetic fuel production, as in the case of crude oil refining, will take place independently of market demand, marketing strategies and competitive trade-offs between various sulfur sources. While 52 percent of current domestic production of sulfur is obtained from uncombined sulfur deposits by the Frasch process, the long range expectation is for a major shift to by-product and co-product sources as a result of the increased use and refining of sour crude sour natural gas and synthetic fuels from coal and shale.

We will examine three synthetic fuel scenarios and compare their implications regarding sulfur availability with the current and projected market for sulfur to the year 2000. The analysis will consider three production levels of synthetic fuels from coal and oil shale. A low sulfur Western coal will be utilized as a feedstock for indirect liquefaction producing both synthetic natural gas and refined liquid fuels. A high sulfur Eastern coal will be converted to naphtha and syncrude via the H-Coal direct liquefaction process. Standard retorting of a Colorado shale, followed by refining of the crude shale oil, will round out the analysis. Insights will be developed from the displacement of imported oil by synthetic liquid fuels from coal and shale.

Sulfur Demand

The following forecast, (Table I), based on published information by J. Shelton of the USBM (1), was used to predict the sulfur demand to the year 2000. The figures chosen on the top line are for probable demand based on a probable average annual growth rate of 4.3 percent between 1978 and 2000. The bottom line figures are for a growth rate of 2.3 percent annually.

TABLE I
SUMMARY OF FORECAST OF U.S. SULFUR DEMAND
(Thousands Short Tons)

	YEAR					
	1978	1979	1985	1990	1995	2000
*	13,889	15,102	19,028	23,810	29,834	37,479
**	----	----	----	18,246	19,984	22,905

*4.6% annual growth as predicted by Shelton (1)

** 2.3% annual growth

Sulfur Markets

The distribution of sulfur markets for 1979 are displayed in Figure 1. Sulfuric acid is the most important product derived from sulfur. About 84 percent of the sulfur consumed was either converted to sulfuric acid or produced directly in this form. About 60 percent of the sulfuric acid in turn is used for agricultural purposes, mainly in phosphoric acid production, and intermediate in fertilizer manufacture. Another important use of sulfuric acid is in petroleum refining. Chemical uses, including plastics, paper and paint, account for 8 percent of sulfur production, sulfuric acid again being a major outlet. Ferrous and non-ferrous metal production consumes 8 percent and miscellaneous uses add up to 18 percent.

Sulfur market forecasts for the year 2000, as illustrated in Figure 1, show a relative decrease in the agricultural use of sulfur as a result of the development of new uses for sulfur representing as much as 29 percent of the projected market (1). Some of these include sulfur-asphalt paving materials. This blend shows lower temperature susceptibility than straight asphalt and this use is particularly interesting because of the decrease in asphalt availability as a result of upgrading to distillate fuels. Another promising use of sulfur is in sulfur concrete blends. Together, these uses could consume 11×10^6 tons of sulfur in the year 2000.

Synfuels Technology

Coal and oil shale are the most likely raw materials to be used in the U.S. for the production of additional quantities of liquid and gaseous fuels as substitutes for imported crude oil. In addition, direct utilization of coal is anticipated to increase substantially in the period 1985-2000. While it is assumed that direct utilization of coal will require Flue Gas Desulfurization (FDG) to meet environmental standards, projected utilization of these systems suggest that this technology will not contribute significantly to elemental sulfur production in the considered time frame. However, if regenerative FGD systems are the preferred configuration then additional quantities of sulfur will be generated from this source. Coal liquefaction and coal gasification technologies, as well as shale retorting procedures, are in various stages of development.

Full scale synthetic natural gas (SNG) plants based on standard Lurgi gasifiers (250 mm scf/D) can be built now to operate on noncaking or weakly caking coals. The developmental gasifiers which are candidates for demonstration will be ready for commercial deployment by 1988 for the conversion of all types of coals with potential reduction in capital and operating cost of 15 to 20 percent. Advanced processes with additional improvements will not be ready for commercialization until the 1990's.

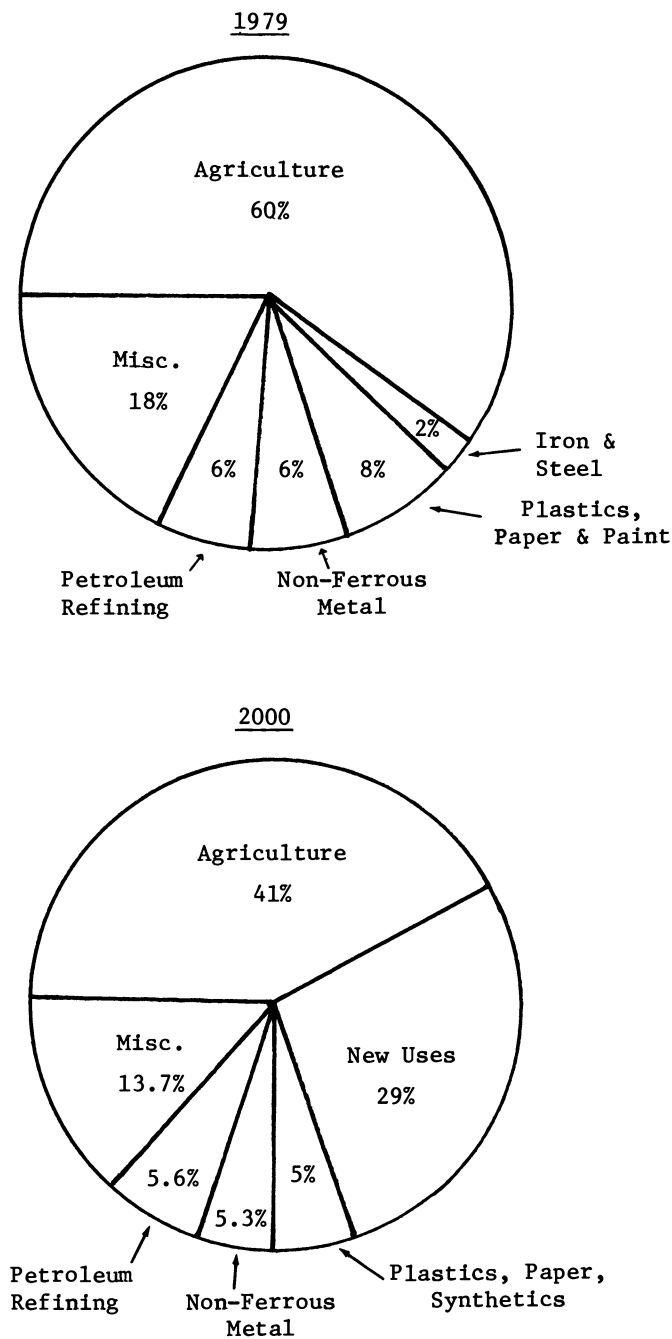


Figure 1. Sulfur markets.

Commercial coal liquids plants based on indirect liquefaction could be built now by adopting developments of SASOL-Fischer-Tropsch in South Africa with the same limitations of coal types as stated for Lurgi gasifiers. Similar comments apply to the Mobil methanol to gasoline process, which could also use Lurgi gasifiers as a first step. This latter process has the advantage over SASOL-Fischer-Tropsch of producing very high yields of high octane gasoline. The developmental direct liquefaction processes will be ready for commercial scale testing by 1988 to 1990, provided current demonstration and large pilot plant programs are successfully implemented.

The extraction of oil from mined shale by retorting is an established technology. The major above ground retorting processes have been under development intermittently for over 50 years. A variety of processes are presently candidates for full scale commercialization.

Figure 2 represents a schematic of the two main routes to coal conversion technology. Route 1, the indirect liquefaction approach, consists of gasification of the coal with steam and oxygen to produce a raw medium Btu gas which after shift conversion and purification yields a synthesis gas consisting essentially of carbon monoxide and hydrogen with various quantities of methane depending on the coal gasification process used. This synthesis gas can be methanated to produce a substitute natural gas (SNG), which is essentially 99 percent methane. Alternatively, the synthesis gas can be converted to liquid hydrocarbons using conventional Fischer-Tropsch technology or to methanol by conventional technology. The methanol could then be converted to high octane gasoline via the Mobil methanol to gasoline process.

The purification step in the route 1 approach removes all of the H_2S and COS in the raw product gas from the gasifier in addition to the carbon dioxide. Sulfur acts as a catalyst poison to Fischer-Tropsch, methanation and methanol catalyst systems, so pure sulfur-free gases must be used in these synthesis reactions.

The acid gas stream from the purification process is sent to a sulfur recovery unit which is usually a Stretford or a Claus unit. The product from these units is elemental sulfur.

In route 2, the direct liquefaction approach, coal is slurried with a process solvent and the slurry is pumped into a pre-heater/reactor and heated to temperatures of 750-850⁰F at a pressure of 1500-3000 psi of hydrogen. A catalyst can be used either in the reactor itself or external to the reactor to hydrogenate the process solvent. Almost all the organic constituents of the

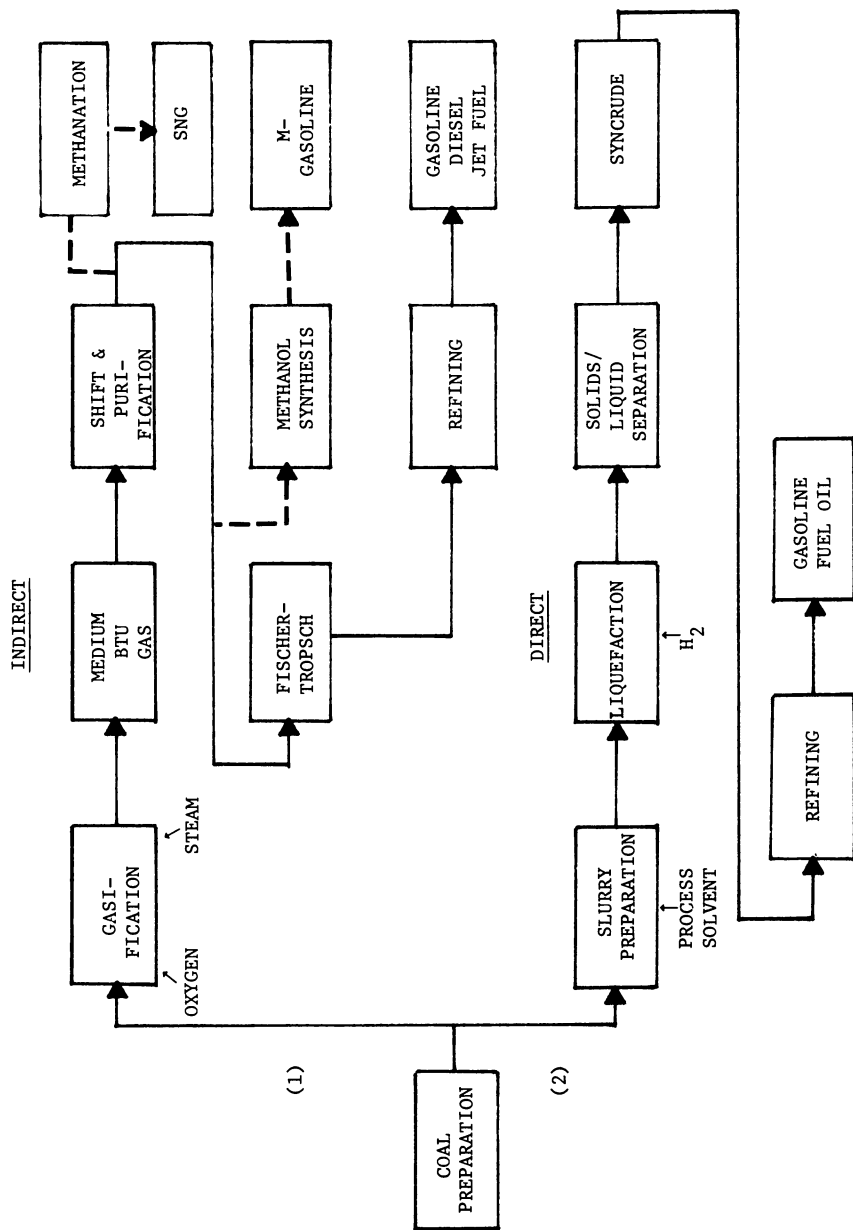


Figure 2. Indirect vs. direct liquefaction technology.

coal dissolve under these conditions and are converted into gas, light hydrocarbons, distillate and resid. The unconverted coal and ash is then separated from the liquid products and these liquids are further separated by fractional distillation. A portion of the liquid product is recycled for slurry make-up oil and the synthetic crude and naphtha products are then further refined to produce finished transportation fuels and specification fuel oils. The heavy residual oil and insoluble organic matter is gasified with steam and oxygen to provide process hydrogen for the coal hydrogenation reactor and the downstream hydrofining steps.

Removal of H_2S and acid gases from the hydrogenation reactor process stream and also from the raw gases obtained from gasification of the heavy residual is required. The incentive for H_2S removal and recovery of elemental sulfur in this case is environmental.

The organic material in oil shale, called kerogen, consists of high molecular weight organic species closely associated with the fine grained sedimentary rock. The only practical recovery method for this organic material is by heating the shale rock to high temperatures in the range of 900-1000^oF. This heating is accomplished using retorts of various designs. The raw shale oil and gas evolved during the retorting process are recovered. The gas is purified by removing H_2S and other acid gases while the raw pyrolysis liquids are usually hydrotreated on site. For environmental reasons all H_2S containing streams are sent to sulfur recovery units where elemental sulfur is produced.

We will consider three processes in more detail to show how the sulfur in the original feedstock material (coal or oil shale) is recovered as elemental by-product sulfur. In this way yields of sulfur per barrel of product can be computed. The three processes will illustrate examples of coal gasification for production of SNG, methanol or indirect liquids, direct liquefaction for production of naphtha and synthetic crude oil and finally, oil shale retorting for production of hydrotreated shale oil.

Techniques for purification of acid gas streams by removal of H_2S , COS and carbon dioxide are standard technology. Recovery of elemental sulfur from these acid gas streams by use of Claus or Stretford units is also conventional technology. These technologies are being practiced on a large scale by both petroleum refiners and natural gas processors.

Coal Gasification (Indirect Liquefaction)

The system considered here is the Lurgi dry ash coal gasification process as used at SASOL in the Republic of South Africa and proposed for use at the Great Plains gasification project in North Dakota (2). The important steps in the process as far as

sulfur is concerned are the front end gasification and gas purification steps. Subsequent clean gas processing can either yield SNG, methanol or Fischer-Tropsch liquid hydrocarbons. All sulfur is removed prior to any catalytic processing of the synthesis gas.

Figure 3 shows a simple schematic of the main processing steps involved. Data for this plant is taken from Reference 2. The plant processes 26,840 TPSD of low sulfur North Dakota lignite. The sulfur is 1.3 wt%/DAF coal. The coal analysis is shown in Table II. Output from the plant is 268,700 MM Btu/day of SNG, equivalent to 45,000 BOE/day. Total production of by-product elemental sulfur is 161 tons/day. This represents 78 wt% of total sulfur input from the coal feedstock. Since goal gasification and indirect liquefaction facilities are most likely to use Western low sulfur lignite or subbituminous coals, this represents the low sulfur case for coal conversion.

The sulfur distribution from the coal conversion plant is shown in Figure 4. The wt% of sulfur remaining in the ash depends on several factors among which are the relative distribution of organic and inorganic sulfur in the coal and the chemical composition of the ash. High alkaline ashes will capture sulfur as sulphide or sulfate.

The elemental sulfur is removed by conventional technology. The gases are purified by the Lurgi Rectisol process which uses a low temperature methanol wash to remove H₂S, COS and CO₂. The acid gas stream is then passed to a Stretford unit which is preferred to the Claus unit because of the high percentage of carbon dioxide in the stream. Sulfur in the stack gas would be removed by conventional flue gas desulfurization techniques and the sulfur would then remain as sulphite sludge and not be recovered as elemental sulfur.

From the available data, the output of elemental sulfur from this plant is calculated to be 0.0036 tons of sulfur per barrel of fuel oil equivalent.

TABLE II
ANALYSIS OF COAL USED FOR ANR PLANT (2)

<u>Proximate (wt%)</u>		<u>Ultimate (DAF, wt%)</u>	
Mositure	35.98	C	71.5
Ash	7.42	H	4.8
Fixed Carbon	23.39	O	21.0
Volatiles	27.21	N	1.4
Heat Content (Btu/lb)	7,230	S	1.3

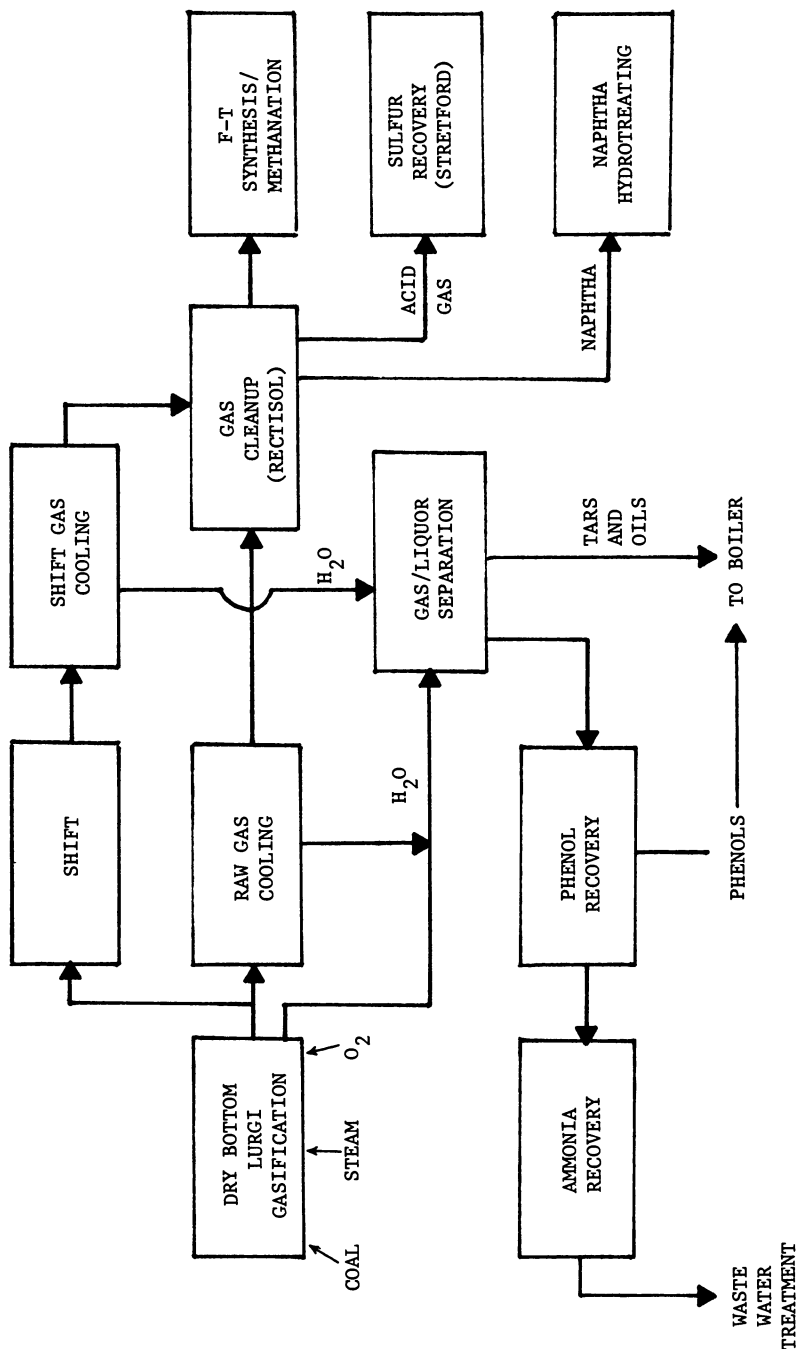


Figure 3. Indirect liquefaction or SNG from coal plant.

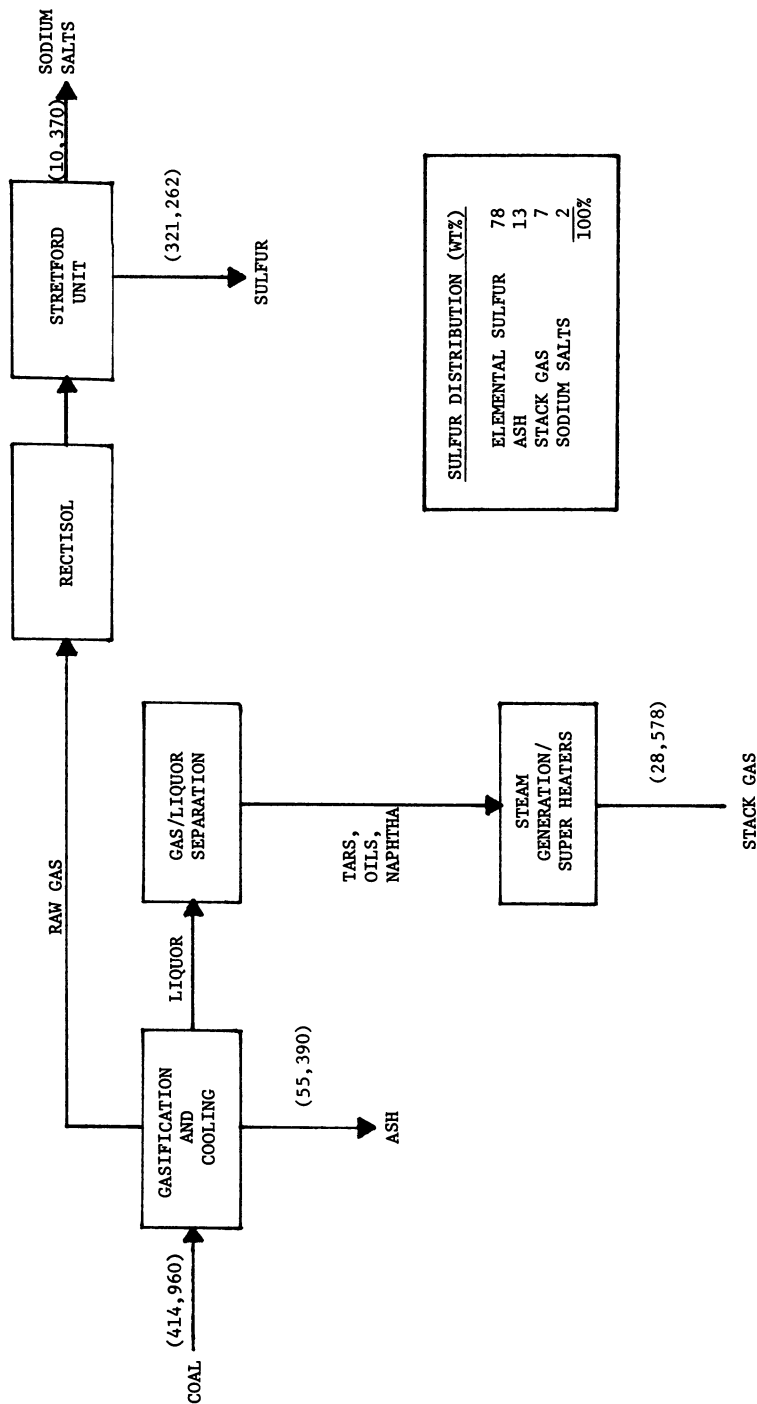


Figure 4. Sulfur balance for ANR Great Plains project. Numbers are pounds of sulfur per day.

Direct Liquefaction

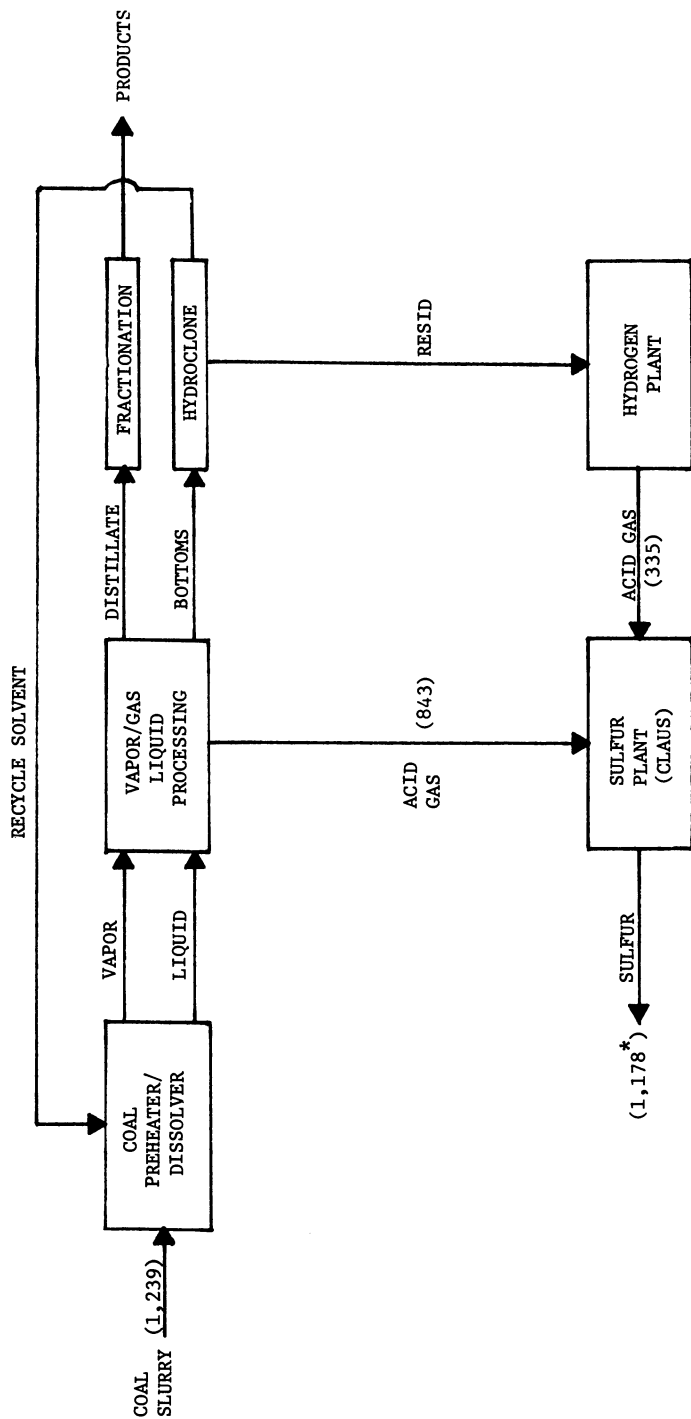
The direct liquefaction process considered for this study is the H-Coal process (3) operated in the syncrude mode (Figure 5). After coal slurry preparation, preheating and hydrogenation in the H-Coal catalytic reactor, the vapor/gas product stream is washed to remove acid gases. H₂S and CO₂ in the process stream are removed by using a physical solvent process in a two step treating operation. In the first step the H₂S is removed together with a small fraction of the CO₂. The acid gas stream discharged from this step contains a high enough concentration of H₂S to allow combustion in the Claus plant furnace for production of elemental sulfur. The second step involves the bulk removal of CO₂ which can then be vented directly to the atmosphere.

Hydrogen for the process is produced by gasification of the heavy residual oil (bottoms) containing insoluble organic matter and ash. The Texaco process could be used and the raw gases sent to a Rectisol or Selexol process for acid gas removal. This H₂S containing gasification stream is also sent to the Claus plant for sulfur removal. The sulfur not recovered in the Claus plant will appear in the tail gas as H₂S, SO₂, COS or as elemental sulfur vapor. Before release to the atmosphere, this tail gas will be treated in a Beavon, SCOT, or Wellman-Lord facility. SO₂ emissions will thus be negligible.

The plant will process 27,836 TPSD of Illinois No. 6 high sulfur bituminous coal containing 4.45 wt% sulfur on an as received basis. The output of fuel products from the plant is 15,531 BPSD of naphtha and 51,325 BPSD of syncrude. 1,178 tons per day of elemental sulfur is produced. This represents 95 wt% of the total input sulfur in the feedstock coal. Most of the remaining sulfur is still present in the liquid synthetic crude oil. From the available data for this proposed plant, the output of elemental sulfur is calculated to be 0.0176 tons per product barrel. Since a high sulfur coal was used this represents a high sulfur production case as it is likely that direct liquefaction facilities will use high sulfur Eastern bituminous coals as feedstock.

Retorting of Shale

The process considered is the Colony hydrotreated shale oil plant using the TOSCO II pyrolysis retort (4). In this process raw shale, crushed to 1/2" or smaller, is contacted with hot ceramic balls in a rotating drum. Downstream of the retort the balls and spent shale are separated by screening. The balls are then transported by an elevator to a vessel in which they are reheated by direct contact with hot combustion gases. The heated balls are then recycled to the rotating retort.



*Elemental Sulfur 95% of Feed

Figure 5. H-Coal direct liquefaction of coal. Numbers are tons of sulfur per day.

The TOSCO II process recovers virtually 100 percent of the Fischer assay yield of gas and liquid hydrocarbons from the shale. The light gases produced (hydrogen and C₁-C₄) account for about 20 wt% of the total product. The plans for the processing of oil shale from the Colony project include upgrading the raw shale oil for the purpose of removing the nitrogen compounds which are abundant in the crude liquid (≈1.9 wt% compared with ≈0.6 wt% for crude oil). The sulfur content of the raw liquid is about 0.7 wt%. The nitrogen compounds are catalyst poisons in refining processes such as reforming, catalytic cracking and hydrocracking and must be removed before raw shale oil can be upgraded to finished transportation fuels. During hydrotreating to remove nitrogen, the sulfur is almost completely eliminated.

Figure 6 illustrates the shale oil plant. Data for this plant is taken from Reference 4. 66,000 TPSD of crushed shale are re-torted to produce 44,400 BOSD of hydrotreated shale oil. The re-tort gases are purified for removal of acid gases and these are sent to a sulfur plant (Claus or Stretford) for recovery of elemental sulfur. The feedstock shale composition is shown in Table III. The H₂S produced during hydrotreating of the raw shale is also sent to the sulfur recovery unit.

TABLE III
APPROXIMATE COMPOSITION OF 25 GPT OIL SHALE (4)
(Weight %)

<u>Organic Matter</u>	
Content of Raw Shale	<u>13.8</u>
<u>Ultimate Composition</u>	
Carbon	80.5
Hydrogen	10.3
Nitrogen	2.4
Sulfur	1.0
Oxygen	5.8
TOTAL	<u>100.0</u>
<u>Mineral Matter</u>	
Content of Raw Shale	<u>86.2</u>
<u>Estimated Mineral Constituents</u>	
Carbonates, principally dolomite	48
Feldspars	21
Quartz	13
Clays, principally illite	13
Analcite	4
Pyrite	1
TOTAL	<u>100</u>

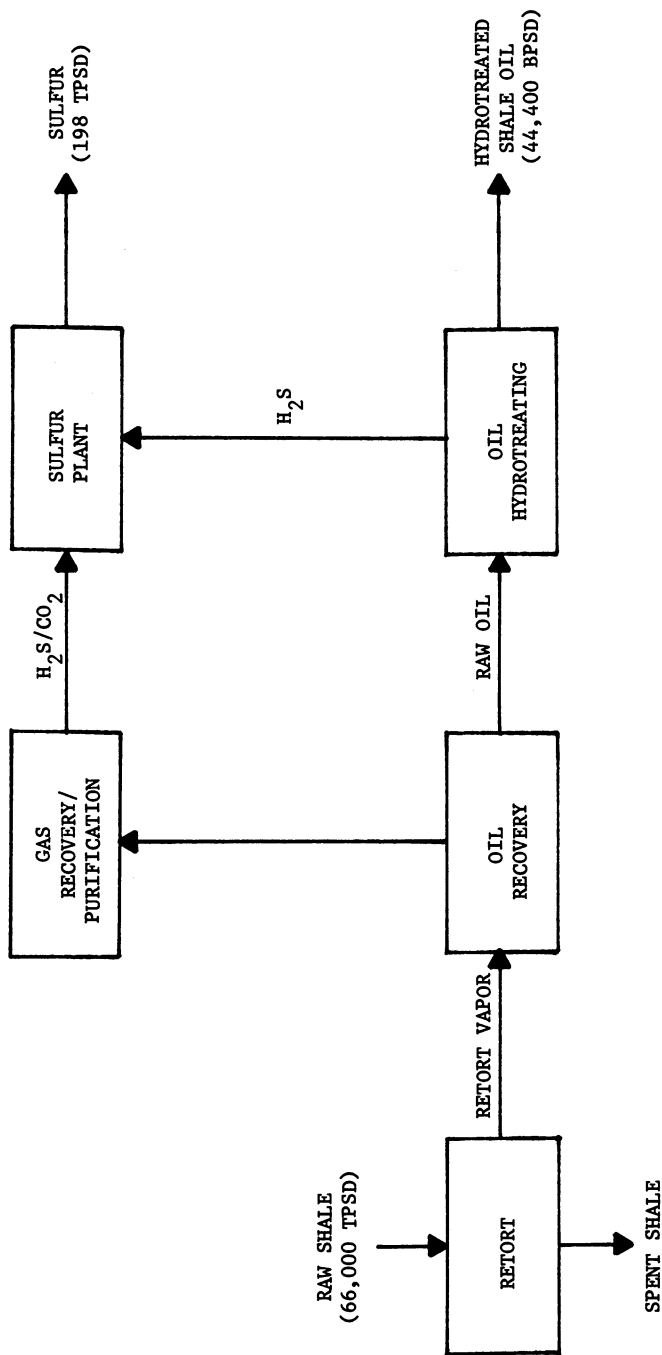


Figure 6. Colony hydrotreated shale oil plant.

The plant will produce 198 TPSD of elemental sulfur. This represents a sulfur output of 0.0045 tons of sulfur/barrel of hydrotreated shale oil.

The three examples chosen produce the following quantities of elemental sulfur per barrel of product:*

- Indirect Liquefaction (Gasification Lurgi) - 0.0036
- Direct Liquefaction (H-Coal) - 0.0176
- Shale Oil (TOSCO II) - 0.0045

Scenarios of Synthetic Fuel Use

Three scenarios of possible contribution of synthetic fuels to the U.S. Energy scene were used in this study. The first two projections were those of the Energy Information Administration's Annual Report to Congress, 1979 (5). The projections in 1979 dollars were for mid and high range oil import price figures of \$32 and \$39 per barrel for 1985; \$37 and \$44 per barrel for 1990; and \$41 and \$56 per barrel for the year 1995. The third projection, the potential contribution of shale and coal liquids was derived by assuming that the rate at which plants can be constructed will ultimately be limited by the capability of A&E firms to undertake the construction task and the ability of equipment suppliers to meet the demand for the required heavy equipment. An architect engineering company has investigated these limits in a preliminary study. They concluded that construction of 20 coal plants and 7 shale facilities having an installed total capacity of 1.5 MM bpd by 1990 was a realistic though taxing undertaking. We have assumed that construction manpower requirements are representative of the overall limit of construction capacity.

The nominal MITRE estimate of potential plant construction by the year 2000 has been developed by assuming a build up transient similar to that assumed by the A&E firm but continuing the peak level construction manpower achieved in the sixth year through to the end of the century. This level of construction activity is capable of producing a total of 3.6 MM bpd of synthetic liquids by the year 2000. Table IV shows the potential contribution of the three synfuel scenarios until the year 2000. These projected levels of synfuel activity will produce by-product sulfur and the projected quantities are shown in Table V for each of the three scenarios.

Figure 7 shows the impact of this by-product sulfur produced as a result of the synthetic fuels activity displayed as a percent-

* If the Illinois #6 coal was used as feedstock for both the indirect and direct liquefaction plants, then approximately the same amount of sulfur per barrel would be produced.

tage of the projected sulfur demand up to the year 2000. The impact of even the high oil price EIA projection only amounts to just over 10 percent of projected sulfur demand up to the year 1995. The MITRE synfuels scenario, an optimistic estimate of the use of synfuels, would predict that 30 percent of projected sulfur demand would be met by by-product sulfur from synthetic fuels by the year 2000. If sulfur demand growth is only 2.3 percent, then 50 percent could be met by synfuels in 2000.

TABLE IV
SCENARIOS OF SYNTHETIC FUELS AVAILABILITY
(Units MM B/D)

SOURCE	1985		1990		1995		2000	
	MID	HIGH	MID	HIGH	MID	HIGH	MID	HIGH
<u>EIA</u>								
Shale Oil	.01	.05	.25	.40	.40	.80	---	
Gas From Coal	.05	.05	.14	.18	.32	.32	---	
Coal Liquids	<u>0</u>	<u>.03</u>	<u>0</u>	<u>.03</u>	<u>.23</u>	<u>.26</u>	---	
TOTAL	.06	.13	.39	.61	.95	1.38		
<u>MITRE</u>								
Shale Oil	---		.30		.80		1.20	
Indirect Coal	---		.45		1.10		1.20	
Direct Coal	---		<u>.10</u>		<u>.50</u>		<u>1.20</u>	
TOTAL			.85		2.40		3.60	

TABLE V
SULFUR PRODUCTION FROM SYNTHETIC FUEL USE
(Units M Tons Per Year of Sulfur)

SOURCE	1985		1990		1995		2000	
	MID	HIGH	MID	HIGH	MID	HIGH	MID	HIGH
EIA	82	340	595	1,086	2,555	3,405	---	
MITRE	---		1,727		5,971		11,257	

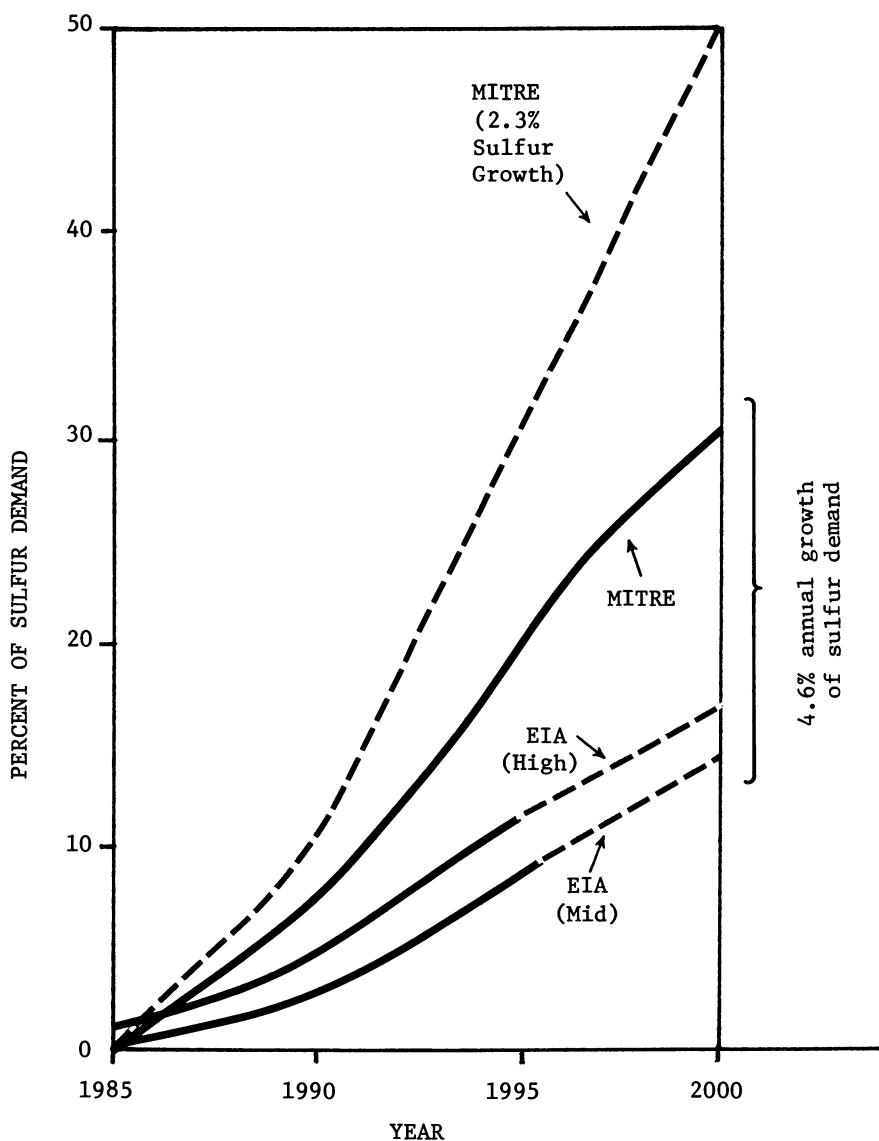


Figure 7. *Impact of sulfur recovered as by-product of synthetic fuels industry on projected sulfur demand to year 2000.*

Conclusions

In 1979 sulfur obtained as a by-product from petroleum refining accounted for 19.7 percent of total sulfur produced in the U.S. The requirement to desulfurize residual fuels or alternatively to refine them to finished transportation fuels will result in a substantial increase in sulfur produced at refineries even if medium sweet crudes continue to be the primary refinery feedstock. However, most experts predict that crudes will become sourer in the future. The contribution from natural gas is an additional uncertainty. Conventional wisdom predicts that natural gas demand will maintain current levels or possibly decline over the next 20 years. The combination of these factors may increase conventional by-product sulfur from petroleum and natural gas by a factor of three or more by the year 2000. This would bring its sulfur contribution up to approximately 12 million tons by 2000, the same as that predicted by the MITRE estimate for synthetic fuels sulfur production. Thus, a possible total contribution of 60 percent of projected sulfur demand could be met by the combination of these by-product sources of sulfur.

With the advent of new uses for sulfur in the near future, there is no present evidence that by-product sulfur from synthetic fuel plants will swamp the sulfur market in this century. If Frasch production still continues to decline the new markets continue to develop, sulfur imports may still be required in the year 2000.

References

1. Shelton, J.E., "Sulfur." U.S. Bureau of Mines. Bulletin 671, Mineral Facts and Problems. 1980 Edition.
2. Great Plains Gasification Project. Final Environmental Impact Statement. U.S. Department of Energy, August, 1980. DOE EIS-0072F, Volume 1.
3. "H-Coal Commercial Evaluation," Fluor Engineers and Constructors, Inc., March 1976. U.S. Department of Energy Report FE 2002-12.
4. Nutter, J.F. and Waikman, C.S. "Oil Shale Economics Update." Presented at A.I.Ch.E., Southern California Section, 14th Annual Technical Meeting, Anaheim, California, April 18, 1978.
5. U.S. Department of Energy, Energy Information Administration, "Annual Report to Congress 1979. Volume 3: Projections." DOE/EIA 0173(79)/3.

RECEIVED October 5, 1981.

Sulfur from the Hydrometallurgical Processing of Sulfide Materials

A. T. WILSON

Duval Corporation, Tucson, AZ 81502

In the classical pyrometallurgical smelting of metal sulphide concentrates most of the sulphur is driven off as sulphur dioxide. This process is becoming increasingly unacceptable from an environmental point of view. An alternative is to process the concentrates using hydrometallurgical techniques. In these processes the metal sulphides are reacted with a saline acid solution containing ferric or cupric chlorides or sulphates. This results in the solubilization of the metal as a complex ion while the sulphide sulphur is converted to elemental sulphur. The sulphur remains in the leach residue mixed with pyrite and siliceous material which were the contaminants of the original metal sulphide flotation concentrate. As the nonferrous smelting industry changes from pyrometallurgy, large quantities of hydrometallurgical sulphur will become available from the processing of copper, lead and zinc sulphide concentrates. The sulphur produced from hydrometallurgical processes will be more impure than Frasch sulphur but in some cases it can be upgraded for use in sulphur burning acid plants. In its impure state it could also find a use in sulphur extended asphalt highway or sulphur concrete construction.

The classical pyrometallurgical method of processing metal sulphide concentrate is to heat the material in air and drive off the sulphur as sulphur dioxide. This process is becoming increasingly unacceptable from an environmental point of view. An alternative that is rapidly emerging is to process the concentrate using hydrometallurgical techniques. Aqueous solutions of certain metal salts will chemically attack most metal sulphides, taking into solution the constituent metals and leaving behind a residue of elemental sulphur. Because of the large

0097-6156/82/0183-0101\$05.00/0

© 1982 American Chemical Society

tonnages of metal sulphides processed each year one might expect by-product sulphur from this source to make a significant contribution to the total sulphur available in the future. The present development of hydrometallurgical processing of metal sulphides not only stems from the difficulty pyrometallurgical smelters have in meeting current environmental limits on sulphur dioxide emissions but also the fact that it is only relatively recently that suitable corrosion resistant materials such as plastics and metals (e.g. titanium) have been available to make such hydrometallurgical processing technically feasible.

Hydrometallurgical Processes

The most likely minerals to be processed using hydrometallurgical techniques would probably be sphalerite (ZnS) and chalcopyrite (CuFeS₂). Duval Corporation in Tucson already has a 40,000 ton (of copper per year) hydrometallurgical plant producing about 38,000 tons/year of hydrometallurgical by-product sulphur (1). Since about 2×10^6 tons of copper as sulphide mineral are smelted each year in the United States and Canada there is the potential for 2×10^6 tons/year of sulphur produced as the by-product of such processing if a total conversion is made to hydrometallurgical processing. The impact would be especially great in the copper producing areas of the world such as Western U.S. and Canada, Chile and Africa. Of course the development of a non-polluting process such as Duval's CLEAR process could move the smelting operation away from the mining areas and nearer to the centers of population.

Lead sulphide (galena - PbS) is another likely candidate for hydrometallurgical processing particularly in the United States where, apart from the problems of the sulphur dioxide emissions, the lead toxicity problem is making it very difficult for the lead smelters to operate their conventional pyrometallurgical process and comply with EPA and OSHA standards. The total amount of lead mined in the United States is about 600,000 tons per year which, if fully converted, would yield about 100,000 tons per year of by-product sulphur. The Bureau of Mines in Reno, Nevada, have an active pilot plant study to produce lead via a hydrometallurgical process (2). In this process the common lead mineral galena is dissolved in an acid brine solution of ferric chloride.

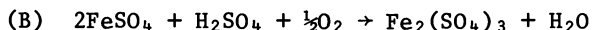
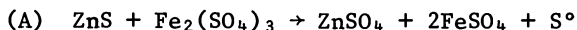


A liquid/solid separation yields a residue and a solution. The solution is cooled to produce crystalline PbCl₂ which is later electrolyzed to lead metal and chlorine in a fused salt cell. The residue consists of elemental sulphur, pyrite and gangue.

The solution is reoxidized to convert the ferrous iron back to ferric iron.

Sphalerite (zinc sulphide) is a strong contender for hydrometallurgical processing. North America mines 2×10^6 tons of zinc per year as zinc sulphide which represents a potential of 600,000 tons of by-product sulphur per year. Sherritt-Gordon and Cominco are active in developing a hydrometallurgical process for processing zinc ores (3)(4)(5), and Cominco has constructed a 65,000 ton/year Zn (20,000 tons/year S°) plant in Trail, British Columbia.

The zinc pressure sulphate leach system has the overall reaction:



The residue from this reaction consists of two easily separated types of solids, one being an elemental sulphur-metal sulphide-pyrite fraction, the other being an iron oxide-lead sulphate (or jarosite)-gangue fraction. The sulphur in the Trail plant is recovered from a separation autoclave by continuous decantation of the aqueous zinc sulphate phase along with the oxide-gangue portion of the solids, and continuous or periodic removal of the molten elemental sulphur from the bottom of the vessel. The molten sulphur contains pyrite and a small amount of metal sulphides, and so is filtered to produce essentially pure sulphur. The zinc sulphate solution is processed through the normal purification and electrowinning circuits to produce elemental zinc and spent liquor which is returned to the pressure leaching step. The sulphur produced in the Cominco plant is currently burnt in their sulphuric acid plant.

Although the production of by-product sulphur from hydrometallurgical processing of sulphide minerals would appear to have a potentially large impact on sulphur production, it probably will not always compete directly with conventional sulphur but will probably generate its own end uses. For example, Duval's CLEAR Plant near Tucson in Arizona currently produces 38,000 tons/year of by-product sulphur which might be compared with Arizona's current consumption of only 6,000 tons/year. Only a part of Duval's chalcopyrite production is processed in this plant and Duval is only one of many copper mines in the Tucson area. To put the problem in perspective and to illustrate the type of product produced, Duval's CLEAR process is described below although generally the same considerations would apply to any hydrometallurgical treatment of a metal sulphide concentrate.

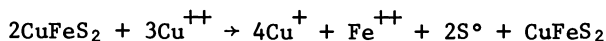
Duval's CLEAR Process

The CLEAR process is designed to completely leach the copper values from a copper concentrate consisting of any combination of copper sulphide or copper iron sulphide mineralization. The most abundant copper mineral is chalcopyrite whose composition is

CuFeS_2 . The reaction is carried out in a nearly saturated solution containing copper, potassium and iron as active essential constituents together with sodium and magnesium as non-reactive cations to maintain the high chlorinity.

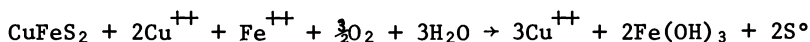
The digestion reaction is carried out in two steps:

(A) The reduction reaction:-



In practice it is difficult to dissolve all the chalcopyrite in a reasonable time as indicated in the above reaction so the solids from the reaction are separated and passed to another reaction vessel where oxidizing conditions are maintained.

(B) The oxidizing reaction:-



The liquor from the first reaction is used as a pregnant liquor to be fed to electrowinning cells. An important electrical current benefit is realized in that it is only necessary to convert cuprous copper (Cu^+) to copper rather than the conventional electrowinning process where cupric copper (Cu^{++}) is converted to copper. In an alternative process developed by Cymet (6), the cuprous chloride is crystallized from this liquor by cooling. The cuprous chloride is later reduced to copper in a furnace using hydrogen.

In the oxidizing reaction vessel the partially reacted concentrate from the first stage is completely reacted in an oxygen enriched atmosphere. The iron is produced as beta-ferric hydroxide or hematite (Fe_2O_3) depending on the reaction temperature. In the preceding reactions all the sulphur is produced as elemental sulphur; in practice a small amount is oxidized to sulphate which must be purged from the circuit. In the Duval process this is done by having potassium in the solution which, together with iron and sulphate, leads to the precipitation of potassium jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$). This material is an inert insoluble material similar to the mineral of the same name found in nature. The corresponding aluminum mineral alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$) is perhaps better known. The iron, therefore, is produced from the overall process as a mixture of potassium jarosite and beta-ferric hydroxide which mixed with sulphur can be readily filtered forming a solid, relatively dry, cake.

Hydrometallurgical By-Product Sulphur

The mineral concentrate feed to any hydrometallurgical process is usually the product of a flotation process. This process

involves treating the finely ground ore in a flotation cell to which suitable chemicals are added and bubbles of air are blown through the suspension. The chemicals and conditions (e.g. pH) are arranged such that the mineral desired is rendered aerophylic and attaches itself to the bubbles and is carried off in the froth leaving the rock gangue behind in the mineral suspension. There is, however, always a small amount of siliceous material locked to the mineral particles and this is carried through the process to end in the residue. Further in practice most mineral ore contains some pyrite (FeS_2) and although this is intentionally suppressed during the flotation process a small amount is carried forward with the desired metal sulphide. Pyrite is refractory to hydrometallurgical solutions and largely survives the CLEAR process to end with the residue. Thus the sulphur from the hydrometallurgical process is produced mixed with ferric hydroxide, jarosite, siliceous gangue and pyrite.

The residue from any hydrometallurgical process would be similar. Clearly, if iron was not a part of the starting material some would usually be added to remove the sulphate either as sodium or potassium jarosite and there would be less ferric hydroxide and a greater proportion of sulphur.

Uses of Hydrometallurgical Sulphur

One possible approach to the use of hydrometallurgical by-product sulphur would be to separate the sulphur by froth flotation. It is possible to enrich the sulphur with respect to the beta-ferric hydroxide, jarosite and siliceous gangue but difficult to completely separate it from the sulphides which are refractory to the hydrometallurgical solutions [e.g., pyrite (FeS_2) and molybdenite (MoS_2)]. The sulphur could always be solvent extracted at a cost to produce pure sulphur but being of mineral origin will always be more impure than Frasch sulphur which is of microbiological origin. It might, therefore, not be suitable for modern catalytic sulphuric acid plants because of arsenic and other impurities which would poison the catalyst. There will be an incentive to use the hydrometallurgical by-product sulphur in its impure state or partly enriched state. The most obvious use would be to use the sulphur either as is, or chemically modified as a partial replacement for asphalt in highway construction. Asphalt is expected to become not only more expensive but in short supply especially as the petroleum industry builds hydrocracking facilities to convert more of the asphaltic fraction of the crude oil into other more valuable products. The hydrometallurgical by-product sulphur could be used close to its point of production which would most often be remote from the sources of asphalt and hence have a transport cost advantage. Recent work by the Southwest Research Institute in San Antonio, Texas, has produced a synthetic asphalt type material from sulphur [called Sulphlex (7)]. This asphalt replacement contains no asphalt and is made

from elemental sulphur, chemically cross linked with organic materials such as cyclopentadiene. Manufacture of materials of the Sulphlex type may be a possible use for the impure hydro-metallurgical by-product sulphur.

Another attractive use for the sulphur-siliceous-gangue-pyrite-ferric hydroxide-jarosite product might be in sulphur concrete type materials. Sulphur concrete is essentially rock aggregate where the voids are filled with elemental sulphur which has been chemically modified by reaction with a plasticizer such as dicyclopentadiene. For an account of sulphur concrete see the excellent review by M.E.D. Raymont (8). Sulphur concrete possesses many useful features exhibited by other aggregate-containing materials as well as some unique properties such as speed and ease of fabrication and low cost. For example, curbs and gutters can be laid continuously using sulphur concrete. Extensive use has already been made in Canada of sulphur concrete for median barriers, bumper bars, and in fact almost any use for which conventional concrete can be used where the object is not likely to be subjected to temperatures above the melting point of sulphur and where the likelihood of a fire hazard is small.

Conclusion

Hydrometallurgical processing of sulphide minerals may in the future provide an important source of sulphur. This sulphur even when purified will be more impure than Frasch sulphur. As produced from the hydrometallurgical process the sulphur will always be contaminated with siliceous gangue and pyrite. In some cases, it will be upgraded for use in sulphur burning acid plants, but there will be a strong incentive to use the material in its impure state for sulphur extended asphalt highway construction and sulphur concrete applications.

Literature Cited

1. Atwood, G. E., Livingston, R. W., "The CLEAR Process, a Duval Corporation Development", Erzmetall 33 (1980), 5, 251-255.
2. Haver, F. P., Won, M. M., "Ferric Chloride-Brine Leaching of Galena Concentrate", U.S. Bureau of Mines Rep. Invest., 1976, 1805.
3. Veltman, H., Bolton, G. L., "Direct Pressure Leaching of Zinc Blende with Simultaneous Production of Elemental Sulphur. A State-of-the-art Review", Erzmetall 33, 1980, 2, 76-84.
4. Parker, E. G., and Romanchuk, S., "Pilot Plant Demonstration of Zinc Sulphide Pressure Leaching", Lead-Zinc-Tin '80, Proceedings of World Symposium, 109 AIME Annual Meeting, Feb. 24-28, 1980, Las Vegas.

5. Parker, E.G., "Oxidative Pressure Leaching of Zinc Concentrates", Fifth Annual District Six Meeting of CIMM, Kimberley, B.C., Oct. 23-25, 1980.
6. Goens, D.N., Kruesi, P.R., "Process for the Recovery of Cuprous Chloride in the Presence of Metal Impurities", U.S. Patent No. 4,013,457, Mar. 22, 1977.
7. "Test Road Paved with Plasticized Sulfur", Chemical and Engineering News, (1980), 58 (35), 25.
8. Raymont, M.E.D., "Sulphur Concretes and Coatings", Sulphur Development Institute of Canada, Calgary, 1978, New Uses for Sulphur Technology Series Number Four.

RECEIVED October 5, 1981.

Sulfur Supply and Demand and Its Relationship to New Energy Sources

M. C. MANDERSON

Manderson Associates, Inc., Winter Park, FL 32789

C. D. COOPER

University of Central Florida, CEES Department, Orlando, FL 32816

World sulfur supplies are expected to grow at roughly 3.7% per year over the coming decade as compared with 2.6% per year from 1973 to 1980. Sulfur production will grow markedly in the United States, primarily due to increased recovery of sulfur from natural gas processing and petroleum refining. Canadian sulfur production will show a net decline despite increased recovery at refineries and smelters. The greatest increases in supplies overseas are expected to occur in the Middle East, Poland, the Soviet Union and in Japan. Demand for sulfur in the world markets is expected to grow at roughly 4% per year (slightly faster than supply) and will sustain the present tight market and high prices for sulfur for several years into the future.

This paper results from work completed in 1979 (and updated in 1980) to evaluate the emerging supply/demand, cost/price outlook for the fertilizer commodities: phosphate rock, upgraded phosphates, sulfur, and sulfuric acid. Our purpose here is to publish, in part, our analysis of recent trends and events which impact on sulfur supply and demand, and to use these together with available production cost data to project price behavior for sulfur over the near term. Such projections are helpful to managers of large industrial firms as one of several tools available to them in making investment, contract, marketing, or other major decisions. This paper is necessarily limited in scope, and will attempt to summarize the world outlook with emphasis on the North American scene.

Sulfur is a relatively abundant element, occurring as an impurity in many metal ores and fossil fuels. It also occurs in relatively pure form from which it can be mined via the Frasch process. Until recently Frasch mining was the major source of supply in the world with the largest producers being the U.S., Mexico and Poland. In the late 1960's, recovery of sulfur as a by-product from "cleaning" operations began to accelerate rapidly. Sulfur recovery from

0097-6156/82/0183-0109\$05.00/0
© 1982 American Chemical Society

non-ferrous metal smelting, oil refining, sour gas sweetening, and other such operations now is a major factor in the total supply picture, with the U.S., Canada and Japan being major "recoverers" of by-product sulfur.

Sulfur is used in a wide variety of industrial processes, however, its single most important use is as sulfuric acid in the production of phosphatic fertilizers. World demand for sulfur (in all forms) has traditionally grown at a fairly steady pace while world supply has been subjected to various sudden surges and shortfalls. The resulting interplay of supply/demand forces has led to an interesting price history for this commodity both worldwide and in North America.

WORLD SUPPLY OUTLOOK

Over the six years from 1973 to 1978, sulfur production capability on a global basis increased from about 48 million long tons (sulfur equivalent) to about 55 million tons per year (2.8% per year). Since world sulfur demand has historically averaged well above 3 percent per year, the gap between demand and supply narrowed noticeably. It should not be surprising, therefore, that recently sulfur prices have begun to increase.

Table I provides a summary of the outlook for world sulfur supply over the coming decade. This table shows the combined totals of all sources and forms of sulfur: elemental and non-elemental as well as discretionary and non-discretionary, including the use of pyrites. As the bottom line in the table shows, we anticipate that world sulfur supplies will grow at a faster rate over the coming 5-10 years than they have in the recent past. Of particular interest is the considerably expanded sulfur production outlook that we foresee for the U.S. and Mexico over the coming decade, the basis for which will be discussed later in this paper.

The greatest overseas increase in sulfur supplies is expected to occur in the Middle East (especially in Saudi Arabia), in Poland, in the USSR and in Japan. Increases in sulfur from the Middle East and Japan will be due to increased recovery, while Poland's increase will be due to a new Frasch mine. From the standpoint of the impact on world markets, sulfur production in Poland and the Middle East is of greatest significance. New sulfur produced in the USSR will be largely self-contained. The expansion in Japan will be used to supply Japan's internal growth and to supply the Far Eastern market, notably Korea and mainland China, thus helping to offset the anticipated gradual decrease in availability of sulfur from Western Canada.

As the table shows, we have assumed that production of sulfur in Poland would increase by 2.0-2.5 million tons per year by 1985. While there is no official word as yet that Poland will actively move forward with their long anticipated expansion, we believe that the current rise in world sulfur prices will provide adequate incentive for Poland to expand its output. Also, recent negotiations

TABLE I
 WORLD SULFUR PRODUCTION, 1973-1990
 (In millions of long tons of S equivalent)

Continent	Country	Year										Average Annual Increase, %	
		1973	1975	1978	1980*	1982*	1985*	1987*	1990*	1973-78	1978-90		
North America	U.S.	10.9	11.7	11.8	12.0	13.0	16.0	19.0	22.0	1.6	5.3		
	Canada	7.7	7.4	7.4	7.0	6.6	6.5	6.2	6.0				
		18.6	19.1	19.2	19.0	19.6	22.5	25.2	28.0	0.6	3.2		
Latin America	Mexico	1.7	2.2	1.9	2.6	3.0	3.2	3.4	3.6				
	Car.-C.A. So. Am.	0.1	0.1	0.2	0.2	0.2	0.2	0.2	0.3				
		0.4	0.3	0.3	0.3	0.4	0.4	0.5	0.6				
W. Europe	France	2.0	1.9	2.2	2.0	1.9	1.8	1.7	1.5				
	Germany	1.1	1.1	1.6	1.7	1.8	2.0	1.9	1.8				
	Spain	1.2	1.6	1.3	1.5	1.7	1.7	1.5	1.5				
	Other	3.4	2.8	2.6	2.4	2.4	2.2	2.2	2.2				
E. Europe	Poland	3.8	4.7	5.7	5.7	5.7	8.0	8.0	8.0				
	USSR	7.7	9.5	10.8	12.3	13.5	15.5	17.0	19.0				
	Other	1.6	1.8	2.0	2.2	2.4	2.6	2.8	3.0				
Middle East	Iran	0.6	0.5	0.5	0.5	0.6	1.0	1.2	1.5				
	Iraq	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.2				
	Saudi A.	---	---	---	0.1	1.0	1.5	1.7	2.0				
	Other	0.1	0.1	0.1	0.2	0.2	0.2	0.2	0.3				
Africa		0.6	0.6	0.8	1.0	1.2	1.3	1.4	1.5				
Asia-Oceania	Japan	2.8	2.4	2.7	2.9	3.0	3.2	3.5	4.0				
	Other	1.7	21.	1.9	2.0	2.2	2.4	2.6	3.0				
	GRAND TOTAL	47.8	51.4	54.6	57.3	61.6	71.6	76.0	83.0	2.7	3.6		

* Estimate

between Poland and Occidental Petroleum Corporation make it likely than an exchange of Polish sulfur for Oxyphosphate rock (from North Florida) will spur the expansion effort.

WORLD DEMAND OUTLOOK

By far the largest single sulfur consuming sector of the world economy is the fertilizer industry (particularly phosphates), accounting for over half of world sulfur consumption. On a historical basis, the growth rate in sulfur demand has been on a modest decline over the past two decades, largely because of the maturing demand for phosphate fertilizer. Between 1965 and 1975, world sulfur consumption increased by about 5 percent per year. Over the coming decade, we anticipate that increases in world demand will average around 4 percent per year, but there is likely to be an interim pick-up in demand over the next few years, due to the cyclical characteristics of fertilizer demand.

In 1978, world sulfur demand (in all forms) totalled about 49 million long tons. This compares with U.S. sulfur demand in 1978 of about 12 million long tons. Over the coming decade, world sulfur demand is expected to increase to about 78 million long tons, with U.S. demand expanding to about 17 million long tons. Thus, by the end of the next decade, domestic sulfur uses will still account for 20-25% of world consumption.

These demand forecasts assume that no major new uses for sulfur develop over the near term. Although a great deal of research has been devoted to developing new sulfur applications in recent years - and we believe that this work should continue - the recent and likely further rise in brimstone prices over the next few years will temporarily forestall the development of significant new markets for sulfur.

A review of the past and projected sulfur supply, demand, and the supply/demand balance on a global basis is presented in Table II. The bottom line of the table shows the all-important relationship between demand and supply. In 1973, a substantial surplus of sulfur existed world-wide. In that year, the operating rate was about 83 percent. Since 1973, the operating rate has been steadily increasing, reaching 89% by 1978. In 1979 and 1980, the operating rate approached 100% - resulting in spot shortages and rapidly escalating prices.

We anticipate that the demand/supply gap will continue to stay narrow over the next several years and that sulfur prices and profit margins will remain high. The recent supply dilemma has been alleviated partially by reduction of inventories, primarily in Western Canada and at Frasch sulfur stockpiles in the U.S. Mexico and Poland. But, since no new major sources of sulfur will be available over the near term, the world operating rate will probably continue to stay above 90% in the early 1980's.

TABLE II
 WORLD TREND IN SULFUR SUPPLY/DEMAND BALANCE, 1973-1990
 (In millions of long tons of sulfur equiv.)

Item	Year								Average Growth, % 1979-1990
	1973	1975	1978	1980*	1982*	1985*	1987*	1990*	
<u>SUPPLY</u>									
• Discretionary: Elemental (Frasch)	15	17	16	17	18	20	20	20	2
Non-Elemental (Mostly pyrites)	$\frac{10}{25}$	$\frac{9}{26}$	$\frac{10}{26}$	$\frac{10}{27}$	$\frac{11}{29}$	$\frac{12}{32}$	$\frac{13}{33}$	$\frac{15}{35}$	$\frac{3}{2.5}$
SUBTOTAL									
• Non-Discretionary: Elemental (Mostly sour gas & oil)	14	16	19	20	22	27	29	33	5
Non-Elemental (Mostly smelting)	$\frac{9}{23}$	$\frac{9}{25}$	$\frac{10}{29}$	$\frac{10}{30}$	$\frac{11}{33}$	$\frac{13}{40}$	$\frac{14}{43}$	$\frac{15}{48}$	$\frac{3}{4}$
SUBTOTAL	$\frac{23}{48}$	$\frac{25}{51}$	$\frac{29}{55}$	$\frac{30}{57}$	$\frac{33}{62}$	$\frac{40}{72}$	$\frac{43}{76}$	$\frac{48}{83}$	$\frac{4}{3.5}$
TOTAL (Rounded)	(48%)	(49%)	(53%)	(53%)	(53%)	(56%)	(57%)	(58%)	
(NON-DISCRETIONARY SHARE)									
<u>DEMAND</u>									
• Fertilizer	20	22	24	27	29	33	37	42	5
• Industrial	$\frac{20}{40}$	$\frac{22}{44}$	$\frac{25}{49}$	$\frac{27}{54}$	$\frac{29}{58}$	$\frac{31}{64}$	$\frac{33}{70}$	$\frac{36}{78}$	$\frac{3}{4}$
TOTAL	(50%)	(50%)	(49%)	(50%)	(50%)	(52%)	(53%)	(54%)	
(FERTILIZER SHARE)									
<u>OVERSUPPLY (DEFICIT)</u>									
Operating Rate (Demand/Supply)	$\frac{8}{83}$	$\frac{7}{86}$	$\frac{6}{89}$	$\frac{3}{95}$	$\frac{4}{94}$	$\frac{8}{89}$	$\frac{6}{92}$	$\frac{5}{94}$	

* Estimated

NORTH AMERICAN SUPPLY OUTLOOKUnited States

Discretionary Sulfur Sources - Frasch Sulfur. Over the past few years, the production of Frasch sulfur has been on a decline, primarily due to slightly declining prices in face of sharply rising costs of energy. Another important, yet less significant, factor has been the decline in productivity and reserve quality at some of the older Frasch sulfur mines. Between 1976 and 1978, 4 Frasch sulfur mines were closed. Three of these closures were made by Texasgulf, and one was made by Freeport Minerals Company. However, sulfur prices began to rise rapidly last year, creating a strong possibility that one or more of the Frasch producers will be stimulated to develop marginal reserves and to push the output of existing mines. It is conceivable, therefore, that production by the U.S. Frasch industry could rise from the 6.5 million ton level of 1979 to 7.5-8.0 million tons per year in the early 1980's.

By-Product (Non-Discretionary) Sulfur Sources - Petroleum Refining. When sour crude oil (crude is considered sour when it contains more than 0.5 wt% sulfur) is refined, some of the sulfur is removed from the oil as H₂S. In most modern refineries, this H₂S is collected and processed to recover the sulfur in elemental form. It is well known in a qualitative way that U.S. sulfur recovery at refineries has been expanding in recent years due to a combination of factors: higher overall crude rates, a higher percentage of sour crudes processed, and more intense desulfurization to meet increasingly rigorous environmental guidelines.

Historical data were obtained on U.S. refinery operations and the production of sulfur from U.S. refineries from 1971-1977. A two-parameter model was developed correlating past levels of sulfur recovery with the quality and rate of crude processed and the qualities and amounts of end products. An overall correlation coefficient of 0.91 was obtained.

We elected to consider three refinery operating scenarios with the main difference relating to the production of heavy fuel oil. The results of varying heavy fuel oil yield, along with our best estimates of some other variables, are summarized in Figure 1. In brief, we estimate that sulfur recovery from U.S. refineries by 1990 will likely range from between 4.3 to 5.0 million long tons per year. We elected to use the higher of these figures in our subsequent estimates of U.S. supply, because we believe that the recent upward trend in heavy fuel oil yield at U.S. refineries is likely to reverse itself. This reversal will be brought about in part by national policy to curb foreign crude imports and in part by the likely high cost of fuel oil for electric power generation, as compared with natural gas and coal.

By-Product (Non-Discretionary) Sulfur Sources - Sour Natural Gas. Historically, there has been limited incentive for companies to develop sour gas reserves. The additional cost of removing the

Publication Date: March 29, 1982 | doi: 10.1021/bk-1982-0183.ch008

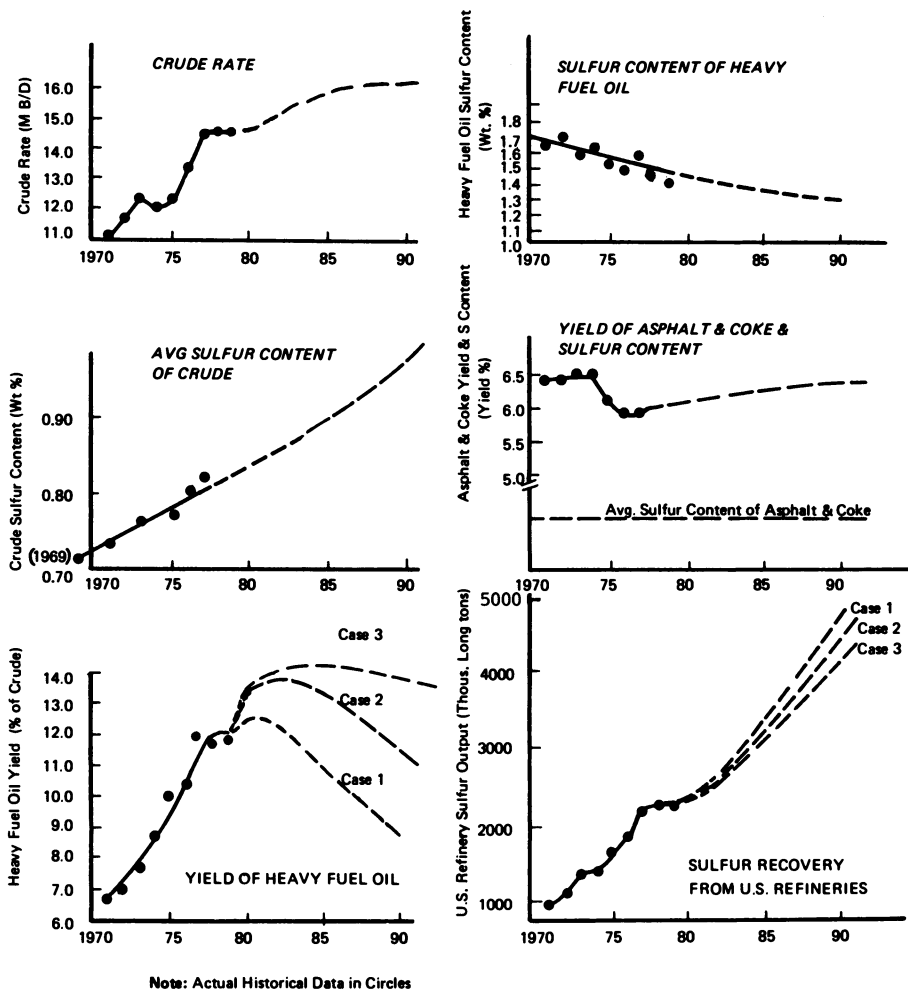


Figure 1. Refinery sulfur model: past and projected trend of key variables and resultant refinery sulfur production in the U.S., selected cases.

sulfur to produce a marketable product has oftentimes placed the sour gas project in an unfavorable economic position. Now, however, there appears to be increasing interest in exploring for and developing large bodies of sour gas, due to the growing price spread between domestic gas and imported oil. We held discussions with a number of petroleum companies to discuss their views of the likely increase in sour gas developments, both in the U.S. and in Canada. The results of these interviews are reflected in our estimates of future sour gas sulfur production in the U.S. as discussed below.

During the interval from 1970 through 1978, sour gas sulfur production in the U.S. increased from about 660,000 long tons per year to about 1.7 million long tons per year. A significant portion of this increase occurred in the Gulf Coast region. Based upon projects now underway in this region, we anticipate that additional production of between 400,000 and 500,000 tons will be realized by 1983. Due to the significant reserves of quite deep sour gas in the Smackover Formation in this region, we anticipate several more such projects will materialize by the end of the coming decade.

The most interesting North American sour gas development is already starting to unfold in the Intermountain Area, especially in Southwestern Wyoming and Northeastern Utah, which contains part of the Overthrust Belt. Since the drilling experience in this area is still in its early stages, gas reserve quality and quantity are not yet well known. However, present indications suggest that the H₂S content ranges between 10-20% and the probable reserves exceed 20 trillion cubic feet which is large not only by U.S. standards, but by world standards.

There are several negative factors which should be taken into account in assessing the rate of development in the Western Overthrust Belt. The terrain is extremely rugged. Drilling costs are high and drilling in this area is risky. Some of the area that offers the greatest potential is in protected wilderness areas controlled by the U.S. government.

After weighing these various factors, we have concluded that there will be a significant expansion in sour gas production and processing in the area over the coming decade, starting in 1983. Amoco and Chevron will likely be the first major developers of sour gas deposits in the Overthrust. Other companies will probably begin to participate significantly sometime in the middle 1980's.

By 1990, we estimate that eight to ten large sulfur recovery plants will be in operation. While this may prove to be conservative long range, we believe that it would be difficult to design and install more than an average of one sour gas plant per year in this mountainous area over the coming decade. Finding markets for the gas should not be a problem, because plans are underway to build a pipeline into the area.

By-Product (Non-Discretionary) Sulfur Sources - Smelting Non-Ferrous Metals. In recent years the nation's move toward improvement in air quality has resulted in requiring essentially all of the

non-ferrous metals smelters in the U.S. to sharply reduce their atmospheric emissions of sulfur dioxide. The most economically and technically practical method for recovery of this SO_2 is to convert it into sulfuric acid. Since 1970, by-product acid recovery from U.S. smelters has grown from about 500,000 long tons per year to 1.1 million long tons per year (1978) in terms of sulfur equivalent. Most of this increase has occurred at copper smelters in the southwestern U.S., primarily in Arizona. Acid production from domestic lead and zinc smelters has remained essentially static over this same period. Overall, by-product sulfuric acid production from smelters increased by about 10% per annum from 1970 to 1978.

In considering the future prospects for increased smelter acid recovery, it is necessary to focus on future developments of the copper industry in Arizona, New Mexico, Montana and Utah. During our study, we contacted all of the major copper companies to obtain insight into their future plans for increased smelting capacity and/or higher levels of SO_2 recovery from existing smelting operations. We estimate that smelter acid production capability will increase from the current (1978) level of about 6.3 million short tons per year of H_2SO_4 to about 8.2 million short tons per year by 1985. This translates into an increase of approximately 600,000 long tons per year of sulfur over the period.

Table III summarizes the supply outlook for the United States through the study period. We wish to re-emphasize that the major increase in "sour gas" sulfur will occur primarily in the Overthrust region which, because of its long distance from major markets, could cause a substantial shift in regional trade patterns within the United States and Canada.

Canada

Over the past two decades, Canada has changed from being a relatively small sulfur producer to the world's third largest producer and its second largest exporter. Sulfur production, especially from the sour gas area in Western Canada, grew dramatically from the early 60's to 1974. Since 1974, production has begun to taper off modestly - from a peak level of about 6.9 million long tons per year to about 6.0 million long tons in 1974.

Over the coming decade, taking into account potential additions of new sour gas reserves, it now seems likely that sulfur recovery from sour gas operations in Western Canada will continue to gradually drop off. Barring a change in Canada's pricing policy on gas exports, we roughly estimate that production will decrease to about 4 million long tons per year by 1990. Although this drop-off is substantial, it is less pronounced than some experienced observers of the sulfur scene in Western Canada believe. However, considering the fact that the expanding production of tar sands will increase sulfur production and the fact that new sour gas operations in Eastern British Columbia are under development, we are led to believe that brimstone production in Canada will decline gradually rather than abruptly.

TABLE III

U.S. SULFUR SUPPLY OUTLOOK BY MAJOR SOURCES, 1970-1990
(In millions of long tons of sulfur equivalent)

Source or Type	Year										Average Annual Increase, %	
	1970	1974	1978	1980*	1982*	1985*	1987*	1990*	1970-78	1978-90		
<u>Discretionary</u>	7.1	7.9	5.6	6.0 ^a	6.0 ^a	7.0 ^a	7.0 ^a	6.5 ^a				
Frasch												
<u>Non-Discretionary</u> <u>(Recovered/By-Product)</u>	0.8	1.4	2.3	2.6	3.0	3.7	4.2	5.0	14	7		
Refinery	0.7	1.2	1.7	2.0	2.5	3.5	5.0	6.5	13	12		
Natural Gas	0.5	0.7	1.1	1.3	1.4	1.8	2.0	2.5	10	7		
Metals Smelting (as acid)	---	---	---	---	---	0.1	0.4	0.8	---	---		
Coal Gas-Liquid	---	---	---	---	---	---	0.1	0.3	---	---		
Coal Cleaning	---	---	---	0.1	0.1	0.1	0.2	0.2	---	---		
Flue Gas Desulf. (FGD)	---	---	---	0.1	0.1	0.1	0.2	0.2	---	---		
(Sub-Total)	2.0	3.3	5.1	6.0	7.0	9.2	11.9	15.3	12	10		
Total Supply (Rounded)	9	11	11	12	13	16	19	22	3	6		
(% in Recovered Form)	(22)	(30)	(46)	(50)	(54)	(58)	(63)	(70)				

* Estimate.

^a Denotes estimate of capacity operation; mines may not operate at this level of demand or price does not justify. Assumes development of 0.5-1.0 MM tons of new capacity in 1982-1987 period and modest reduction thereafter.

SOURCE: U.S. Bureau of Mines; published and private sources; and Manderson Associates, Inc., estimates.

Sulfur from other sources - primarily from smelter acid and from petroleum refining - will increase relative to the position of sour gas sulfur. There are likely to be growing regional pressures on some U.S. markets due to the substantial expansion in smelter acid production which we foresee taking place in Eastern Canada. In brief, areas around the Great Lakes and along the northeastern coast of the U.S. will continue to be under the most threat from this new source of smelter acid. With anticipated higher brimstone prices during the next few years, domestic producers of acid based on elemental sulfur will be under increased pressure from low-priced acid imports.

Mexico

Aside from the U.S., Mexico is one of the few countries in the world that produces sulfur by the Frasch process. Its output of Frasch sulfur has been on a general decline in recent years. The reverse is true for the production of recovered sulfur - from refineries, sour gas operations, and smelters. Overall, the total sulfur supply from all sources amounted to about 1.9 million long tons of sulfur equivalent in 1978, representing a substantial decline since 1974, when production was 2.4 million tons.

In considering the future, however, we see several positive developments in Mexico's sulfur supply outlook. First, Mexico is making a major effort to rejuvenate its Frasch operations. By the early 1980's, it hopes to increase Frasch output to about 2.5 million tons per year. For example, the Frasch mine which was owned by Gulf Resources and Chemicals Corporation (formerly Gulf Sulfur Company) is now being reopened and rehabilitated.

The outlook for sulfur production from petroleum, and especially from sour gas, is also promising, largely because of the aggressive development plans which the Mexican government now has to expand the petroleum and petrochemical sectors. The projected very large increases in gas processing will be accompanied by a sizeable expansion in sulfur recovery. Plans are now well advanced to expand gas treatment capability from the current level of about 100,000 tons per year of sulfur to about 500,000 tons per year by 1985.

In total, we anticipate that Mexico's sulfur output will expand from the current level of about 1.9 million long tons per year to a potential of about 3.2 million long tons per year by 1985, and to a minimum of at least 3.5 million tons by 1990.

In summary, we estimate that the total sulfur supply in North America will increase from the 1978 level of about 20 million long tons per year to about 31 million long tons per year by the end of the forecast period. U.S. production will account for about two-thirds of this total, and Canadian supplies will account for about 20 percent of the total.

NORTH AMERICAN DEMAND OUTLOOKUnited States

Between 1970 and 1978, U.S. sulfur demand grew from 9.2 to about 12 million long tons per year, equivalent to an average annual rate of increase of about 3.4 percent. Over the forecast period, we anticipate an average annual increase of about this same rate. Our estimate assumes that the U.S. will continue to maintain world leadership as an exporter of upgraded phosphates, and that growth in domestic phosphate fertilizer consumption will average about 3 percent per year.

By relating the supply forecast that has been presented earlier in this paper with the projections of future demand, we can arrive at the trend in the supply/demand relationship over the forecast period. The U.S. has been a small net-importer of sulfur values during most of the past decade. In 1978, the U.S. had a net deficit position of about 400,000 tons. With a short-term upturn in phosphate demand, both domestic and international, we anticipate that the deficit position will widen over the next year or so. Even though U.S. exports will likely increase due to rising prices for sulfur in the export market, U.S. imports will also rise. But, with the advent of large amounts of sulfur starting to come from the Overthrust Belt by the mid-1980's, we believe that the deficit position will reverse itself and place the U.S. in a net export position. In the latter part of the 1980's, we anticipate this surplus to widen considerably.

Canada

Canadian demand for sulfur has amounted historically to about 10 percent of U.S. demand. We expect this relationship to continue. As in the U.S., over half of Canadian sulfur use goes into the production of fertilizers. Other major uses for sulfur are for the leaching of uranium ores, and for use in the pulp and paper industry.

With the advent of large sour gas sulfur production in Western Canada that began in the early 1960's, Canada became a large net exporter of sulfur. In 1979, Canada produced about 6.0 million long tons of sour gas sulfur, compared with local demand of about 900,000 tons, with exports about 5.3 million tons. During the early part of the forecast period, we anticipate that the export position of Western Canada will increase modestly to perhaps 6 million tons per annum, after which it will begin to decline gradually. The huge stockpile in Western Canada has now probably reached its peak of 20-21 million tons, and net withdrawals from inventory will be required if Canada is to maintain exports of 5-6 million tons per year. In this connection, we can expect that Canadian exports to the U.S., which have been running at about 1 million tons per year, will be gradually replaced from incoming production of sour gas sulfur from the Overthrust Belt in the U.S.

Mexico

Demand for sulfur in Mexico is even more oriented toward the fertilizer sector than it is in the U.S. and Canada. In 1978, fertilizer uses accounted for about 75 percent of the total. We expect that the future use of sulfur in Mexico will continue to be oriented heavily toward the fertilizer industry. By 1990, Mexican sulfur consumption should be almost three times the current level.

A surplus position of sulfur existed in Mexico beginning in 1972 through the most recent year of published statistics (1978). If Mexico is successful in upgrading and expanding its Frasch mining activities, and, barring the discovery of new deposits, the surplus position should increase from the present level of about 1 million tons per year to about 1.5 million tons by the mid-1980's.

North American Supply/Demand Summary

Overall, we estimate that surplus production capability in the region will expand from the current level of about 5.4 million long tons per year to about 9 million long tons per year by 1990. By far, the greatest surplus will exist in the mid-continent and Intermountain regions of the U.S., where the current area surplus will rise from about 2.8 million long tons per year of sulfur equivalent to about 7.2 million tons per year by 1990. These supply/demand historical relationships and projections are summarized for each country and for North America in Table IV.

EMERGING PRICE OUTLOOK

Methodology

Our price forecast for sulfur over the next decade is predicated primarily upon two basic assumptions: (1) that the Frasch sulfur producers, although now a less dominant supply source in the North American and world markets, will continue to exert price leadership, especially during periods when a tight supply demand situation exists, such as today, and (2) that the pricing of sulfur in the U.S. will be determined, in large part, by the production economics of the U.S. Frasch industry - that is, the highest cost marginal supplier.

Therefore, we believe that the cost position of Frasch producers will determine the trend in sulfur prices, so long as the Frasch industry remains the marginal supply source - a condition that will continue over the forecast period. If, at some future date, the supplies of by-product sulfur reach a level which will fully satisfy the demand, this assumption may no longer be valid.

Frasch Production Costs

There are only six major producers of sulfur by the Frasch

TABLE IV
 NORTH AMERICAN SULFUR OUTLOOK: PAST AND PROJECTED SUPPLY/DEMAND BALANCE, 1970-1990
 (In millions of long tons of sulfur equivalent)

BASIS: (1) Assumes new U.S. Frasch sulfur capacity of 1 MM tons/yr is developed between 1980 & 1985

Area	Year									
	1970	1974	1978	1980*	1982*	1985*	1987*	1990*		
<u>UNITED STATES</u>										
Supply	9.1	11.2	11.6	12.0	13.0	16.2	18.9	21.8		
Demand	9.2	10.8	12.0	13.1	13.9	15.3	16.0	17.5		
Excess Supply	(0.1)	+0.4	(0.4)	(1.1)	(0.9)	+0.9	+2.9	+4.3		
<u>CANADA</u>										
Supply	4.6	7.5	7.0	7.0	6.6	6.5	6.2	6.0		
Demand	1.1	1.3	1.5	1.7	1.9	2.1	2.3	2.5		
Excess Supply	3.5	6.2	5.5	5.3	4.7	4.4	3.9	3.5		
<u>MEXICO</u>										
Supply	1.0	2.4	1.9	2.6	3.0	3.2	3.4	3.6		
Demand	0.5	0.8	0.8	1.1	1.5	1.7	2.0	2.3		
Excess Supply	0.5	1.6	1.1	1.5	1.5	1.5	1.4	1.3		
<u>TOTAL NORTH AMERICA</u>										
Supply	14.7	21.1	20.5	21.6	22.6	25.9	28.5	31.4		
Demand	10.8	12.9	14.3	15.9	17.3	19.1	20.3	22.3		
Excess Supply	3.9	8.2	6.2	5.7	6.3	6.8	8.2	9.1		

* Estimate

process in the world today. Duval, Freeport and Texasgulf dominate the U.S. picture. Azufrera Panamericana in Mexico is another major producer, and government-controlled organizations in Poland and Iraq mine via the Frasch process.

Since the Frasch industry is small, and has historically been highly profitable during most of its 70 year history, production costs have been closely guarded. It is well known, however, that the economics of Frasch production depend largely upon the amount and cost of energy required to produce superheated water to melt and recover the naturally occurring sulfur from sub-surface deposits. Because the life of a sulfur well is quite short relative to the life of a gas or oil well, the dominant cost factors in Frasch sulfur mining consist of the initial plant investment, the cost of energy and the expense of well drilling and development.

Royalty fees sometimes can be significant. Depending on the location of the Frasch deposit, transportation costs can be an important factor, as can be the availability and cost of fresh water.

Figure 2 has been prepared to show graphically the change in estimated production costs among the three producers since the early 1970's, with forecasts through 1990. As the figure shows, production costs in the early 1970's for all three producers were about the same, with costs well under \$20 per long ton. By 1985, we estimate that average production costs for the Frasch producers will lie in the \$60-\$80 per ton range. By 1990, we anticipate that production costs will range between \$85-\$125 per long ton.

Future Price Outlook

With the recent tightening of the sulfur supply situation, both in North American and worldwide, we can understand why prices increased over the past two years. It is, perhaps, less easy to understand why they expanded so rapidly. However, most of us are aware that prices can shift radically in commodity markets - both up and down - depending on supply/demand shifts, market psychology, regulatory changes, etc. The recent situation in precious metals offers a good example.

When the threat of the large tonnages of sulfur coming from the Overthrust Belt starts to become a reality, it would not be surprising to see a period of price instability and weakness occur, just as happened in the early 1970's after expansion in output occurred in Canada and the U.S. Based on present knowledge, the next period of greatest "stress" will probably occur in the mid-1980's. Many conventional thinkers today foresee an even tighter sulfur situation by the mid-1980's than exists today. Nonetheless, for the reasons stated, we believe that the recent and rapid upward spiral of rising prices and profit margins will be temporary rather than permanent. A view of the past sulfur prices in the Gulf Coast and in Western Canada is presented in Figure 3 along with our generalized price forecasts.

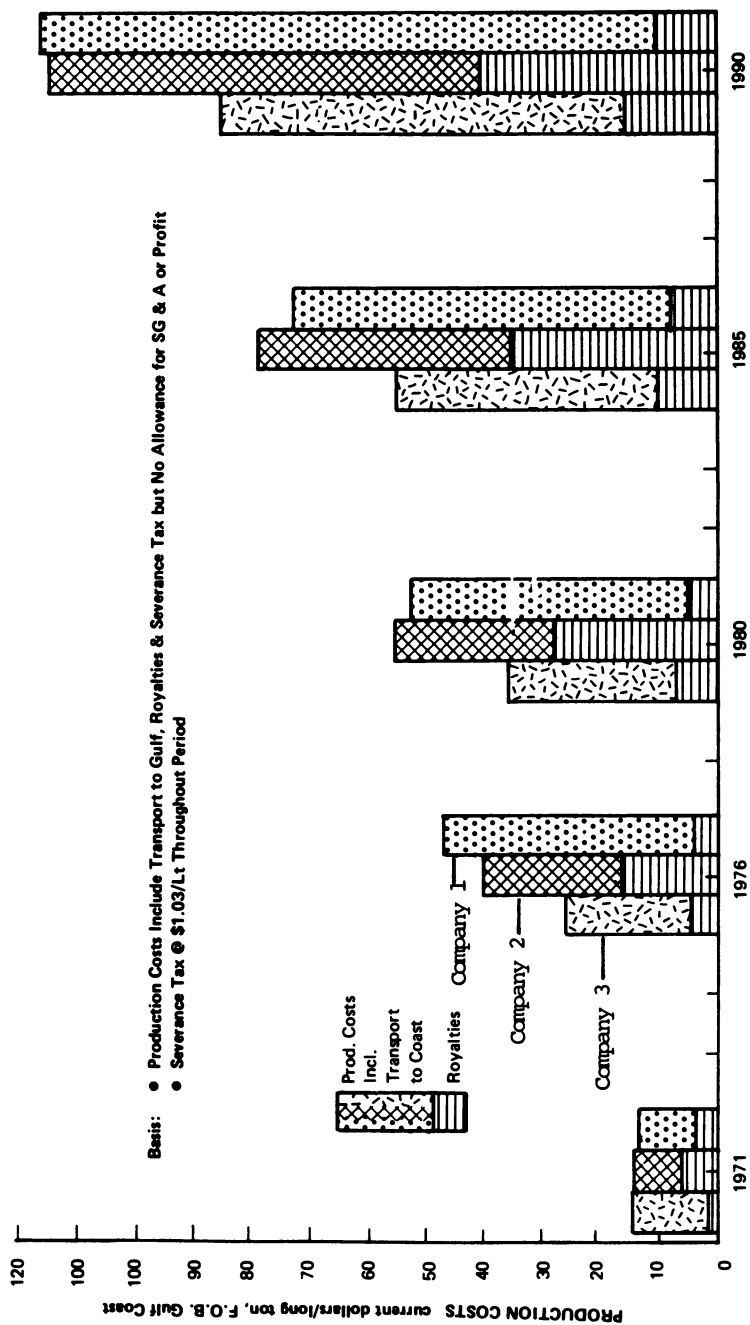


Figure 2. U.S. Frasch sulfur: estimated past and projected production costs by major producer: 1970-1990.

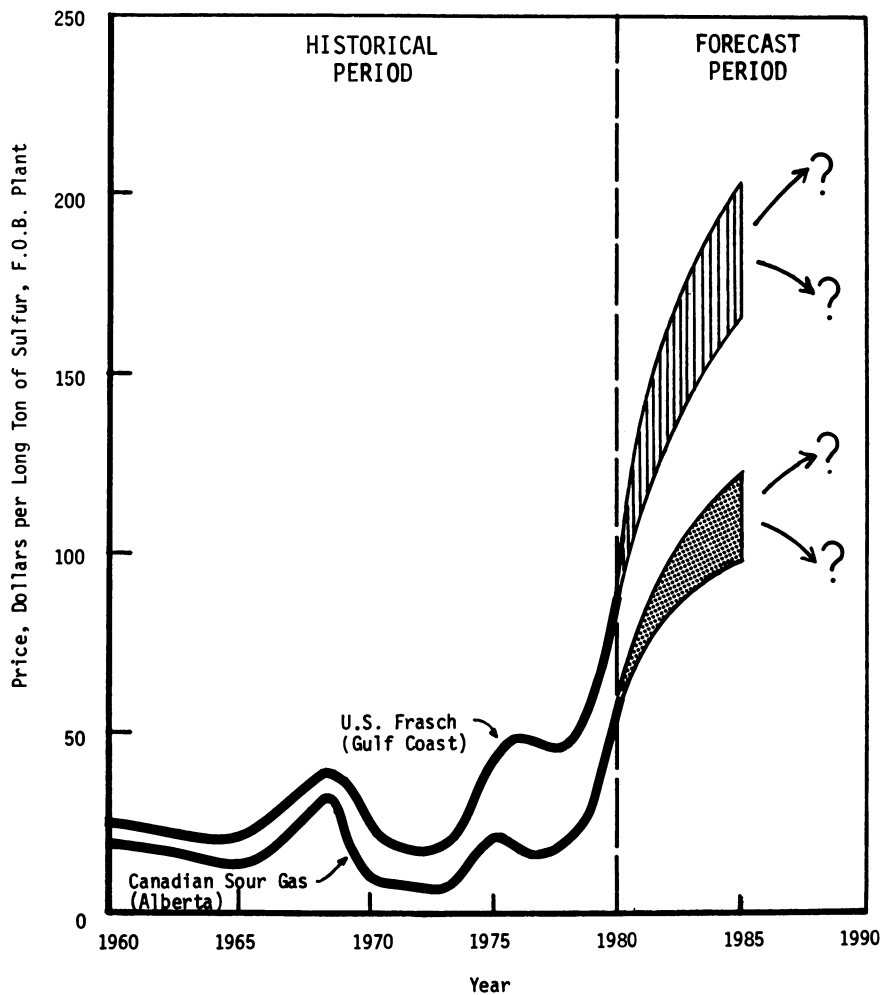


Figure 3. Past and projected sulfur prices in North America: U.S. Frasch vs. Canadian sour gas.

RECEIVED October 5, 1981.

New Product Opportunities for Sulfur

D. R. MUIR

Sulphur Development Institute of Canada (SUDIC),
#1702, 505 3rd Street S.W., Calgary, Alberta, Canada T2P 3E6

Investigation of novel uses of sulphur is not just a recent phenomenon - work was conducted sporadically during the 19th century and with greater intensity during the 1920s. But it was not until the early 1970s that the economic situation and the need for the unique properties of these materials provided sufficient incentive for their development and commercialization.

This paper will review only those technologies which are commercial or are approaching commercialization.

Several sulphur asphalt systems and sulphur concretes offer significant product performance advantages, combined with cost reduction potential, and in some cases, energy conservation. These products are in commercial use today. One other technology which has commercial potential produces small molded blocks, such as tile and brick, from sulphur.

Although not a new use *per se*, the agricultural importance of sulphur must not be overlooked. Its value as a micronutrient, although long recognised, is now taking on new significance in the light of world food needs and increasing costs of food production.

Approximately 87% of all sulphur is used as a processing chemical in the form of sulphuric acid and the bulk of the remaining 13% is used in one combined form or another for specialized chemical applications. Over the years though, researchers have been intrigued by the prospects of exploiting the unique chemical and physical properties of elemental sulphur in special product applications. In fact, research was conducted sporadically during the nineteenth century and with greater intensity during the 1920s. Three important factors, however, worked

0097-6156/82/0183-0127\$05.00/0
© 1982 American Chemical Society

against successful widespread commercialization - elemental sulphur was not widely available; it was expensive relative to other materials it could replace; and in general the technological demands of the marketplace were low (relative to today) so that the value placed on quality improvements to be gained through sulphur technology was correspondingly low - too low in fact to offset the adverse economics.

These constraints do not exist today. Research efforts were renewed in the early 1970s and have been successful in bringing a number of new products to the commercial or near-commercial stage.

This research was spurred by an extended period of serious over-supply of sulphur on the world markets. Although this situation has undergone substantial correction and supply/demand is in much closer balance, the results of this development work will have significant impact both on the product markets and the sulphur producer. The products themselves fill identifiable technological needs in the marketplace and thus provide definite advantages and benefits to the user. And as the products become more broadly used on a commercial basis, the value of sulphur will be upgraded and the cyclical supply/demand swings will be somewhat dampened, providing greater market stability for this commodity.

The whole field of new product markets cannot be adequately dealt with in a single paper. This presentation will be confined to a brief discussion of three products which are now at the commercial stage (two types of sulphur asphalts, for both road paving and patching, and sulphur concretes) and one product concept, molded sulphur blocks, which is believed to have good commercial potential. And, although the use of elemental sulphur in agriculture is neither a new product nor a new use, this application of sulphur will be reviewed because of its importance and the research attention it is currently receiving.

These are not the only areas in which research has been conducted. Several other sulphur technologies have been developed to the commercial stage, including insulating sulphur foams, sprayable protective coatings and sulphur paving mixes which use sand in place of aggregate. Because the major market for these products is outside North America, and in one case, the impact on the sulphur picture will be minor, these technologies will not be covered in this paper. As well, several other technologies are the object of preliminary studies directed towards determining economic and technical viability - this category includes for example the use of sulphur in plastics and building products.

The Commercial New Uses

Sulphur Extended Asphalt Paving Mixes. On average a conventional road paving mix consists of 5%/wt. asphalt cement (AC) and 95% graded aggregate, with the AC binding the aggregate together

to form a cohesive "flexible" structure. The hot mix is prepared simply by mixing hot liquid AC and preheated dried aggregate together, generally in the temperature range of 120-150°C (250-300°F), transporting the mix from the paving plant to the job site in dump trucks and uniformly applying it to the road surface with a paving machine. As the placed material cools through the temperature range of 80-100°C (180-210°F) it is densified by multiple passes with compactive rollers.

Molten sulphur can be emulsified into hot liquid AC and this emulsion used in place of regular AC as the binder in the paving mix (1). Such a system provides a number of potential advantages:

Reduction in AC usage - Stable sulphur asphalt emulsions can be produced with up to 40%/wt. sulphur. Since binder volume is the critical factor in the paving mix, and since the relative density of the emulsion binder is greater than regular AC, the substitution of AC by sulphur is not a one-to-one relationship. With a 40:60 emulsion, AC usage is reduced by approximately 27%/wt. This can provide a significant cost saving as well as a lesser dependence on not-always reliable asphalt supplies.

Lower fuel consumption - Binder rheology is favorably altered with the addition of sulphur. Of greatest importance is the downward shift in the viscosity/temperature relationship. Since paving plant mixing efficiency is dependent on binder viscosity, this means that the paving plant can often be operated at a lower-than-normal temperature. In addition, the pavement can be densified with less compactive effort. Both these advantages offer a potential fuel savings to the paving operation.

Improved pavement performance - After the densified pavement has completely cooled, the emulsified sulphur droplets solidify and act as a solid filler for the binder film. This system now exhibits certain improved properties over a regular asphaltic material. The stiffness/temperature relationship for the sulphur asphalt mix, while unaffected at lower temperatures, shows greater stiffness at high temperatures. As a result a sulphur asphalt will show no greater tendency towards cold temperature cracking, but will display much greater resistance to deformation at high temperatures; in practice there is a significant improvement in rutting resistance. Water stripping is greatly improved, and sulphur asphalt pavements exhibit a higher load bearing capacity which may enable a reduction in pavement thickness under appropriate conditions.

The manufacture of sulphur extended asphalt paving mixes is relatively straightforward. Except for production of the emulsion binder itself, no mechanical change is required in the paving plant and normal procedures are followed.

The several technologies which have been developed in this area focus on methods of manufacture of the emulsion binder and stabilization of the emulsion (2-4). While the technologies do vary in complexity, all work quite satisfactorily if employed under suitable conditions.

Stability of the emulsion is of prime importance. If the emulsion breaks, the advantages of adding sulphur are completely lost, with the impact on strength and durability properties particularly detrimental. As sulphur in asphalt emulsions are unstable by nature, due attention has to be paid to this point. One technology utilizes the addition of a surface-active agent to enable the production of a very fine emulsion and to avoid coagulation and subsequent separation of the components.

The driving force behind the commercial acceptance of sulphur extended asphalts is the cost reduction potential. Improved pavement performance, while of importance, is a secondary consideration. AC prices have been soaring recently in tandem with crude oil prices and continued rapid price escalation is forecast together with geographic shortages of asphalt. In many parts of North America a partial substitution of asphalt by sulphur will result in a reduction in cost per tonne of hot mix, and of course the use of sulphur will offset asphalt shortages (of up to 27%), wherever these shortages may occur.

Field development and evaluation of sulphur extended asphalts has been going on since the mid-seventies. The first commercial placements of sulphur extended asphalts under competitively bid contracts took place in North America in 1980. Of the approximately 160,000 tonnes of hot mix involved, over half used the additive technology mentioned above, the remaining projects used a number of different approaches.

A rapid growth is expected in sulphur extended asphalt's share of the market: The National Asphalt Pavement Association (NAPA) is forecasting sulphur extended asphalt use to reach 58 million tonnes by 1990 in the U.S. alone (5). In light of the world energy situation, this is a very timely and important product which should be in routine use in many parts of North America within the next several years.

Sand-Asphalt-Sulphur Road Patching Mixes. One sulphur asphalt product was developed specifically for road patching applications and is being used commercially in Canada (6, 7). The product consists of about 6%/wt. AC and 13% sulphur with the remainder aggregate or fine sand, depending on the patching application. The liquid AC, molten sulphur and hot aggregate are simply mixed in the correct proportion and placed in the pothole or depression using normal techniques. The mix itself is self-compacting and does not have to be densified to develop strength. Consequently, a leveling of the surface is all that is required to obtain a strong, durable patch. The mix can be used equally successfully for asphalt or concrete pavement repair.

A considerable economic benefit is offered by this product. Based on several years' experience one provincial highway department estimates that the installed cost is 60% less than for other conventional patching materials (7). In addition, the patches are proving to have a life span 2-3 times longer than normally experienced for conventional patches.

To date, use of this product has been limited for the purpose of developing economic and commercial data. Once this phase is completed, wider promotion should readily broaden the use of this material.

Sulphur Concrete. Sulphur concrete consists simply of modified sulphur and aggregate, with sulphur comprising 10-15%/wt. of the mix, depending upon aggregate type and gradation and end-use application. The product is made by mixing hot aggregate and molten sulphur together and pouring the mix into molds or forms and allowing it to cool (8, 9).

Sulphur concrete possesses a number of advantages over regular portland cement (PC) concrete. On the processing side, it sets as soon as it cools and gains full strength in one day versus the 28 days normally required for PC concrete. Unlike regular concrete, ambient temperature conditions are not a critical factor, so pours under winter conditions can be made without any special precautions. The product has very high resistance to corrosive acid and salt environments and offers significant advantages in those applications where regular concrete has a poor performance record.

Limitations on the use of sulphur concrete are imposed by its high temperature and fire susceptibility. Although it will not sustain combustion, under applied flame the sulphur will burn to produce SO_2 . At temperatures above the melting point of sulphur, the product loses structural integrity. Thus sulphur concrete is best suited for outdoor and underground use as well as indoor construction applications where fire hazard is not a concern and building codes are not applied.

The advantages of sulphur concrete have been known for a number of years, but one major technical problem - the durability of the product under temperature cycling - has prevented broad commercialization. A system of pure sulphur and aggregate simply does not have the capability to relieve stresses caused by cooling and setting and temperature fluctuations without cracking. Several technologies have been developed which significantly improve the durability properties by plasticizing the sulphur through reaction with other chemicals (10-13). Unfortunately this chemical plasticization is not permanent and will reverse within a time span as short as several months with one technology to as long as several years with another.

Depending on the specific end use, this reversion may not be a negative factor. Products such as flooring and sewer pipe will experience the most stress build-up during the initial period of time while the chemical plasticization is effective. Once in use further stress due to severe temperature changes is not likely to occur. However, other products such as bridge decking, highway pavement and curb and gutter can experience continuous stressing because of rapid climatic changes. In these cases, permanent plasticization is essential for product durability.

A recently developed technology takes a different approach to solving the stress problem (14). Rather than chemically plasticizing the sulphur, non-reactive additives are used to holistically plasticize the sulphur concrete mix. In essence these additives are lubricants which operate at the sulphur/aggregate interface to allow slippage and stress relief without disruption and cracking. The apparent permanency of this plasticization approach has been demonstrated by extensive testing over a four year period.

By varying the level of plasticizer, the stress/strain characteristics of sulphur concrete can be designed to fit the specific needs of the end use application. The range covers from high strength material similar to regular concrete to flexible material comparable to asphaltic concrete. As noted previously, with chemical plasticization reversion to the high strength brittle product occurs with time, regardless of plasticizer loading.

The current state-of-the-art has significantly advanced the performance properties of sulphur concrete to a point where it is commercially acceptable. However there still are limitations on the durability of the product in extreme temperature regimes. Very recent research has developed methods of imparting a considerably higher durability to sulphur concretes (15). Results indicate a superior performance to PC concrete in this regard, and as this technology is further developed the last restriction on the utilization of sulphur concrete (other than high temperatures) will have been removed.

Applications for sulphur concretes fall into two broad categories: utility uses and high corrosion performance uses. Utility applications refer to those for which PC concrete performance is relatively satisfactory, such as parking bumpers, precast curb and gutter, paving slabs and highway median barriers. In these applications in-place economics rather than performance is the criterion that will determine commercial use. As a general rule of thumb, when sulphur and portland cement are the same price, sulphur concrete should be economically competitive for these applications.

It is in the high corrosion performance uses where portland cement concrete rapidly deteriorates that sulphur concrete will enjoy a very strong position - this includes uses such as industrial flooring, acid storage tanks, electrolytic cells, sewer pipes and bridge decking where highly corrosive environments are encountered. Table 1 shows an example of potential savings to be gained in using sulphur concrete flooring in a corrosive environment. Estimates indicate that up to 70-75% of the cost of other flooring material can be saved over a ten year lifetime when replacement costs are taken into account.

Field evaluation of sulphur concrete has been conducted in a number of application areas - not always successfully because many field placements also involve process development work.

TABLE I. Estimated relative costs of flooring in corrosive environments.

	<u>PC Concrete with Acid Re- sistant Brick</u>	<u>PC Concrete with Acid Re- sistant Coating</u>	<u>PC Concrete</u>	<u>Sulphur Concrete (SC)</u>
Installed Cost (\$/ft. ²)	11	6	3	3
Estimated Life (yrs.)	10	5	2.5	10
Placements in 10 yr. Service	1	2	4	1
Discounted Cost for 10 yrs. Service (\$/ft. ²)	11	10	10	3
Relative to SC	3.7	3.3	3.3	1

Much more needs to be done, but sulphur concrete is being used now on a small commercial scale in specialized applications. And with recent advances in modifier technology, rapid commercial development and extension of the uses of sulphur concrete can be anticipated.

Moving Towards Commercialization - Molded Sulphur Blocks

Although hot-poured sulphur concrete is very suitable for poured-in-place and precast applications, the material cannot at this time be press-molded and is thus not amenable to high speed/high volume production of small blocks. Although a potentially large market exists for blocks of this kind, such as tile and brick, it was not until the late 1970s that an attempt to develop a cold mix/press-mold sulphur based technology was successful.

This technology (16, 17) produces sulphur concrete blocks by a manufacturing process very different from a hot poured sulphur concrete system. Solid sulphur, aggregate, liquid and a mineral binder are mixed together cold and compacted into a mold. Because of the presence of the small amount of liquid and mineral binder, the product retains its shape, although at this point the sulphur is not binding the product together in any way. The block is then dried to remove the liquid and heated in an oven to melt the sulphur.

Products made in this way meet or exceed specifications for PC concrete blocks and in addition have a much higher resistance to corrosion than the PC products. The sulphur-based blocks and bricks should therefore find ready usage in walls, storage sheds, agricultural buildings, warehousing, floors and patios as well as for low cost housing in those countries which already use block construction extensively.

The economics of this technology appear promising, although further work is necessary to determine accurate costs. The raw materials are inexpensive and readily available, and the manufacturing equipment can be adapted from currently available brick and block process units. The system has at least one process advantage over conventional block manufacture which will positively affect the economics: because sulphur-based blocks reach full strength on cooling, the blocks can be used within a few hours of mixing the raw materials. By comparison, conventional concrete blocks require a minimum of several days' storage for curing.

Most of the laboratory development work for this technology on mix design, formulations, processing conditions, property determination and durability evaluation has been completed. In addition, conceptual design and optimization of process conditions for a semi-commercial hydraulic block machine have been worked out.

Sulphur in Agriculture

Agricultural fertilization with sulphur is not a new concept - at the research level at least, sulphur has long been recognised as an essential plant nutrient. However because the complex role of sulphur - in soils, in plant material and in interaction with other essential element cycles - has never been fully understood, sulphur fertilizers have been used mainly on an empirical basis. As a result, sulphur fertilization has shown somewhat erratic performance: Measured sulphur deficiency in soils has not always been correlated with poor crop yield and, as a corollary, sulphur fertilization of sulphur deficient soils has not always improved poor crop yields. Thus it has been difficult to routinely demonstrate an economic benefit to the farmer.

Considerable research has been conducted on the uses of sulphur in agriculture and of course cannot be dealt with within the scope of this paper. But one program in progress in Canada is examining a very fundamental aspect of the use of sulphur in agriculture - a model that will allow prediction of sulphur requirements, losses and gains is being developed (18). Eventually this model could provide a complete mathematical explanation of the role of sulphur in the soil system and be applicable in any agricultural area.

This work will greatly enhance the reliability and effectiveness of sulphur fertilization and greatly improve the efficiency of agricultural food production. In light of present and forecasted world food needs, this will be a significant accomplishment.

Summary

Recent research has led to a number of new products - several of which have been reviewed here - that are being used commercially or are close to commercialization. There is little doubt that these will gain broad use. Although forecasting market size in the short term is very difficult, a recent publication by the U.S. Bureau of Mines (19) estimates that the probable annual demand for sulphur by new uses in the U.S.A. will be 10 million tonnes by 2000. In light of long term trends, this is not an unreasonable figure and if realized, certainly implies significant commercial success for these new products.

Literature Cited

1. Rennie, W.J., New Uses for Sulphur, 2(2nd Ed.) Sulphur Development Institute of Canada (SUDIC) 1979.
2. Garriques, C., Signouret, J.B., Chambu, C., U.S. Patent 3,970,468 (1976)
3. Pronk, F.E., U.S. Patent 4,154,619 (1979)
4. Kennepohl, G.J.A., Logan, A., Bean, D.C., U.S. Patent 4,155,654 (1979)
5. Foster, C.R., NAPA Special Report, National Asphalt Pavement Association, (July, 1980)
6. Kopvillem, O., MacLean, J.W., Canadian Patent 945,416 (1974)
7. Culley, R.W., Saskatchewan Highways & Transportation Technical Report 29 (1979)
8. Shrive, N.G., Gillott, J.E., Jordaan, I.J., Loov, R.E., Potential & Properties of Sulphur Concretes, American Chemical Society Meeting, Atlanta (1981) (This volume)
9. Raymont, M.E.D., New Uses for Sulphur (4), Sulphur Development Institute of Canada (SUDIC) (1978)
10. Sullivan, T.A., McBee, W.C., U.S. Department Interior Bureau of Mines Report No. 8160 (1976)
11. Leutner, B., Diehl, L., U.S. Patent 4,025,352 (1977)
12. Vroom, A.H., U.S. Patent 4,058,500 (1977)
13. Gregor, R., Hackl, A., Adv. in Chem. #165 (ACS), 54 (1978)
14. Gillott, J.E., Shrive, N.G., Jordaan, I.J., Loov, R.E., U.S. Patent 4,188,230 (1980)
15. Gillott, J.E., Shrive, N.G., Jordaan, I.J., Loov, R.E., U.S. Patent Application. Unpublished
16. Terrel, R.L., U.S. Patent Application 073,503 (1980)
17. Terrel, R.L., Babaei, K., Proc. Int. Conf, Sulphur in Construction, Canada 519 (1978)
18. Bettany, J.R., "Sulphur Transformation in Relationship to Carbon and Nitrogen in Soil Organic Matter Studies", Saskatchewan Institute of Pedology. Not yet published.
19. Shelton, J.E., "Sulfur - A Chapter from Mineral Facts and Problems, 1980 Edition", Preprint from U.S. Department Interior Bureau of Mines Bulletin 671 (1980).

RECEIVED October 5, 1981.

The Potential and Properties of Sulfur Concretes

N. G. SHRIVE, J. E. GILLOTT, I. J. JORDAAN, and R. E. LOOV

University of Calgary, Department of Civil Engineering,
2500 University Drive N.W., Calgary, Alberta, Canada T2N 1N4

Sulphur concretes have been used for low-cost housing in developing countries and have potential for various other applications. Field trials have been conducted of sulphur-based curbs and gutters, sewer pipes, median barriers, linings for acid containers and road bases. Recent research has been concentrated on stress-strain behaviour, durability in environments aggressive to portland cement concrete, and durability in cycles of freezing and thawing. Various researchers have used different approaches in attempts to solve performance problems. Polymerization of the sulphur in a pre-mix operation has produced strong durable concretes with age-dependent stress-strain behaviours. Additives which alter intercrystalline and sulphur-aggregate boundaries have also been used: strain softening materials are obtained at the expense of strength. Mix design has also received attention. Strength is sensitive to mix design and the techniques used for asphaltic and portland cement concretes are not directly applicable. In the paper, the advantages of the different approaches to the problems are examined. New data are also presented and interpreted with previous results to provide a comprehensive view of sulphur concrete behaviour.

Sulphur concretes are materials in which the binder is principally elemental sulphur. These concretes are therefore different to sulphur extended asphaltic concretes and sulphur infiltrated portland cement concretes, which will not be discussed in this paper.

In sulphur concretes, the mechanical properties of the sulphur binder are usually altered from those of the "pure" crystalline (orthorhombic) element - the thermodynamically stable form of sulphur at room temperatures. The property alteration is

0097-6156/82/0183-0137\$05.00/0
© 1982 American Chemical Society

accomplished by polymerization of the sulphur or by the addition of small quantities of other materials to alter the intercrystalline or matrix-aggregate bonds.

In an earlier state of the art report (1) various properties of sulphur concretes were outlined. In the last few years, researchers have concentrated on the topics of durability (moist environment, biological and chemical attack, cycles of freezing and thawing), stress-strain behaviour and mix proportioning. Some work has been done on fatigue and a number of field trials have taken place. We will review these five latter topics in relation to recent work by various researchers, and then discuss the potential applications of various sulphur concretes.

Durability

When swelling clay is present in the aggregate, moisture can cause cracking or complete disintegration of the concrete (2). The problem can be overcome by using aggregates free of swelling clay, by treating the aggregate with a polyol, crude oil, or most suitably, selected fractions of crude oil (3). Mechanisms by which these additives provide resistance to moisture have been proposed (3). One possibility is that the polyol fixes the interlayer spacing of the clay mineral. However, the quantities of additive required to provide resistance to given amounts of swelling clay have not yet been determined in detail.

Sulphur concretes resistant to moisture show good durability in the presence of various acid and salt solutions which are normally aggressive to portland cement concretes (4, 5, 6). Care must nevertheless be exercised with the aggregates to be used.

Bacteria of the genus thiobacillus attack sulphur in the presence of moisture, oxygen and warmth (except thiobacillus denitrificans which grows without oxygen). The acid produced may cause long term problems close to the concrete if the buffering capacity of the soil is low (7). Damage to specimens is usually restricted to the surface.

The problem of durability in cycles of freezing and thawing has received much attention. In cold climates, cyclic freezing and thawing is certainly one of the more common causes of durability failure of exposed concrete and other building materials. The currently accepted mechanisms of failure in portland cement and sulphur concretes are different. Both mechanisms are discussed for subsequently obvious reasons.

With portland cement concretes, deterioration takes the form of horizontal cracks, pop-outs, D-cracking, spalling and scaling. Salts used as deicing agents compound the problem. Early theories attributed the mechanism of failure to the 9 per cent volume increase when water converts to ice. "Critical saturation" - moisture filling more than 91 per cent of the voids was considered important.

More recently, moisture migration towards growing ice cry-

stals has been regarded as a principal factor. Pressures great enough to exceed the tensile strength of the material have been attributed to an osmotic-type mechanism (8) and to differences in vapour pressure between the more stable ice and unfrozen water adsorbed on internal surfaces (9). Ice is now believed to form in large voids, cracks or external surfaces whereas the freezing point of surface adsorbed water is depressed. Because the internal surface area is high, the amount of adsorbed water is considerable.

While the properties of the cementitious binder are known to be important, it is also recognized that certain aggregates cause further problems especially in the presence of salts and deicing agents. The decrease in durability has been attributed to both physical mechanisms (10) and chemical processes (11). Salt solutions are known to corrode the surfaces of some aggregates (12).

In sulphur concretes, the mechanism of deterioration caused by frost action has been attributed to entirely different causes to those above. The material has low permeability to moisture and as water is not used in mixing, it was not considered that water played a major role in deterioration. Sulphur has a very high coefficient of thermal expansion ($\alpha \approx 55 \times 10^{-6}/^{\circ}\text{C}$) and low thermal conductivity ($0.27 \text{ W/m}\cdot\text{K}$). Hence the poor durability performance in cyclical freezing and thawing has been attributed to the development of high stresses due to thermal gradients (5, 13, 14, 15, 16). A contributing factor was thought to be the weakening effect of residual stresses resulting from the crystallographic inversion from the monoclinic to the denser thermodynamically stable orthorhombic form on cooling below 95.5°C . Attempts to improve durability have therefore been based on plasticization of the sulphur. The intention is to reduce brittleness and lower the level of internal stress (5, 13, 14, 15, 16).

Recent work at the University of Calgary has shown that whilst the permeability is low, moisture does gain access to the interior of sulphur concrete specimens continuously exposed to moisture. Previous work (2) had indicated that specimens subjected to temperature variations alone suffered little deterioration. It was thus thought that the mechanism of failure was not that described immediately above but might be more akin to that proposed for portland cement concretes. We therefore have attempted to air-entrain sulphur concretes. Laboratory tests on these "air-entrained" concretes have shown significant increases in the average number of cycles of freezing and thawing to failure. ASTM C666 freezing and thawing in water, was the test used.

Some specimens have withstood over 500 cycles. Untreated specimens of these concretes commonly failed the test at approximately 80 cycles. The elastic modulus criterion (less than 60% of original by resonant frequency analysis) was used to determine failure. Specimens often failed the test with no visible cracking or spalling. Strength retention in these specimens was usually high (50% or more).

With other sulphur concrete technologies, different results were obtained. Specimens of one technology failed the test within 90 cycles whereas specimens supplied by the U.S. Bureau of Mines failed on average at about 250 or 300 cycles (two types of concrete). It is interesting to note that these latter materials (both forerunners of the current U.S. Bureau of Mines "rigid" materials) had the same durability when tested at six months and at 14 months. The stress-strain behaviour altered significantly in that time (see next section). This would confirm the supposition that durability in cycles of freezing and thawing is not totally dependent on stress-strain behaviour.

Stress-Strain Behaviour

The variety of potential applications of sulphur-based materials - from coatings to pavements to structural components - dictates that great care has to be exercised in declaring that one or other stress-strain property of the material is "good". For example, creep has an adverse effect on the behaviour of a prestressed concrete member but is irrelevant when considering curbs and gutters since these are subjected to very small sustained stresses.

Other illustrations are given in Figure (1). Figures (1) (a) and (b) show cases where the material of interest (here, sulphur concrete) is called upon, respectively, to support load and to endure strain. The requirements for the material are quite different: in the first case, strength is the main requirement, while in the second case the required properties are flexibility, strain capacity (without damage), and ductility. These two cases are mirrored in the second pair of sketches in Figures 1 (c) and (d), in which we have depicted a paving material covering a surface under which a weakness has developed. In the first case, the weakness is bridged - as might happen if the paving material were conventional portland cement concrete. In the second case, the material deforms (preferably with little damage) so as to accommodate itself to the new shape dictated by the weakness, which would be the case for asphalt concrete.

The kind of test that is appropriate in the two cases is different; in the first case, load should be increased until failure while in the second, some sort of deformation (or strain) control is appropriate. (A practical case of the latter is the Marshall stability test for evaluating the performance of asphalt concrete). In reality some combination of stress and strain capacity is required.

The strain-control test has the advantage that information on the strain capacity is obtained, as well as the maximum stress that can be sustained, the latter value being similar to that obtained in a conventional test with constant loading rate. In the following we shall discuss behaviour in compression in tests with a constant strain rate.

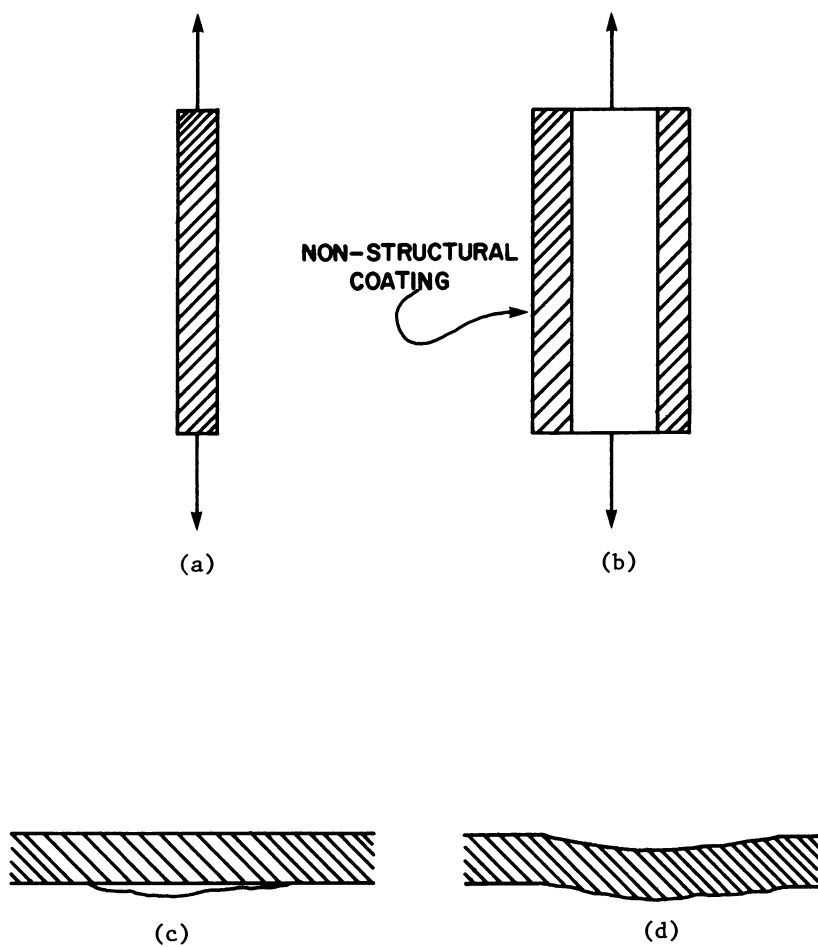


Figure 1. Illustration of different material applications requiring different stress-strain behavior. In a and b, vertical load-bearing members are depicted; in c and d, a paving material covering a surface weakness is shown.

It is possible to conduct theoretical exercises using various material properties so as to analyze physical situations like those illustrated in Figures 1 (c) and (d). This would permit one to make reasoned arguments regarding potential behaviour in an application, but requires a mathematical formulation of the stress-strain relationships, including the definition of limiting (unacceptable) states. In the past few years, the technology of sulphur concretes has seen quite rapid changes and our approach is to use experimental results to estimate potential behaviour. Subsequent field trials will provide confirmation or otherwise, of these ideas.

Sulphur concrete (without additives) will typically have a near-linear stress-strain curve up to failure, which occurs explosively at a strain usually between 0.0005 and 0.002. The peak stress varies from 20 to 70 MPa depending on the mix design. Sulphur concrete is thus a strong but brittle concrete material; the brittleness need not necessarily be a grave disadvantage; cast iron was used for a long period of time as a construction material. Any modification to the stress-strain behaviour should be evaluated carefully to see whether the modification is potentially useful. Two different approaches have been used to modify stress-strain behaviour. The modifications are (a) polymerization of the binder (4, 5, 17) and (b) use of the thermodynamically stable orthorhombic sulphur as the binder with alteration of the bond behaviour (3, 18). The matrices of both types of concrete are thus "modified" sulphur.

Polymerization of Binder: Polymerized sulphur usually gives materials with greatly enhanced strengths and ductile stress-strain diagrams - see Figures 2 and 3. The figures illustrate the behaviour of sulphur concretes produced at the University of Calgary with 4% DCP (dicyclopentadiene) by weight of sulphur and also that of the two types of concrete (designated A and B) supplied by the U.S. Bureau of Mines. It should be noted again that these latter materials were not of the current (1981) technology.

A major disadvantage of the materials using polymerized sulphur as the binder, is the time-dependence of their behaviour; the polymerized sulphur is metastable and in all cases the ductility disappears within a relatively short period of time (a few months to about 15 months, Figures 2 and 3). This time-dependence was also found previously by Currell and his co-workers (19). Data on Sulphlex (17) show similar trends.

Metastability is often incorporated in engineering materials but ways have to be found to ensure that the time-frame during which desired properties persist is reasonable from an engineering point of view. In favour of the modified materials, it should be noted that the high strength appears to remain for the periods examined here, even though the ductility disappeared. One modified material, Sulfurcrete (5, 20) does show increased strength but is consistently brittle.

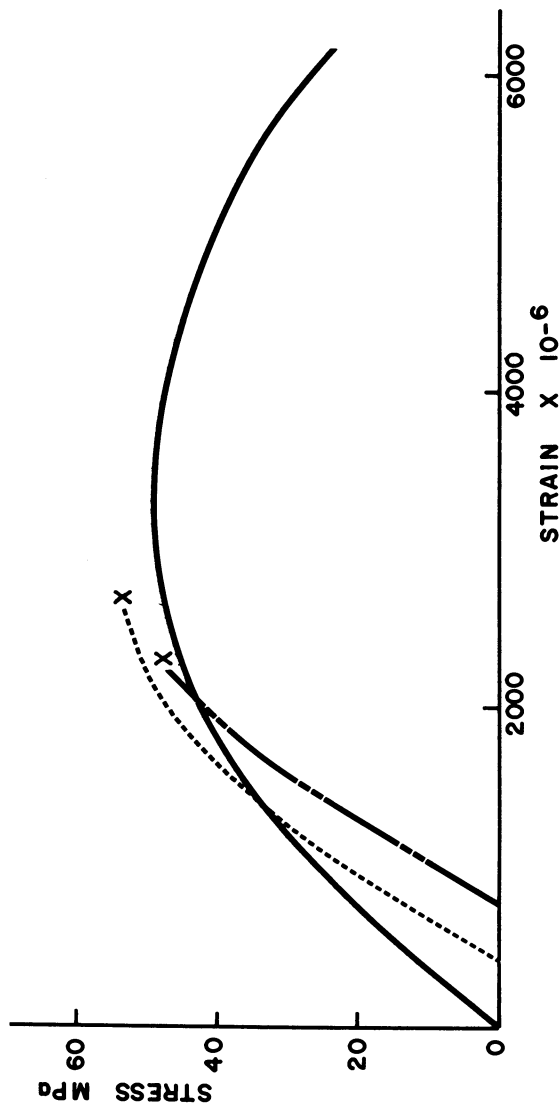


Figure 2. Change in stress-strain behavior with time, with dicyclopentadiene polymerized sulfur used as the binder. Key: —, 2 weeks; - - -, 4 months; ·····, 12 months; and X denotes sudden brittle failure. Note: 4 and 12 months curves are offset by 400 and 800 micro-strain, respectively.

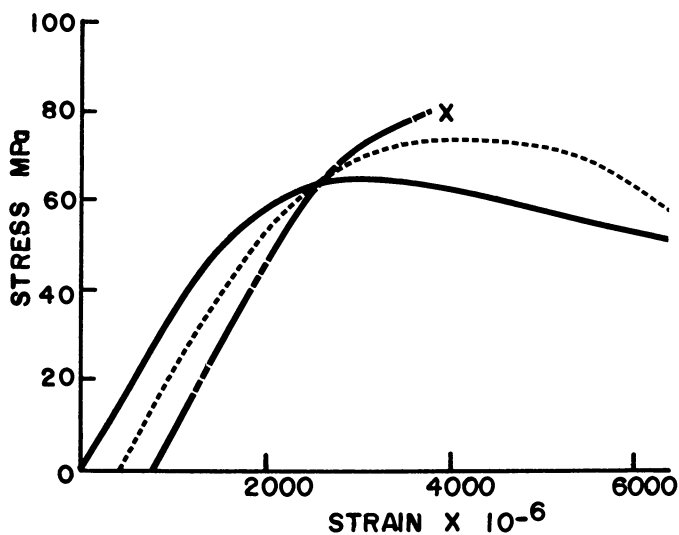
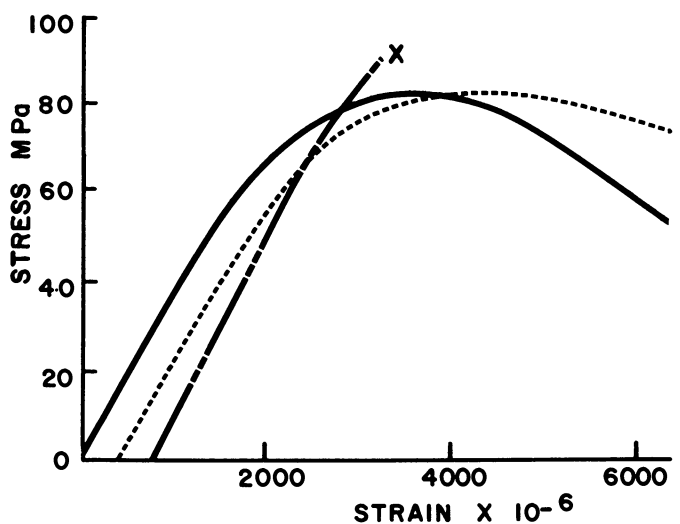


Figure 3. Change in stress-strain behavior with time, with specimens supplied by the U.S. Bureau of Mines, Type A (top) and Type B (bottom). Key: —, 2 months; ---, 5 months; and - - - -, 14 months; where X denotes brittle failure. Note: 5 and 14 months curves are offset by 400 and 800 micro-strain, respectively.

Bond Behaviour: This type of modification is thought to involve alteration of the bond characteristics between the sulphur matrix and the aggregate and between sulphur crystals within the matrix (3). The general behaviour of these materials can be seen in Figure 4. Percentages noted are selected fractions of crude oil by weight of sulphur. The additive reduces strength but substantially increases strain capacity. Also, the modified behaviour has not altered noticeably within 3 years (Fig. 5) (the 3 year old specimens were from a different batch to the 1 week and 1 year old specimens). The curves in Figure 4, and others that we have obtained, show that with high levels of these modifiers the stress-strain curve of sulphur concrete becomes similar to that of asphalt concrete (18). This suggests potential application in paving materials; a range of strategies between those exemplified in Figures 1 (c) and (d) becomes possible. However, the response to various stress and strain cycles with measurements of the consequent damage to the material, as was done by Spooner and Dougill, (21), should prove invaluable in evaluating the potential of such strategies.

Fatigue

The phenomenon involving failure of a material subject to repeated loading is called fatigue. Failure occurs at stress levels below those observed in the "static" tests described above. Lee et al (22) examined the characteristics of some sulphur concretes subject to fatigue. Fatigue lives (the number of cycles to failure) considerably in excess of those for portland cement concretes were observed. Polymerization of the sulphur with dicyclopentadiene was observed to reduce fatigue life.

Preliminary results of work at the University of Calgary confirm the high fatigue life with unmodified sulphur as the binder. In 1/3 point bending tests at a load nominally 95% of static strength, the fatigue life was on average 1670×10^3 cycles. A reduction in fatigue life was observed when the binder was modified by the addition of selected fractions of crude oil. The frequency distribution became bimodal with peaks at 200×10^3 and 1400×10^3 cycles. However, even these reduced fatigue lives of sulphur concrete exceed that for portland cement concretes.

Mix Design

The importance of mix design has been recognized for some time. The strength of sulphur concretes seems to be sensitive to the gradation of the aggregate used and to the quantity of sulphur in the mix. Since the sulphur matrix is the most expensive component, it is logical to reduce this to an appropriate practical minimum to provide more economical products.

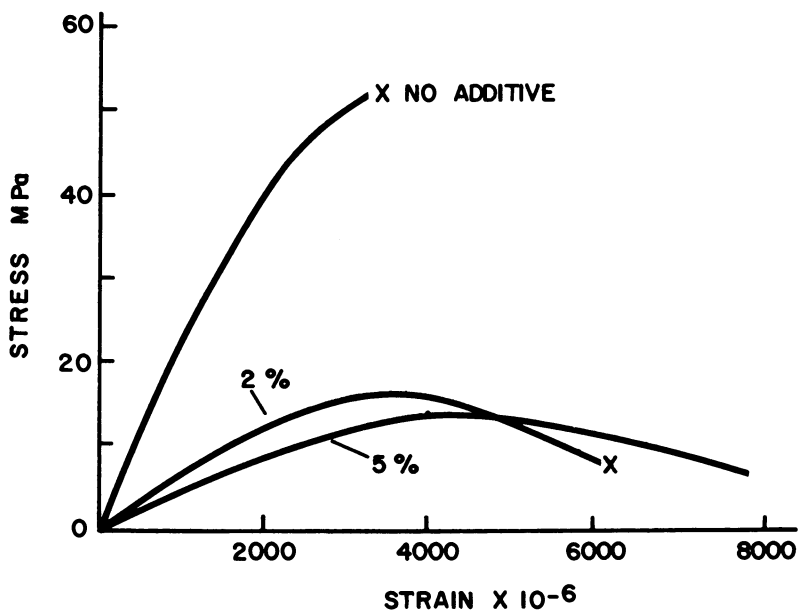
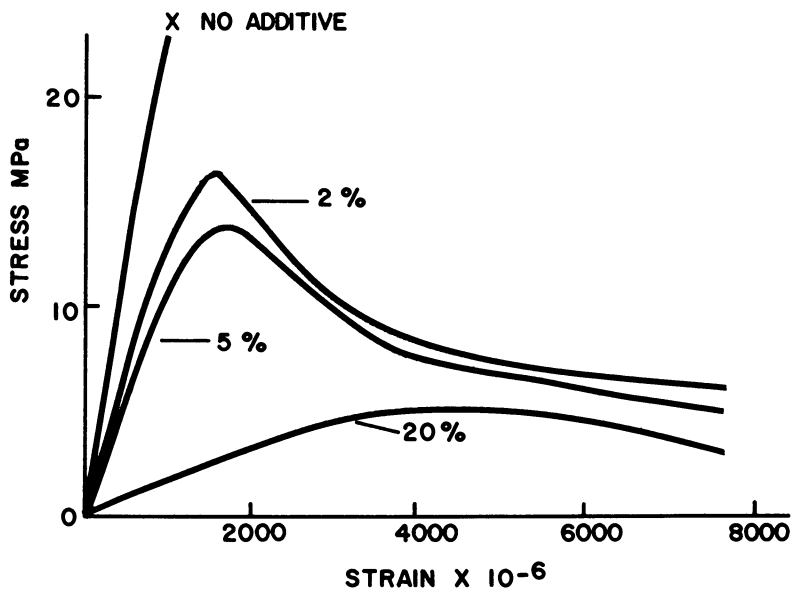


Figure 4. Stress-strain behavior of a mortar and a concrete of the University of Calgary (Sudicrete) materials with varying percentages of additives. Top, flyash concrete; bottom, flyash mortar; and X denotes sudden brittle failure.

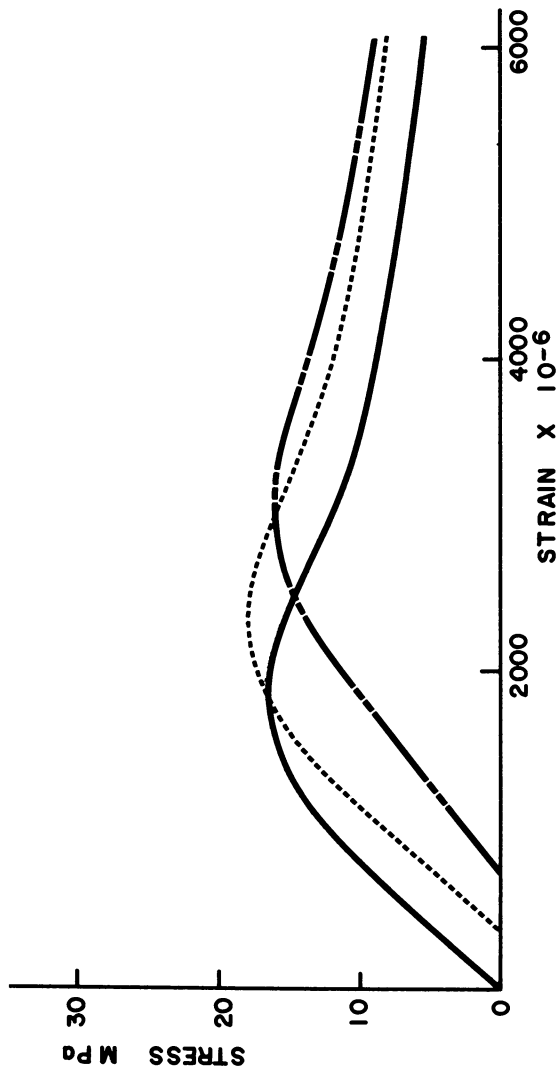


Figure 5. Stress-strain behavior of University of Calgary (Sudicrete) material with 5% additive as a function of age. Key: —, 1 week; ---, 1 year; ····, 3 years. Note: 1 and 3 year curves are offset by 400 and 800 micro-strain, respectively.

American Chemical
Society Library
1155 16th St., N.W.
Washington, D.C. 20036

Other researchers (23, 24) have shown that continuous gradation as for asphaltic concretes is a suitable basis for grading aggregates for sulphur concretes. The so-called "Fuller curves" are based on theory developed for closely packed spheres. However, with slightly different limits, blends with a lower volume of voids can be obtained for rounded aggregate, and with other limits again, for crushed (angular) aggregate (23).

In our initial work, we used the graphical "trilinear plot" to determine appropriate mixes of coarse aggregate, sand and fly-ash. For aggregates from one local pit, it was determined that no combination of the three aggregates would give a gradation entirely within the limits specified for asphaltic concretes. Therefore, five gradations were chosen to correspond roughly with:

- 1) above the upper limit line
- 2) the upper limit line
- 3) the mid-line between the limits
- 4) the lower limit line
- 5) below the lower limit line.

Since the chosen blends varied considerably about the lines of intended correspondence, mathematical optimization by obtaining the least squares difference from a chosen gradation was employed thereafter.

Aggregates from a different source were blended using the mathematical technique to obtain five curves as before. The grading curves are shown in Figure 6. Mix 2 is almost coincident with the upper Fuller limit and mix 4 with the lower limit. Strengths, voids in the mineral aggregate (VMA), and densities are given in Table 1.

Table I

Blends of Aggregate from Beiseker Pit
and Properties of Resultant Sulphur
Concretes (Binder = Sulphur, no additives)

Mix No.	Coarse %	Fine %	Fly Ash %	VMA (%)	Strength (MPa) ± Std. Devia- tion
1	26.2	40.3	33.5	26	72 ± 2
2	30.9	43.0	26.1	23	65 ± 6
3	41.0	39.3	19.7	17	69 ± 6
4	51.2	35.5	13.3	18	68 ± 2
5	60.4	32.3	7.3	16	51 ± 6

For mix 3, the sulphur content was varied above and below the VMA percentage to determine the affect of this change. The results are shown in Table 2.

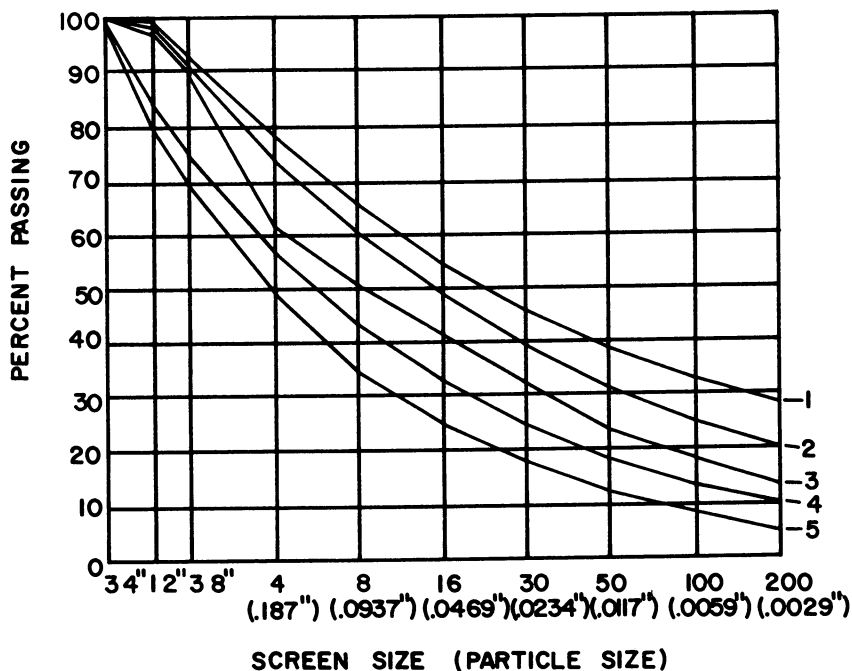


Figure 6. Gradation curves of different aggregate blends. Lines 2 and 4 correspond closely to the upper and lower Fuller curve limits, respectively.

Table II

Strength (MPa) vs Binder Content for Mix 3 of Table 1

Mix No.	% Binder (by volume)	Binder	
		Sulphur	Sulphur + 2% Selected crude oil fraction.
3a	15	66	35
3	17	69	33
3b	19	63	32
3c	21	68	29

Examination of the results obtained from both sources of aggregate indicated some general conclusions.

1. Mixes with a very large proportion of fine particles which fall at or above the upper Fuller curve are relatively expensive because they require a large volume of sulphur to fill the voids. This finding is in agreement with Gregor and Hackl (23). Also, the strength is high.
2. Mixes with a very low proportion of fine particles which fall below the lower Fuller curve appear to have reduced strength. The required sulphur content is low.
3. Mixes falling within the Fuller curves at the fine end appear to be best because they require a low sulphur content and have reasonable strength.
4. The VMA appears to indicate the approximate volume of binder required for a mix. Increasing or decreasing the binder content did not produce a consistent variation of strength.

Conclusion 3 led us to consider whether it is important to follow the Fuller curves all the way. Qualitatively we can argue that the larger particles must be analogous to cherries in a fruit cake and not of great significance in the mix design. (One may question therefore why the gradation of aggregates is based on the size of the largest particle). The fine end is not of significance if the fine particles are just slipping into and not filling the gaps between the larger particles. With too many fines the fine particles interact and push the larger particles apart, thus causing the VMA to increase. The particles which should be important are those around the "average" size which are touching and interacting with each other. In our case, these latter particles range from the 3/8" or No. 4 sieve to the No. 30 sieve. Work involving the slope of the gradation curve in this sieve range has not yet been completed.

We have determined, however, that although existing techniques for the blending of aggregates can produce mixes with low

VMA's, these methods will not necessarily produce a mix with the lowest VMA possible with the aggregates available. The particle shape and surface, boundary effects from the container, compactive effort and the ratio of the "sizes" of the aggregates must all play a part in the blending procedure.

Field Trials

A number of field trials of various sulphur concretes are in progress. Sulphlex has been used for road bases in Texas (17), and the University of Calgary material, under the name Sudicrete, for the same purpose in British Columbia.

The U.S. Bureau of Mines material has been used extensively in applications involving corrosive environments (4). Also Sudicrete is now being tested in such an environment.

The Sulphur Innovations Ltd. material, Sulfurcrete, has been sold commercially as pre-cast products (pipeline weights, median barriers, parking curbs, etc.) and poured in place as road patches, floor slabs, retaining walls, etc. (20).

Because of the precise reproduction of mould shapes, sulphur concretes are ideal for use in interlocking blocks. Housing has been constructed in the United Arab Emirates (25) and Mexico (26) with such blocks. Also an interesting compression mould, post-heat process for simple mass-production of interlocking blocks has been developed at the University of Washington (27) and a number of buildings have been constructed from the product.

It should be noted that results from early field trials should be considered in terms of knowledge of sulphur concrete at the time of the trial. Significant improvements have been made since these tests which should be reflected in field performance in new trials.

Discussion

The properties of a material must dictate the applications in which it will best perform its intended use. All materials made to date with polymerized sulphur show time-dependent stress-strain behaviour. The reversion to the brittle behaviour of orthorhombic sulphur is inevitable as the sulphur transforms from the metastable polymeric forms to the thermodynamically stable crystalline structure. The time-span involved of at most 15 months (to date) would indicate that no such materials should be used in applications dependent on the strain softening behaviour. Design should not be based on the stress-strain relationships observed at an age of a few days. Since the strength of these materials is maintained, however, uses based on strength as the only mechanical criterion would be reasonable.

Strength should not be confused with toughness. Toughness is a measure of the ability of a material to absorb energy prior to failure. A strong brittle material will probably be less tough than a weaker but more ductile material. Under impact load-

ing (eg. a median barrier being hit by a truck) the latter material would be a more suitable choice than the former.

In Sudicrete the gain of consistent stress-strain behaviour with time has been at the expense of strength. However, in road base-course applications, strength is not the dominant criterion: the ability to absorb strain without failure is more important. Since the fatigue life is high, Sudicrete shows singular promise for this type of application. The material would also be suitable for pre-cast and other products requiring toughness.

Sulphur concretes appear well suited for use in environments corrosive to portland cement concretes. The extensive work by the U.S. Bureau of Mines shows their material performs admirably in such environments. When used as a lining, the initial stress-strain behaviour will allow the material to adapt to the main structural element and relieve internal stresses without cracking. Corrosion resistance will be maintained by the material thereafter, even though the stress strain behaviour alters. On its own, the material retains sufficient strength to withstand typical loads involved in this type of application (eg. liquid container). Sudicrete has not been tested much in this area, although laboratory tests show similar promise.

Interlocking construction blocks are also a promising field for sulphur concretes. The various types of blocks produced allow easy construction. The close reproduction of mould shape is a major advantage: mortarless construction has been employed, allowing use of unskilled labour. Improvements in mix design should lead to a reduction in the quantity of binder required and thus a reduction in cost.

Summary and Conclusions

Sulphur concretes have undergone substantial development in the last six years. Recent effort has been directed towards improved durability and less brittle stress-strain behaviour has been achieved. A technology has been developed to produce a material (Sudicrete) with the same stress strain behaviour after three years as that observed soon after casting. Other materials show a consistent reversion to brittle behaviour with time. Nevertheless, there is considerable room for improvement in mix design.

Durability in corrosive environments is impressive. Durability in cycles of freezing and thawing is being improved.

Applications of sulphur concretes should be considered in respect of the material properties. Unfortunately this is not always the case. The major areas of application appear to be:

- 1) in road-bases for materials in which the static stress-strain behaviour does not deteriorate with time;
- 2) in pre-cast and cast-in-place products;
- 3) in corrosive environments.

Acknowledgements

The authors are grateful to Messrs. Harry Pollard, Brad Berg and Jeff Urquhart for their efforts in providing the data used in this manuscript. The work was supported by grants from the National Science and Engineering Research Council of Canada and the Sulphur Development Institute of Canada. We would also like to thank the reviewer for his constructive and helpful comments.

Literature Cited

1. Loov, R.E., Proc. Int. Symp. on Concrete, Monterey, N.L., Mexico 1975. Available as Research Report CE75-2, Dept. of Civil Engineering, Univ. of Calgary, Calgary, Alberta.
2. Shrive, N.G., Gillott, J.E., Jordaan, I.J., Loov, R.E., J.T. Eva, 1977, 5, 6, 484-493.
3. Gillott, J.E., Jordaan, I.J., Loov, R.E., Shrive, N.G. U.S. Patent, 1980, 4,188,230.
4. McBee, W.C., Sullivan, T.A. U.S. Dept. of Interior, 1979. Bureau of Mines, R.I. 8346.
5. Vroom, A.H. U.S. Patent, 1977, 4,058,500
6. Gillott, J.E., Jordaan, I.J., Loov, R.E., Shrive, N.G. A.S.T.M., 1980, S.T.P. 691, pp. 549-559.
7. Laishley, E.J. Alberta Sulphur Research Quarterly Bulletin, 1978, Vol. 15, 2, pp 26-35.
8. Powers, T.C. A.C.I., 1975, S.P.-47, pp 1-11.
9. Litvan, G.G. Cement & Concrete Research, 1976, 6, 3, 351-56.
10. Verbeck, G.J., Klieger, P. Bull. Highway Res. Board, 1957, 150, 1-13.
11. Browne, F.P., Cady, P.D. A.C.I., 1975, S.P. 47, 101-119.
12. Gillott, J.E. A.S.T.M., 1980, S.T.P. 691, 605-616.
13. Duecker, W.W. Chem. and Mech. Engineering, 1934, pp 583-86.
14. Currell, B.R., Polymers, Paint and Colour Journal, 1978, pp 674-8.
15. Sullivan, T.A., McBee, W.C. Proc. Int. Conf. on Sulphur in Construction, Canmet, Ottawa, 1978, Vol. 2, 453-474.
16. Malhotra, V.M. Canmet Report 79-28, 1979, Energy Mines & Resources, Canada.
17. Ludwig, A.C., Gerhardt, B.B., Dale, J.M. U.S. Fed. High Admin. Rept., 1980, RD-80/023.
18. Jordaan, I.J., Gillott, J.E., Loov, R.E., Shrive, N.G., Proc. Int. Conf. on Sulphur in Construction, 1978, Canmet, Ottawa, Vol. 2, 475-488.
19. Blight, L., Currell, B.R., Nash, B.J., Scott, R.A.M. and Stillo, C. Am. Chem. Soc., 1978, Advances in Chemistry Series 165, pp 13-30.
20. Vroom, A.H. Sulphur Res. & Dev., 1979, Vol. 2, 15-18.
21. Spooner, D.C., Dougill, J.W. Mag. Conc. Res., 1975, 27, pp 151-160.
22. Lee, D -Y, Klaiber, F.W., Khosraviani, S. Proc. Int. Conf. on Sulphur in Construction, Canmet, Ottawa, 1978, Vol. 2, 489-502.

23. Gregor, R., Hackl, A. Am. Chem. Soc., 1978, Advances in Chemistry Series 165, 54-78.
24. Johnston, C.D. Proc. Int. Conf. on Sulphur in Construction, Canmet, Ottawa, 1978, Vol. 2, 413-432.
25. Ortega, A. Sulphur Research Dev., 1979, Vol. 2, 12-14.
26. Zucker, L., Architect, Mexico. Communication to Int. Conf. on Sulphur in Construction, Canmet, Ottawa, 1978.
27. Terrel, R.L., Ahmed, M. Proc. IAHS Int. Conf. on Housing Problems in Developing Countries, Dhahran, Saudi Arabia, 1978, Vol. 1, 651-669.

RECEIVED October 5, 1981.

A Review of the State of the Art of Sulfur Asphalt Paving Technology

D. SAYLAK

Texas A&M University, College Station, TX 77843

W. E. CONGER

Chemical Enterprises, Inc., Houston, TX 77024

Construction, maintenance, and rehabilitation costs for pavements have risen sharply during the past decade, while revenue for these purposes has leveled or declined. In an effort to offset these rising costs and reduce dependence on uncertain asphalt supplies, increased research and development activity throughout the world has been devoted to the development and implementation of new and improved materials for use in pavement construction and maintenance. The use of sulfur in asphalt paving materials has proven to be one of the more promising developments to come from these activities.

Sulfur was a natural choice for study because of its unique structural properties, low price, and projected surplus in the future. Although the price of sulfur has increased dramatically in the past few years, producers contend that, allowing for inflation, sulfur prices are not out of reason [1]. Reduced production due to political situations in several producing countries and more slowly developing recovered (secondary) sulfur production have resulted in the present tight sulfur market [2]. This tight market along with higher prices has encouraged expansion of Frasch as well as secondary production of sulfur [1, 2]. Continued expansion of world sulfur production is still predicted to produce surplus and stabilize prices for the long term [1, 3].

Research into the use of sulfur in asphalt paving materials has resulted in the development of two distinct technologies whose basic difference lies in the primary role sulfur plays in the mixture. The first development was Sand-Asphalt-Sulfur (SAS) which involves the use of sulfur as a structuring agent (i.e. playing the role of the aggregate) with poorly graded sands to produce a quality asphaltic paving material. Sulfur-Extended-Asphalt (SEA) is a later development in which sulfur is utilized as an integral part of the binder to effect a partial replacement

0097-6156/82/0183-0155\$09.75/0

© 1982 American Chemical Society

or extension of the asphalt cement in conventional asphaltic pavement materials. For more detailed treatment of the historical background of these two concepts the reader is referred to the excellent review by Rennie [4]. This paper will attempt to put into perspective the more recent state-of-the-art in the design, preparation, placement and in-service performance evaluation of SAS and SEA mixtures.

SAND-ASPHALT-SULFUR (SAS) SYSTEMS

Canadian Developments

Shell Canada Limited has been investigating the use of sulfur as a means of producing mixes with low quality aggregates since 1963. This work produced a series of patents [5-13] and experimental field trials [14, 15]. The results of these trials and an extensive research and development program [16-18] led to the development of a number of specialty items two of which are: (1) THERMOPAVE* - a sand-asphalt-sulfur paving material [19] and (2) THERMOPAVE* - a remeltable material used for pavement repair [20]. Whereas the former was developed primarily for use with low quality sands, THERMOPATCH mixes use a variety of aggregates ranging from sand to graded crushed rock or gravel.

In 1964, Shell Canada conducted full scale paving trials in Oakville, Ontario and St. Boniface, Manitoba in which the in-service performance of SAS systems were compared with conventional asphaltic concrete using both well graded aggregates and poorly graded sands. The results of these trials are summarized below:

1. Both solid and liquid sulfur can be used to prepare SAS mixtures using batch-type asphalt hot mix facilities.
2. Mixes which were compacted by conventional rolling following placement, experienced early damage, whereas those which were not compacted performed very well.
3. Mixtures prepared with one-sized sands performed equal to those prepared with the dense-graded systems.
4. Because of the pourability of SAS mixtures, whose slump characteristics can range from 2-6 inches (ASTM Test Method C-143), pavement thickness control could be a problem necessitating the use of forms as in cement construction. Flowability of the mixes induced an

*Registered Trade Marks of Shell Canada Limited

adverse shoving effect on the surface of the mat due to the interaction with the paver screed. This required an alteration to be made to pavers on future SAS construction projects in which screed height was hydraulically controlled to balance upward lift and downward pressure so as to maintain a uniform pavement thickness.

5. Screed temperature control must be maintained within the suggested working range of the mixture (260 to 300°F) for optimum workability and minimum generation of noxious fumes.
6. SAS mixes with S:A ratios of 1.0 to 2.5:1.0 are recommended for use in flexible pavement mixture designs, while S:A ratios greater than 5:1 can be used in situations requiring rigid pavement designs. A typical SAS formulation is 82 parts sand, 6 parts asphalt and 12 parts sulfur by weight.

Based on the success of these early trials and the additional data base provided by concurrent laboratory programs, Shell undertook a number of subsequent field trials in Richmond, British Columbia (1970) [14], Oakville, Ontario (1971), St. Antoine, Quebec (1972), Tillsonburg, Ontario (1972) and McLean, Saskatchewan (1974). In addition, a number of small scale field trials were conducted to evaluate various paver modification schemes.

One concept which evolved out of these field trials was a truck with a heated dump body. The bodies are totally enclosed, propane heated with double-walled steel or aluminum shells. These trucks are utilized to keep the temperature of the mix between 265 and 300°F during hauling.

Other modifications came in the form of paver kits which provide the screed control discussed in item 4, above and changes to the strike-off bar to minimize tearing in very fine, one-sized sand mixes. These modification kits have been designed primarily on Barber Greene series 100 and Blaw-Knox pavers. Successful demonstrations of these innovations were made by Shell in a number of small scale trials during 1976 and 1977. The most recent concept utilizes a totally self-contained paver-mixer developed by Shell in cooperation with Midland Machinery Co., Inc. of Tonawanda, New York which eliminates the need for heated dump bodies [21]. Although most of the developments in SAS technology in Canada emanated from Shell, feasibility studies involving THERMOPAVE utilization have been under evaluation in a joint Shell/SUDIC program since 1974 [4].

Development in the United States

Interest in the United States in the SAS concept was generated by two factors: (a) the decreasing availability or total absence of quality aggregates in a number of regions around the country such as the Gulf States and (b) the projected surplus of sulfur anticipated from secondary sources in connection with pollution control processes. The Texas Transportation Institute (TTI) under the co-sponsorship of the Sulphur Institute and The Bureau of Mines instituted a program to introduce the SAS concept to the United States [22]. Volume III (Revised 1978) of the final report was prepared as a user's manual and sets forth some preliminary specifications, recommended mix design, construction and quality control procedures to be used on SAS highway systems. A preliminary structural analysis using layered-elastic theory of SAS systems was conducted by Saylak, et. al. [23, 24] which indicated excellent fatigue life compared to conventional asphalt concretes. The Bureau of Mines made independent studies of SAS mixes using blow sands and mine tailings. Patches of these materials placed within the city limits of Boulder City, Nevada in 1975 are still performing well to date [25]. The Bureau also used an SAS mix to repair a portion of McCarran International Airport in Las Vegas [26].

Two experimental field projects evolved out of the Shell and TTI studies; (a) LA. 108 in Sulphur, Louisiana - January 1977 [27] and (b) U.S. 77 in Kenedy County, Texas - April 1977 [28]. A part of the Kenedy County construction report includes an extensive analysis of emissions generated during construction. The results tend to verify the conclusions established earlier by Shell, that as long as mix temperatures are maintained below 300°F, concentrations of H₂S and SO₂ are well within the safety limits suggested by the American Conference of Governmental Industrial Hygienists [29]. All of the field trials conducted both in the United States and Canada utilized conventional batch type hot mix plants and paving equipment. These field sections have been under post-construction evaluation for more than four years and are still performing satisfactorily.

Preparation and Mix Design Methods for SAS Mixtures

The preparation of SAS materials involves a two cycle process as shown in Figure 1. The operation begins with all three ingredients; aggregate, asphalt and sulfur preheated to a temperature above the melting point of sulfur (240°F) and below 300°F. The upper limit is the temperature above which sulfur undergoes an abrupt and very large increase in viscosity which could adversely affect mix workability. Although acceptable mixes have been prepared at temperatures as high as 380°F, 300°F is also considered to be the maximum mix processing temperature for averting toxic fumes emissions [16, 18].

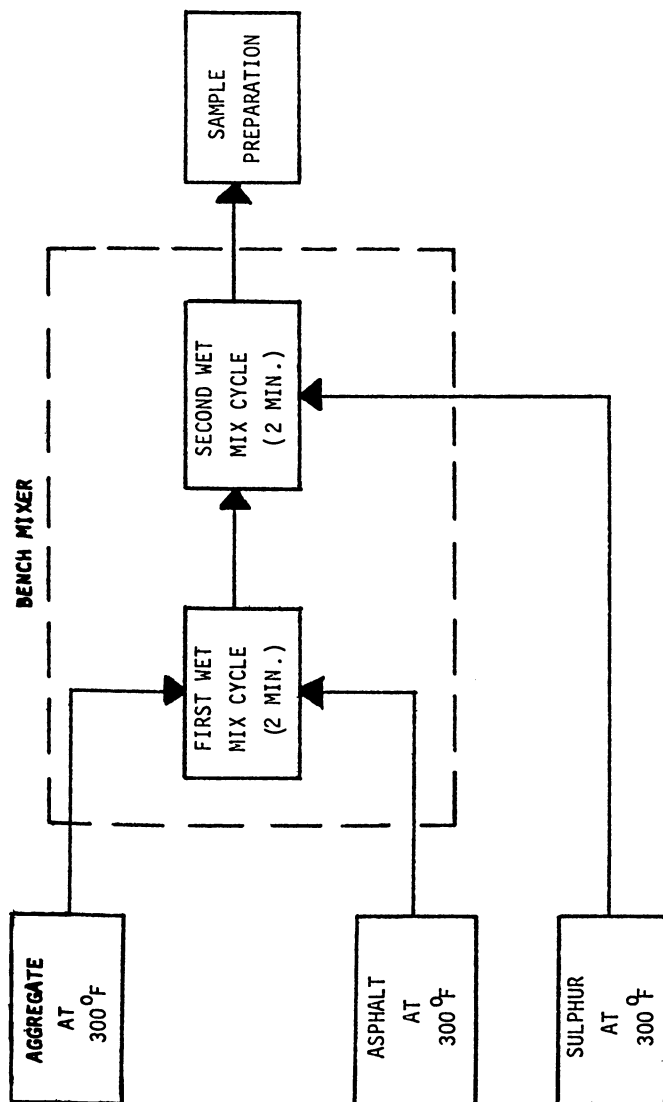


Figure 1. Schematic of SAS mixture preparation.

In the first cycle aggregate and asphalt are mixed to coat the particles with asphalt. Liquid sulfur is then added and mixed with the asphalt and aggregate until the three ingredients are dispersed throughout the mix. Upon cooling, the sulfur which does not dissolve in the asphalt solidifies within the voids of the mixture creating a mechanical interlock from which the material derives its strength. A photo-micrograph of a polished mix section surface is shown in Figure 2 and illustrates how the sulfur occupies the void spaces between the asphalt-coated aggregate particles. An excellent series of photo-micrographs of the SAS mixtrix is also given in Reference 15. The solidification of the sulfur is very critical to the structural integrity of SAS systems. By acting as a conforming filler the crystallized sulfur induces such a high degree of mechanical stability to the mix that high quality paving materials can be achieved using poorly graded aggregates such as single-sized sands. Since normal densification procedures tend to disturb the solidification process, conventional compaction methods such as rolling and vibration are not recommended in SAS pavement construction.

SAS mixes are optimized using a slightly modified Marshall Method (ASTM Method D 1559) and represent a series of trade-offs between stability and flow, air voids content and permeability and fatigue life [15]. The major departure from the Marshall Method is that only 2 hammer blows rather than the conventional 75 blows per face are used. The light compaction is used only to expel entrapped air and to achieve more uniform sample configurations without disturbing sulfur soldification within the aggregate voids.

The effect of sulfur and asphalt contents in SAS mixtures on Marshall Stability is shown in Figure 3 [15]. The stability values tend to increase with sulfur content but decrease with asphalt addition. It is interesting to note that without the sulfur and asphalt, sand mixes would have little or no stability. The data also indicate a wide variety of mix designs are possible whose stabilities are consistant with Asphalt Institute suggested values for conventional asphaltic mixes.

A characteristic of single sized sands is their comparatively high air void contents which usually exceed 30 percent. Since sulfur's role in SAS mixtures is to fill these air voids without the aid of mechanical densification, both economic and performance considerations would require analysis of the maximum permissible air void content the mixture may possess and still be relatively impermeable to water without sacrificing structural integrity. Figure 4 [15] shows the relationship between air voids content and permeability for both SAS and asphaltic concretes as determined

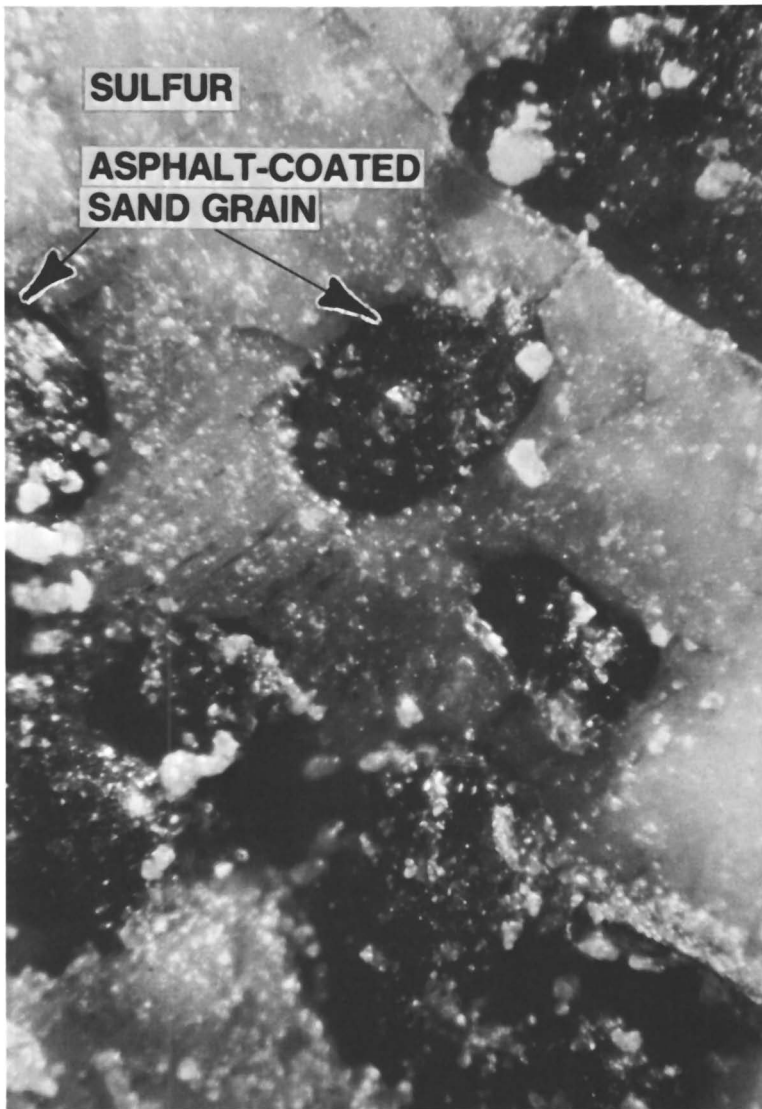


Figure 2. Photomicrograph of sand-asphalt-sulfur matrix showing the mechanical interlock of sand particles provided by the sulfur (Mag: 108X).

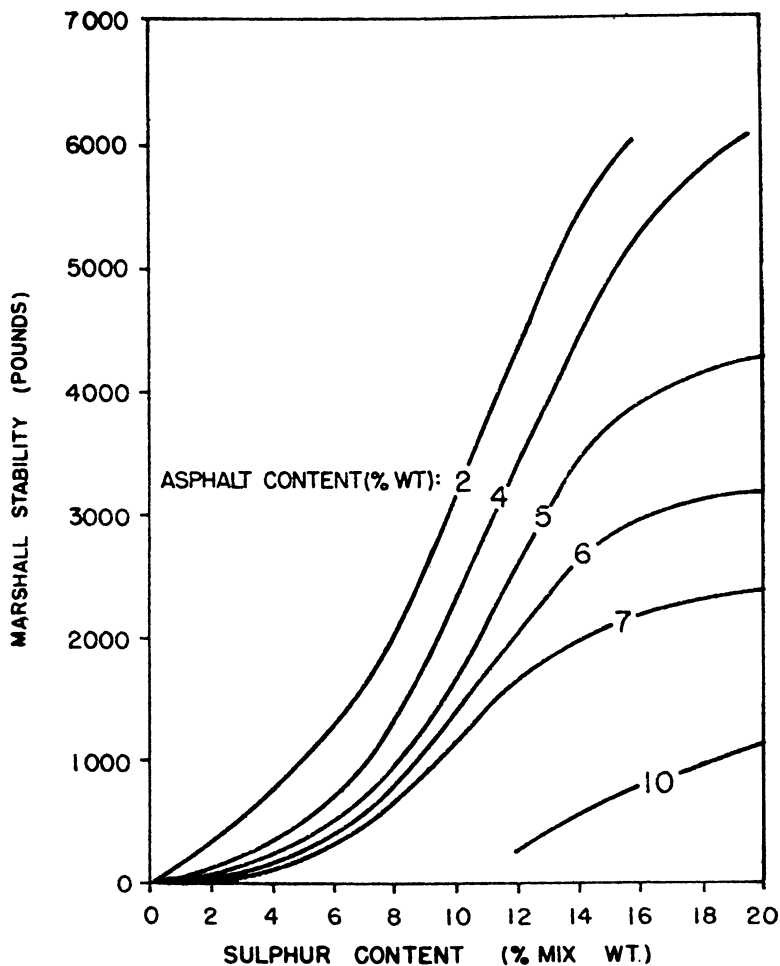


Figure 3. Marshall stability as a function of sulfur and asphalt contents in sand-asphalt-sulfur mixes (15). Materials used were medium-coarse sand and 150/180 pen. asphalt. All specimens were prepared with 2 hammer blows on one face only.

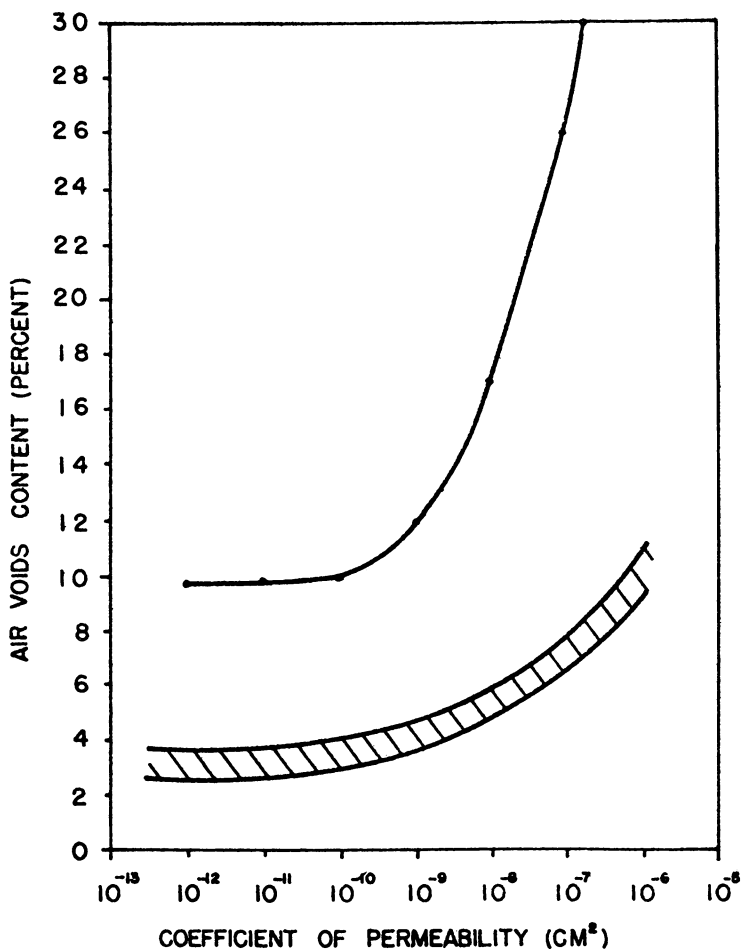


Figure 4. Comparison of coefficient of permeability as a function of air-voids content in sand-asphalt-sulfur and asphaltic concrete mixes (15). Sand-asphalt-sulfur mixes were prepared with medium-coarse sand and 150/180 pen. asphalt. Key: —, sand-asphalt-sulfur mixes; and ▨▨▨, asphalt concrete.

using a constant head permeameter₂ [16]. Mixes whose coefficients of permeability are below 10^{-8} cm are considered to be impervious. Therefore, the maximum allowable air void content for SAS mixtures is approximately 15 percent as compared to 6 percent for dense graded asphalt mixes. This also indicates that the voids in SAS mixtures are individually discrete and isolated and the presence of the solid sulfur inhibits the passage of water.

The stability and permeability of a mix are not sufficient criteria to reflect how a material will perform under the repeated loads generated by traffic. Therefore, any mix design selection process should include an examination of the material's fatigue resistance. Figure 5 shows the relationship between sulfur content and fatigue life for some SAS mixtures at two strain levels [15]. These tests were run at constant stress in third point flexure. Both curves go through a maximum at a sulfur content of 14 percent.

An examination of the above criteria would indicate that an optimum SAS system would have sulfur and asphalt content between 12 and 14 percent and 5 and 7 percent, respectively. The final decision will be dictated by the air void content and gradation of the aggregate, the latter of which has a bearing on the tear resistance of the mat during placement. For a fine in-depth treatment of the aggregate selection process and SAS construction procedures, the reader is referred to Volume III of Reference 22.

Summary of SAS Status

On the basis of the results of extensive laboratory and field studies of SAS paving materials, it can be concluded that, when prepared and placed using established recommended practices, they can be expected to perform as well as, if not superior to, conventional asphaltic concretes. Three major drawbacks appear to hinder the general acceptance of SAS materials for greater usage in the paving industry.

1. The need for heated dump bodied trucks (see Figure 6 [28]) represents an unpopular investment which detracts from the general acceptance of SAS construction. More recent developments in which the mixes are prepared at the paver [21] eliminate the need for these trucks.
2. SAS materials with excellent engineering properties can be prepared in the laboratory using poorly-graded sands. In the field, however, the surface tearing problem especially with mixes prepared with fine, one-sized sands, requires blending with more expensive graded sands. Claims of eliminating this problem by modifying the paver strike-off bar [4] need to be verified in documented field trials.

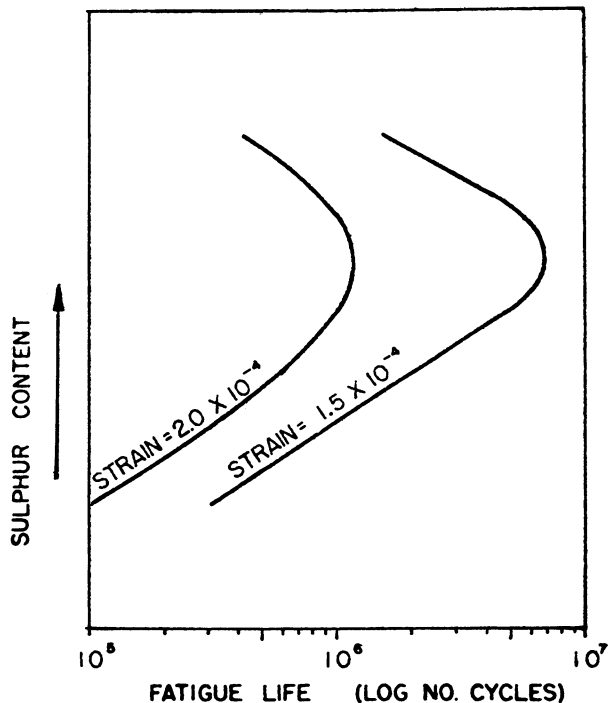


Figure 5. Fatigue life as a function of sulfur content for a sand-asphalt-sulfur mix. Test temperature: 50°F (10°C). Test frequency: 60 Hz. Materials: medium-coarse sand, and 150/180 pen. asphalt. Asphalt content: 6% wt (15).



FHWA

Figure 6. Heated dump body truck developed by Shell Canada, Ltd. used for hauling sand-asphalt-sulfur paving mixtures. [Photographed at the Kenedy County Texas field trials in 1977 (28)].

3. The cost advantage of using sulfur to off-set the cost of high quality aggregates is disappearing.

Sulfur inventories and pricing will be major factors which will ultimately dictate the future of SAS systems in the paving industry. To the author's knowledge no major field projects involving SAS materials are being planned for the near future. A summary of the number of SAS paving trials placed since 1964 are given in Table 1.

Table 1. Number of SAS Paving Trials (May 1981)

	Canada	United States	Total
1960-1965	2	-	2
1966-1970	1	-	1
1971-1975	4	3	7
1976-1980	-	3	3
1981-	-	-	-

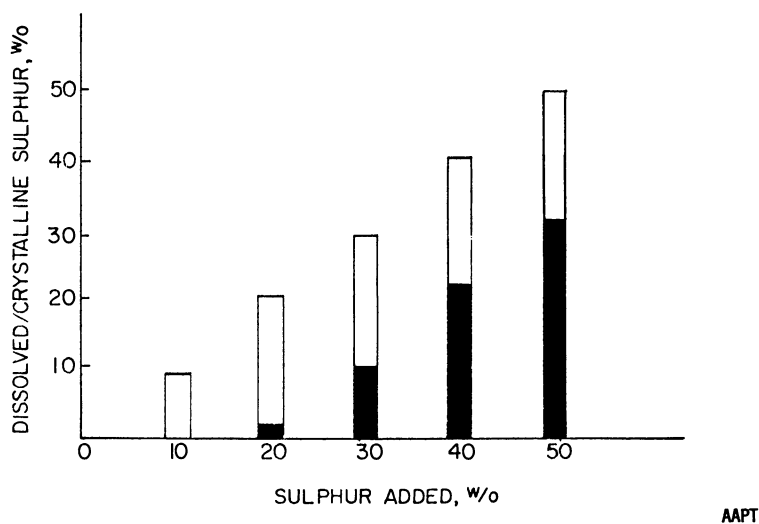
Sulfur Extended Asphalt (SEA) Systems

Although commercial processes for modifying properties of asphalts with sulfur have been in existence for more than a century, the current developments in the use of SEA binders originated with the work of Bencowitz and Boe [30] in 1938. Using a wide variety of types and sources of asphalts, they produced stable blends containing 25 percent sulfur. Blends with as much as 40 percent sulfur were also achieved with some asphalts.

These early studies along with more recent investigations [31-34] established some conclusions regarding the effect of sulfur on the properties of SEA binders and the hot-mix concretes in which they were used.

- (1) Depending upon the temperature and the amount present, sulfur will go into solution with the asphalt, chemically react with the asphalt to form aromatic polysulfides and form a solid-liquid dispersion with the binder.

- (2) At binder S:A ratios up to 20:80 percent most of the sulfur will be dissolved by the asphalt at blending temperatures between 240 to 300°F. As more sulfur is added, that which does not react with the asphalt will exist in the dispersed phase as shown in Figure 7.
- (3) Because the specific weight of sulfur is about twice that of the asphalt, the solid sulfur particles will settle out unless the blend is continually agitated. The rate of settling is dependent on the viscosity - temperature properties of the asphalt. Figure 8 shows a typical sulfur settling rate in a 30/70 SEA binder maintained at 285°F for 6 hours. The curve indicates the height of the column of settled sulfur in the bottom of the test tube in each time station. Figure 9 shows the rate of settling is directly related to the amount of sulfur present in the blend. The first signs of settling occur about one-half hour after the binder was prepared.
- (4) The general trend of physical properties for SEA blends is shown in Figure 10 which shows the effect of Sulfur Asphalt Ratio on Specific Gravity, Penetration, Ring and Ball Softening Point and Viscosity. Except for the Specific Gravity whose increase with S/A ratio reflects the two-to-one difference in the densities of sulfur and asphalt, the other three parameters show trend reversals. These reversals are attributed to the increasing amounts of solid sulfur particles present in the blends as the S/A ratio exceeds 20 percent. These sulfur fines act as filler in the binder. All tests were run within 24 hours following the preparation of the binders.
- (5) The engineering properties of mixes prepared with SEA binders vary with sulfur content while maintaining their load bearing characteristics over a wide range of pavement temperatures. Figure 11 shows that SEA binder mixes can be placed at temperatures below sulfur's solidification temperature, 240°F. However, with sulfur contents in excess of 35 volume percent (52 weight percent) the mixes become sensitive to compaction temperatures below 240°F. At this point the sulfur content becomes significant enough that a mechanical interlocking process similar to that encountered with SAS system becomes a factor. This is considered the maximum permissible substitution level for normal compaction conditions. At levels below 15 volume percent (26 weight percent) properties are similar to conventional asphalt mixtures.



AAPT

Figure 7. Typical proportions of dissolved and crystallized sulfur in sulfur-extended asphalt blends (32). Key: □, dissolved sulfur; and ■, crystalline sulfur.

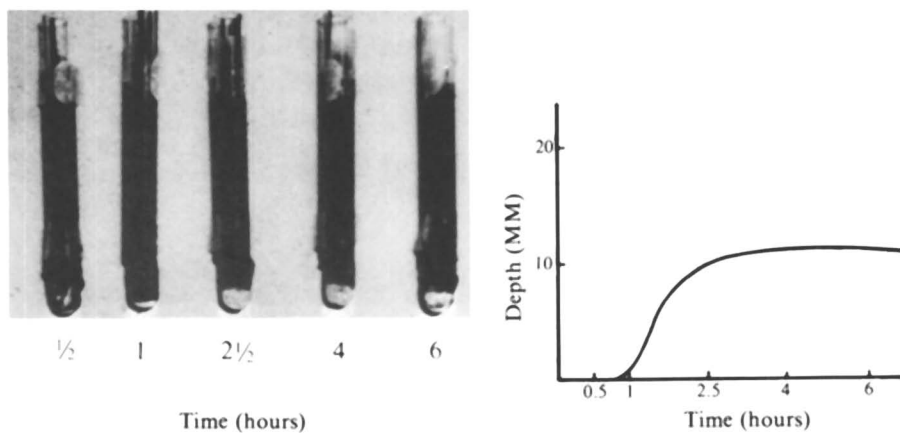


Figure 8. Typical settling of sulfur from a sulfur/asphalt (30/70) emulsion maintained at 285°F.

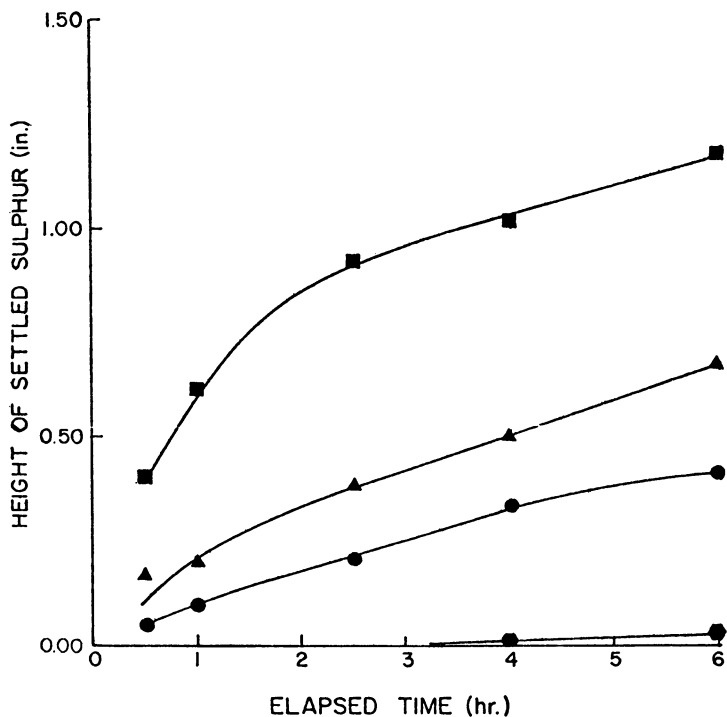


Figure 9. Relative sulfur settling in SEA blends with different sulfur/asphalt ratios maintained at 285°F (31). Key: \blacklozenge 20/80; \bullet 30/70; \blacktriangle 40/60; and \blacksquare 50/50 of sulfur/asphalt (w/o).

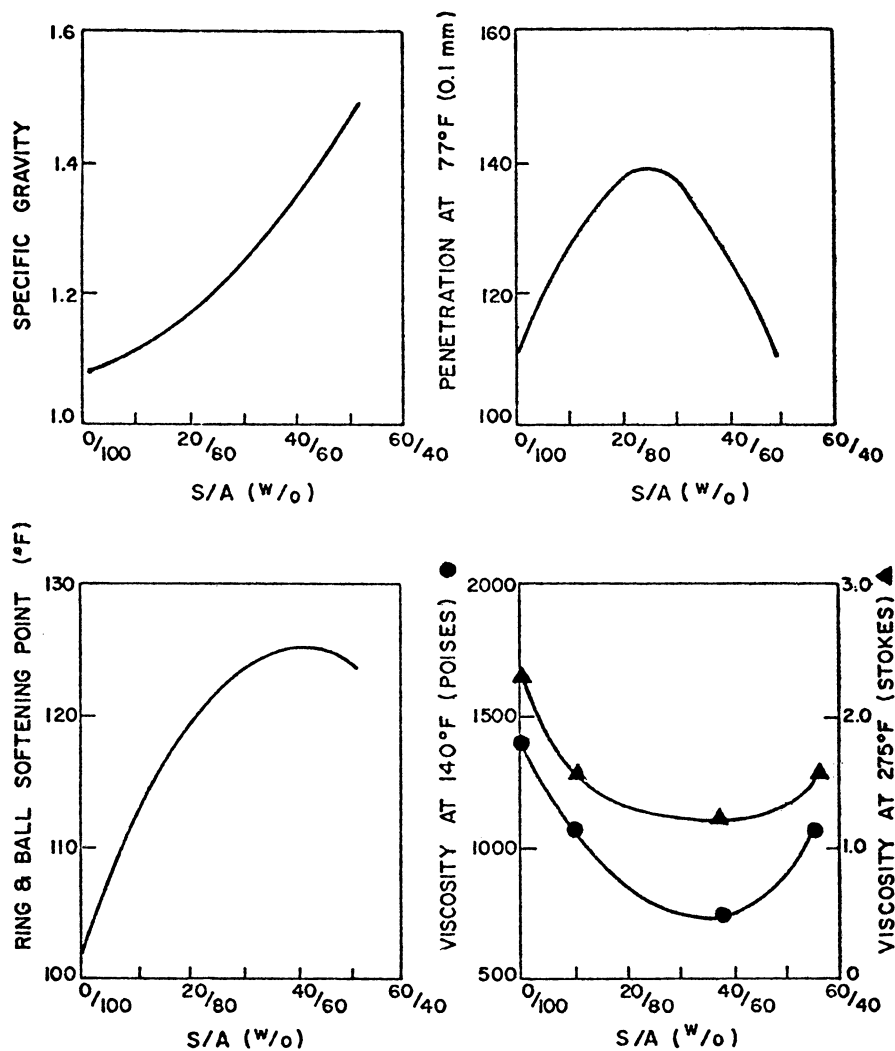
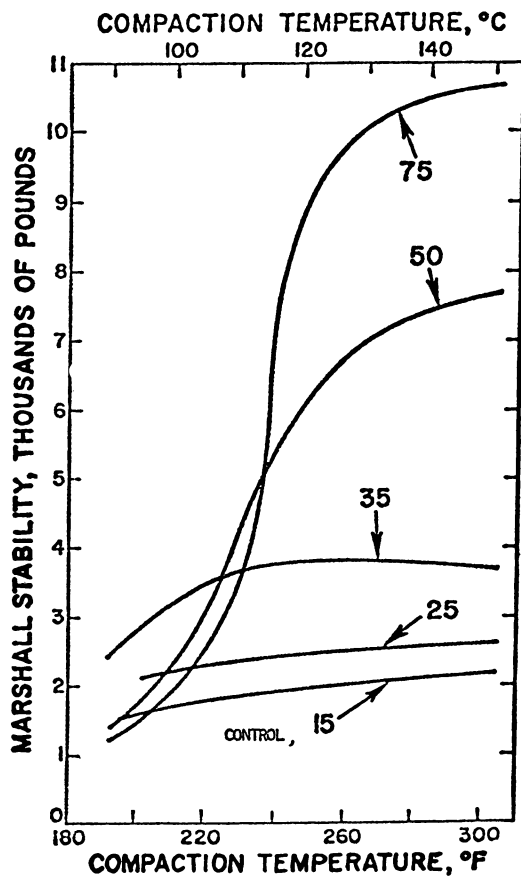


Figure 10. Variations in physical properties of SEA binders with S/A ratio (31).



American Society for Testing and Materials

Figure 11. Influence of compaction temperature on stability of SEA mixtures at different sulfur contents. Numbers indicate volume percent sulfur (33).

- (6) SEA mixes also exhibited good resistance to water absorption and lower air void contents. The former is attributed to the added presence of the solid sulfur and the latter is achieved by virtue of higher degrees of compaction possible with the lower viscosity SEA binders.

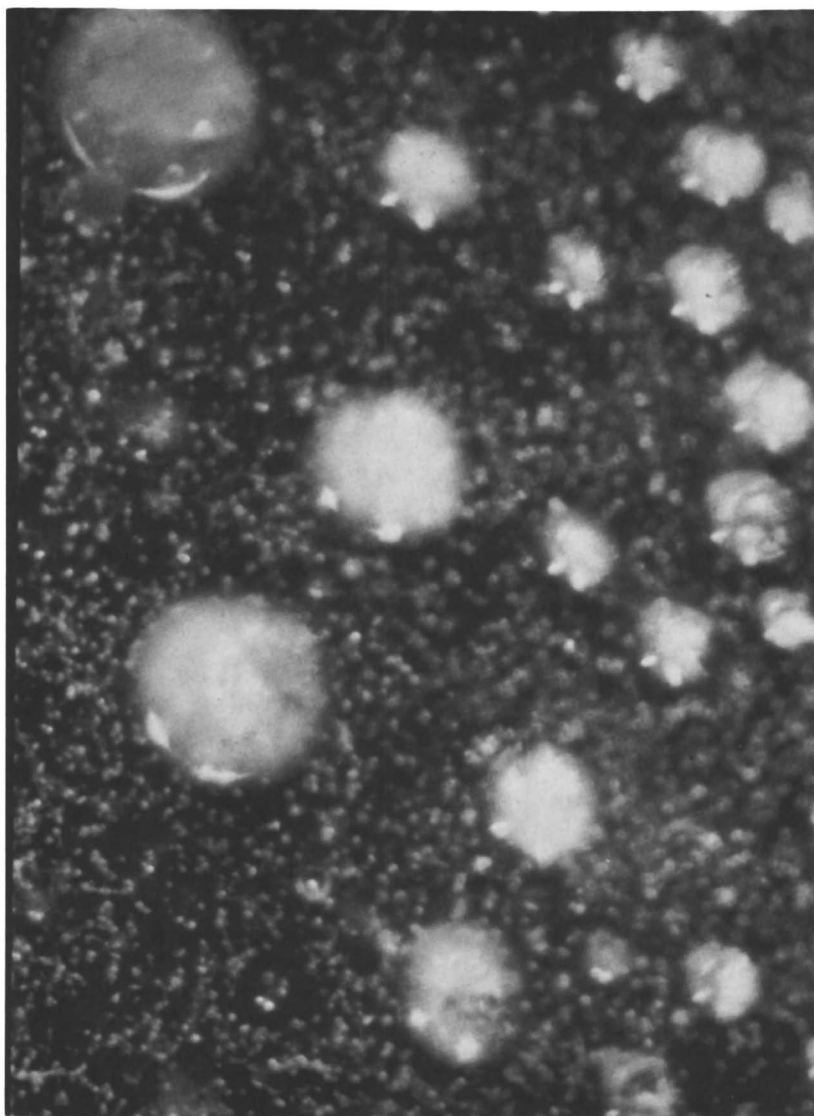
Although these early findings showed that significant beneficial effects could be derived from mixes prepared with SEA binders, very little attention was maintained in this area until the mid-1970's, or more directly, the advent of the Oil Embargo from the Middle East. In anticipation of reduced crude supplies on the future price and availability of asphalt, coupled with the lower cost and projected surpluses of sulfur, the paving industry revived its interest in SEA binder technology.

Preparation and Mix Design Methods for SEA Mixtures

A sulfur-extended asphalt blend requires a fine, uniform dispersion of the liquid sulfur in asphalt as shown in Figure 12. The basic difference between the techniques for SEA binder preparation used by Bencowitz, et. al. and those in current use is the emphasis of the latter on high shear rate mixing to generate the desirable sulfur particle size (3 to 10 microns). The size range is consistent with that required to maximize solubility of the sulfur into the asphalt and enhance long term stability [34]. SEA binders produced by Bencowitz were agitated at 325 rpm for 2 hours, whereas the latest methodology relies on colloid mills [35], emulsifiers [36, 37] turbines [38], homogenizers [39] in-line mixers [40] or combinations of the above [35, 41]. In all of the above the sulfur and asphalt are preblended prior to entering the mix plant as shown in Figure 13.

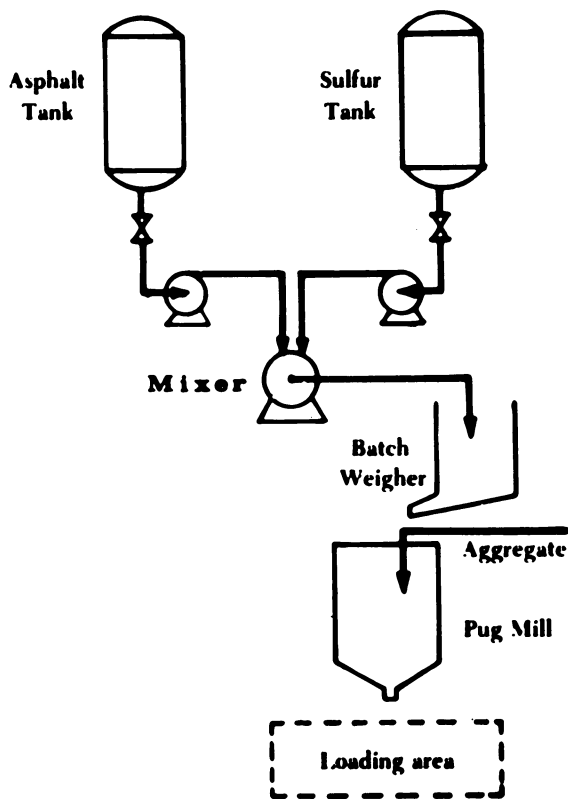
Other investigators [42, 43] have determined that sufficient shearing action can be produced by the interaction between the aggregate and binder during mixing. This method, referred to as direct substitution, requires that the sulfur, and asphalt be stored and metered separately into either the weigh buckets or directly into the mixing unit (Pugmill or Drum mixer) - See Figure 14.

Both processes have been used successfully in field trials. The 1978 trial in Brazos County, Texas [35] used both on the same job for comparison purposes. After three years no significant difference in performance has been noted. Only 2 of the last 18 field trials placed in the United States during 1979 utilized the preblending method, exclusively [33] indicating a preference for the direct substitution method.



AAPT

Figure 12. Photomicrograph of SEA binder showing small (3–5 μm) finely dispersed sulfur along with large globules produced on aging (32).



AAPT

Figure 13. Schematic of mixing station for preparing SEA mixes—preblending method (32).

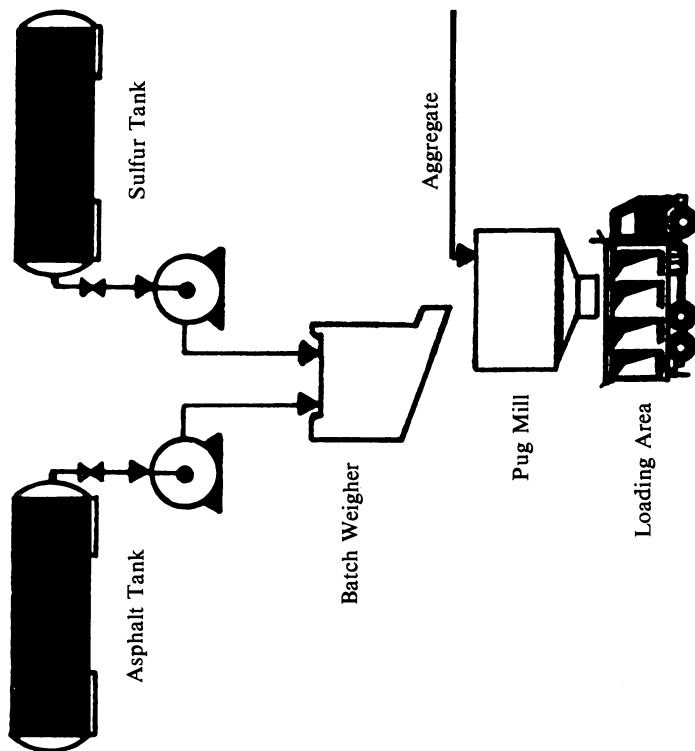


Figure 14. Schematic of mixing station for preparing SEA mixes—direct substitution method.

Since sulfur is about twice as dense as asphalt, a given weight of sulfur occupies one-half the volume of the same weight of asphalt. Early mix design procedures evolved on the basis of an equal volume substitution (i.e. a S:A substitution weight ratio of 2 to 1) of sulfur for asphalt. However construction experience in the United States and Canada indicates that, due to the improved aggregate coating capability provided by the lower viscosity of SEA binders, substitution weight ratios as low as 1.4 to 1 may be feasible [33]. An added benefit is also derived from the structuring effect provided by the undissolved sulfur particles in high sulfur content binders.

Probably the most detailed treatment of mix design and construction procedures was developed in a state-of-the-art guideline manual by The Bureau of Mines [44] under the sponsorship of FHWA and the cooperation of The Sulphur Institute. This manual deals with all technologies currently in use in the preparation of SEA binders. The authors propose the following formula for establishing the Equivalent SEA Binder Content to replace, on an equal volume basis, the asphalt in a conventional asphaltic concrete mix design:

$$\text{Equivalent SEA Binder Content, weight percent} = \frac{10,000 AR}{10,000R - 100P_s(R-1) + AP_s(R-1)} \quad (1)$$

where:

A = weight percent asphalt in the conventional design

R = sulfur substitution ratio

P_s = weight percent sulfur in the SEA binder

This equation will produce the equivalent volume replacement of asphalt with sulfur by the substitution:

$$R = \frac{G_s}{G_a}$$

where:

G_s = specific gravity of sulfur at ambient temperature

G_a = specific gravity of asphalt at ambient temperature

An approximate of the equivalent SEA binder content provided by Equation (1) is given by

$$\sim \frac{200 A}{200 - P_s} \quad (2)$$

The optimum or minimum allowable substitution ratio is then established by means of a series of justification tests at different binder contents. Figure 15 shows a comparison between the Marshall design properties of a conventional mixture using an asphalt binder and a 30:70 SEA binder. As indicated the optimum substitution ratio based on the maximum stability and equivalent air voids is about 1.7:1. Since minimizing the substitution ratio has a direct impact on the economic benefits to be realized by replacing the asphalt with sulfur these justification tests are to be recommended in all mix designs.

Based on the above, the determination of the optimum binder content for SEA concrete mixtures can be summarized as follows:

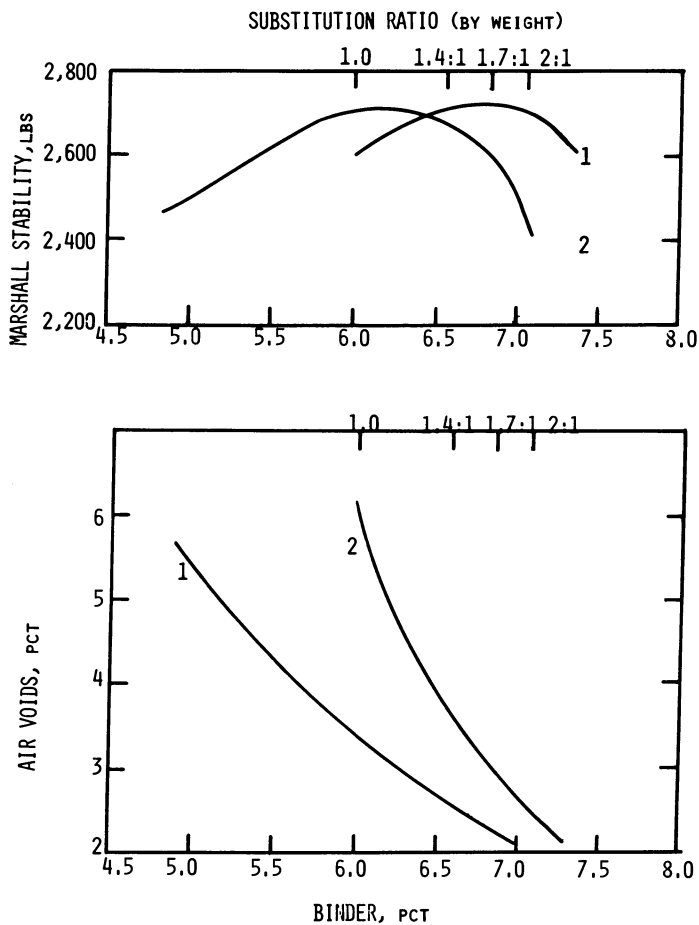
1. Establish optimum binder content for a conventional asphaltic concrete mix.
2. Calculate the Equivalent SEA Binder content using the formula given above.
3. Using the results of steps 1 and 2 above as the maximum and minimum binder contents prepare mixes at a number of intermediate levels.
4. Perform justification tests as shown in Figure 15 and select the optimum binder content.

Once the binder content has been established, the preparation and placement of the SEA mixtures is accomplished using conventional construction procedures.

Field Construction of SEA Mixes

The direct mixing method requires no special equipment in the field for SEA binder preparation. On the other hand a number of uniquely designed processing units have been developed for preblending sulfur and asphalt. Four of the more common preblending concepts used in the United States were developed by Societe Nationale Elf Aquitaine (SNEA), Gulf Canada Limited, Sulfur Development Institute of Canada - Pronk and Texas Gulf, Inc. and are shown in Figure 16 through 19, respectively. In some construction jobs, which incorporated the preblending method, an accumulation tank was used for temporary storage of the SEA binder prior to being pumped to the mixer [36]. Virtually all current operations prepare the binder "on demand" and this eliminates the need for their accumulation.

Both batch and drum mixing plants have been used on SEA pavement construction projects throughout the United States,



American Society for Testing and Materials

Figure 15. Sulfur-extended asphalt (SEA) justification test data. Curve 1, asphalt binder; and Curve 2, SEA binder (30-70) (33).

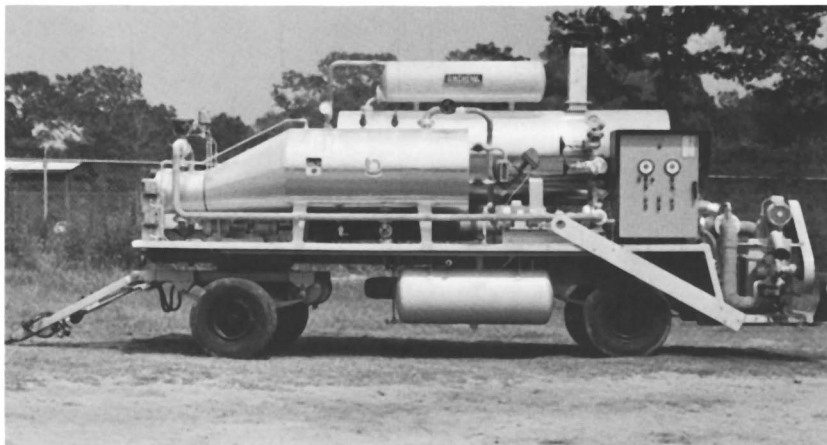


Figure 16. SNEA emulsification unit, Lufkin, Texas, 1975.



Figure 17. Gulf portable sulfur asphalt module (SAM).

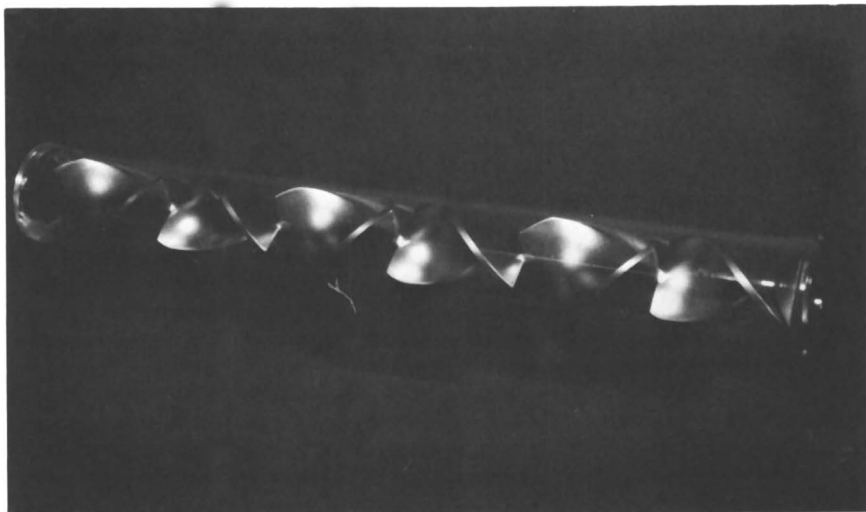


Figure 18. Pronk static in-line static mixer.



Figure 19. Texas Gulf portable sulfur asphalt emulsifier.

Canada, Europe and the Middle East [45]. New projects are continuing to be added and even more are in the planning stages. For more detailed discussion of these projects the reader is referred to the individual States Highway Department construction reports.

Two of the more recent innovations for using sulfur modified binders are in conjunction with recycling old asphalt pavements and the construction of open graded friction courses (OGFC). This opportunity for using SEA binders for recycling has been investigated to capitalize on the viscosity reduction achieved by blending sulfur with asphalt (Figure 20) and thus eliminate the need for softening agents normally used in reclaiming old bituminous pavements. This sulfur-recycling concept was developed jointly by the U. S. Bureau of Mines and the Texas Transportation Institute [46, 47]. A comparison of some of the engineering properties of old pavements recycled with asphalt and sulfur modified binders is given in Table 2.

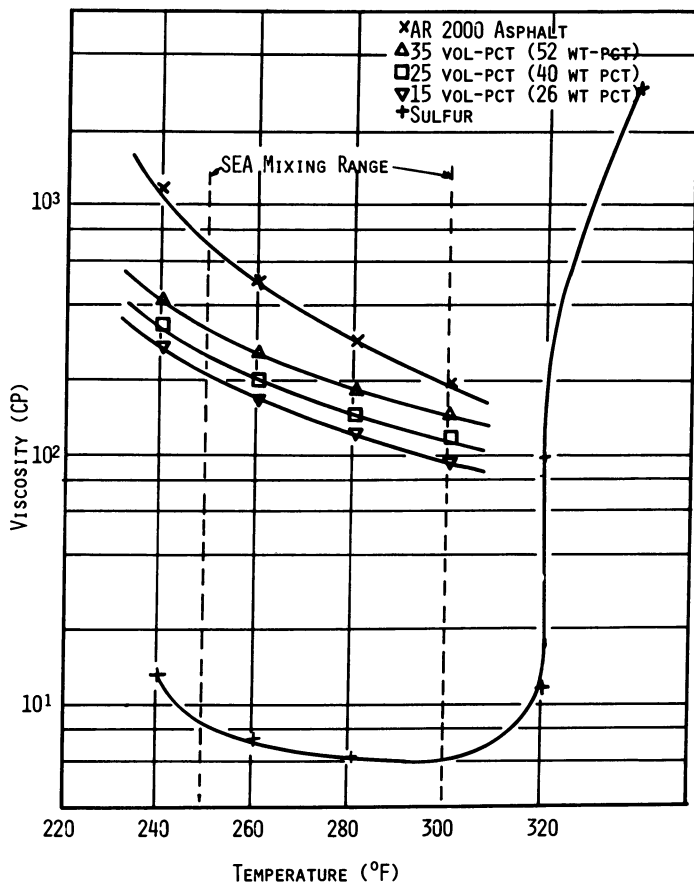
Table 2. Properties of Recycled Asphalt Pavement Using Sulfur/Asphalt Emulsion Binder.

Binder Added, w/o	Marshall		Hveem Stability, pct	Air Void, pct	Dynamic Modulus, psi
	Stability, lb	Flow, 1/100 in			
S/A:30/70					
0	4700	12	62	8	1,500,000
1.5	3400	13	53	3	1,400,000
2	3810	17	42	3	1,450,000
2.5	4020	17	39	2	1,600,000
S/A:40/60					
1.5	4030	15	48	4	1,800,000
2	3910	16	41	3	1,850,000
2.5	3470	20	27	2	1,850,000
S/A:50/50					
1.5	3010	17	40	4	1,750,000
2	2620	22	28	3	1,800,000
2.5	2600	24	24	2	1,950,000

NOTE: a) S/A = weight ratio of sulfur to asphalt in the combination binder
 b) Compaction: 50 blows per side
 c) Asphalt: Texaco AC-20, Port Neches, Texas

1/ w/o refers to weight percent in the total mix.

The properties are consistent with those suggested by the Asphalt Institute [48] for light, medium and heavy traffic categories, except in the area of air void content, which can be adjusted through changes in aggregate grading and binder content. At S/A



American Society for Testing and Materials

Figure 20. Temperature-viscosity chart indicating influence of sulfur contents in SEA binders (33).

of 50/50, and greater, Marshall flow values become excessive when more than 1.5 percent SEA binder is added. The high stiffnesses produced in these sulfur-recycled mixes suggests their use in recycling city streets where the use of cutbacks in maintenance jobs have a tendency to produce mixtures with low stiffnesses.

Conventional recycling requires the old mixture to be reheated prior to the addition of virgin asphalt and rejuvenating agents. This is normally accomplished in heating kilns which involve direct exposure to gas flames. The pollution problems associated with this operation are compounded when SEA binders are used due to the evolution of toxic emissions or by exceeding the upper working temperature limit for sulfur-modified asphalts. This is alleviated by only using the kiln for heating new aggregate. The recycled material enters a storage hopper as cold feed along with the hot aggregate which acts as a heat transfer medium. The dwell time in the hopper prior to its being dumped into trucks for hauling to the construction site (see Figure 21) is sufficient to bring the whole mix to the paving temperature. The aggregate is sized and graded to meet specifications. Current production rates require a ratio of recycled to virgin material of 30 to 70 weight percent to accomplish the above. The "mixer heat-transfer method" as it is called was first used on a conventional asphalt recycling project in Maplewood, Minnesota in 1976. Since then many projects have been completed using this technique. This process has been successfully demonstrated on sulfur-recycling project in Roseville, Minnesota during August 1979. A subsequent sulfur recycling job was placed along I-35W in Burnsville, Minnesota during June 1980, in which sulfur was added to the pug mill in solid rather than liquid form. Both paving sections are reported to be performing well [49]. The Ashland County, Wisconsin sulfur-recycled project, Reference 45, utilized a split feed system in which sulfur was introduced into the drum mixer from the outlet side to eliminate direct contact with the gas flame and mix temperatures in excess of the 300°F (150°C) upper limit.

The development of sulfur-extended asphalt open graded friction courses (SEA-OGFC) is currently under investigation under FHWA sponsorship at the Texas Transportation Institute [50]. This pavement concept is designed and constructed to allow rain-fall to flow through the porous surface layer to the roadway shoulder, and thus minimize traffic tire spray and skidding accidents on wet highways. Unpublished results to date indicate that with minor modifications existing federal and state conventional asphalt OGFC mix design procedures may be used for SEA-OGFC system. Laboratory test results indicate improved structural integrity, drainage and freeze-thaw properties over conventional OGFC mixtures. The improved drainage provided by

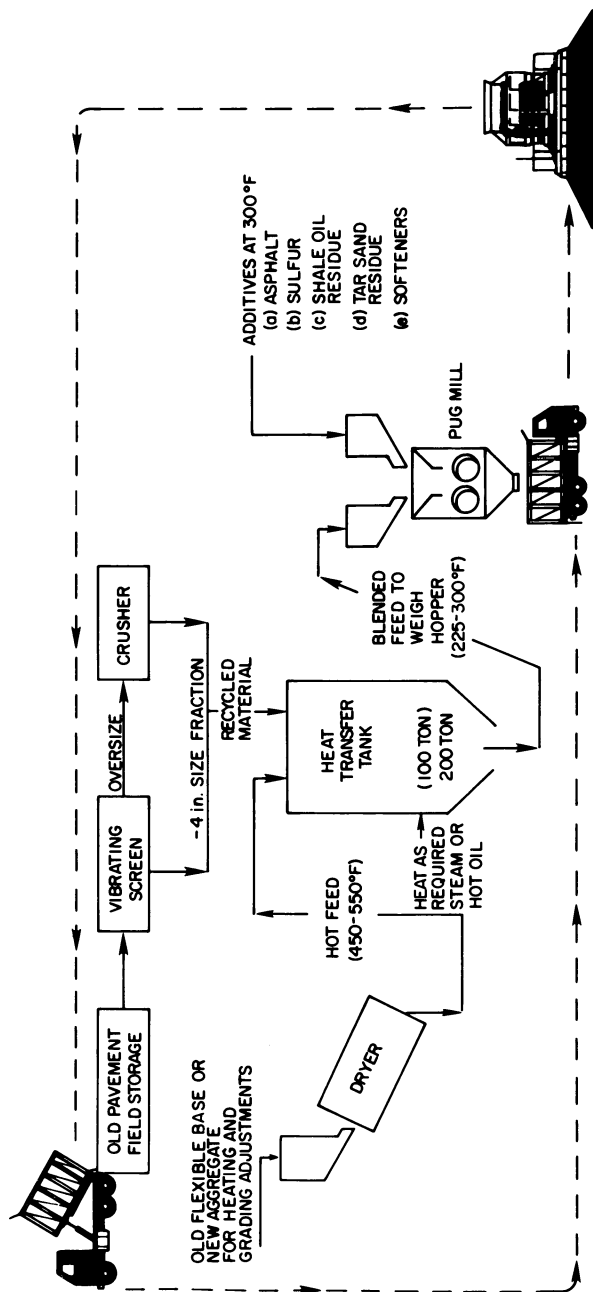


Figure 21. Schematic of a central plant for sulfur recycling of old asphalt pavements.

SEA-OGFC mixes over conventional mixtures is reflected in their higher coefficients of permeability, K_v , and flooding rainfall intensity, I_F shown in Table 3 [50].

Table 3. Permeability Test Results for Limestone SEA Mixes

Asphalt Grade	o/w S in Binder	Coefficient, K_v (cm/sec)	Predicted Flooding Rainfall Intensity I_F , (in/hr)
AC 10	0	.071	.094
	20	.200	.264
	30	.259	.342
	40	.287	.378
AC 20	0	.056	.074
	20	.238	.314
	30	.210	.277
	40	.187	.247
AC 40	0	.107	.141
	20	.262	.345
	30	.230	.303
	40	.248	.327

The techniques developed in the TTI program were utilized in the mix design and construction of an experimental SEA-OGFC test section on Loop 495 in Nacogdoches, Texas during August 1980 [51]. The mix was prepared using an S/A ratio of 35/65 in which separate streams of asphalt and sulfur were added to the aggregate in a dryer drum mixer. The results of limited post construction evaluation activity tends to support the conclusions generated in the laboratory.

Summary of SEA Status

In contrast to the SAS systems, the number of sulfur extended asphalt paving projects in the United States has been consistently increasing since 1977. This is shown in Table 4 along with projects undertaken in Europe, Canada and the Middle East.

Table 4. Number of SEA Paving Projects (May 1981)

	United States	Canada	Europe	Middle East	Total
Before 1977	1	4	7	0	12
1977	2	3	4	2	11
1978	5	2	8	1	16
1979	10	3	2	2	17
1980	12				

The prime impetus for this wide spread activity was the "energy crisis" which produced considerable uncertainty about the future availability of asphalt cement for road building purposes and as a consequence caused bid prices to soar over the past eight years.

The degree to which SEA systems will be utilized by the paving industry will ultimately depend on the relative costs of sulfur and asphalt which over the same eight years have kept pace with each other. As long as asphalt continues to be readily available SEA pavements will tend to remain an excellent, proven alternative. Additional field trials involving the sulfur recycling concept and SEA-OGFC are needed to verify mix design and performance characteristics.

SAFETY AND ENVIRONMENTAL IMPACT

Throughout its development, the use of sulfur in highway paving mixtures has introduced questions regarding the pollutants generated, their environmental impact and worker safety aspects associated with mix preparation and placement. Evolved gas analyses have been incorporated into a number of field trials in Canada and the United States [4]. Probably the most well documented evolved gas analysis of a sulfur asphalt paving construction site was conducted during the SAS trial in Kenedy County, Texas [28]. Using a wide variety of instrumentation, The Texas Transportation Institute working in conjunction with the Texas Air Control Board and The Bureau of Mines monitored emissions at various locations including the storage area, hot mix plant, trucks, vicinity of the paver and downwind of the paving operation. Except for two situations, when the paver screed temperature was permitted to exceed 320°F, all emissions were within the allowable limit of 5ppm (see Figure 22) as established by governmental hygienist [28].

The Texas Transportation Institute has just completed a very extensive two year FHWA sponsored program to look into other aspects of safety and environmental impact of sulfur-asphalt construction [53]. A number of typical sulfur-asphalt and sulfur-concrete paving systems were evaluated to assess their potential environmental impact and establish safety considerations relative to their formulation, construction and maintenance. The environmental impact was investigated from the formulation stages, through weathering, and included considerations of simulated fires and chemical spills.

In the formulation phase the influence of sulfur on nine mixtures was examined against mix temperature and humidity and oxygen content of the air. The results generated in this study tend to support the data generated by others in the laboratory as

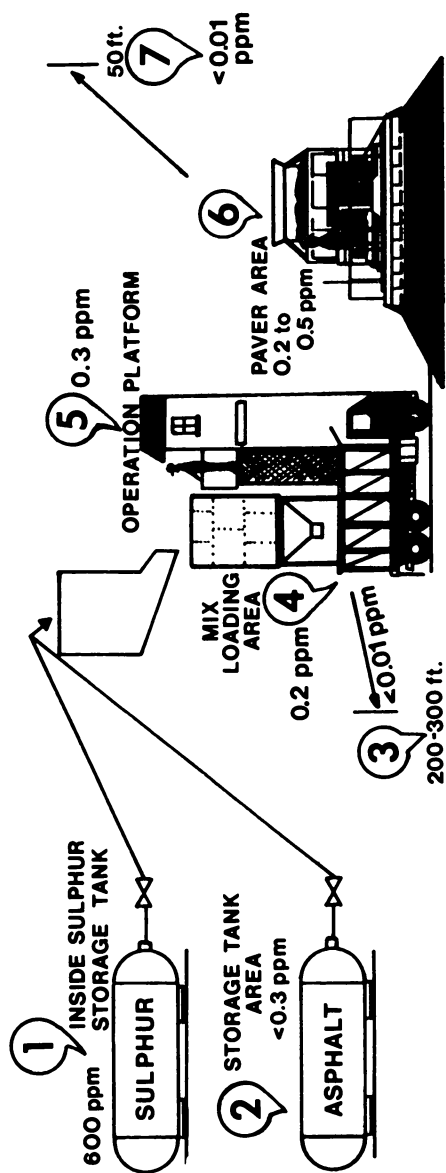


Figure 22. Typical H_2S emissions at various locations of an SEA mix plant and construction site.

was examined against mix temperature and humidity and oxygen content of the air. The results generated in this study tend to support the data generated by others in the laboratory as well as the field; that as long as the mix temperature is kept below 300°F (149°C) evolved gases and pollutants can be maintained within safe limits. These conclusions do not apply when sulfur-asphalt or sulfur concrete are processed in closed environments or stored for prolonged periods of time. Effects of humidity and oxygen were found to be negligible. The recommended maximum allowable temperature limit for continuous handling of sulfur modified paving materials is therefore 300°F (149°C).

It was also found that exposure to the elements had a negligible effect on these pavement materials and run-off either by wind or rain produced little or no effect on the immediate environment. It should be noted that in both the formulation and weathering studies, environmental conditions were designed to maximize the test conditions and thus permitted the results to be considered conservative.

A large number of structural materials were evaluated for possible attack by run-off from a sulfur-asphalt pavement. Of the ten materials studied, copper and steel appeared to indicate a vulnerability. The former or its alloys should never be used in equipment or structures which could bring them in contact with sulfur due to the high probability of producing the sulfates of copper. Steel reinforcing rods would be susceptible to attack by H_2SO_4 produced by moisture on contact.

The possibility of accidental events such as fire and chemical spills revealed some possible short term undesirable effects. These were in the area of obnoxious fumes or short-time-interval pollution. Virtually all of the sulfur pavement materials were difficult to ignite and were self extinguishing.

The effect of simulated brine and gasoline spills on sulfur pavement were studied. Whereas salt based deicers would have minimal effect, organic solvents or naphtha mixtures can solubilize free sulfur in addition to attacking the asphalt.

The results of this study also produced a Field Evaluation Document (Volume II) and an Annotated Bibliography (Volume III) containing over 500 relevant sources. The Field Evaluation Document was designed for use by contractors and state agencies to establish the relative safety and for identification of potential hazards at the various locations and work elements on a sulfur-asphalt construction project. Recommended clothing and first aid procedures were included in this document.

In summary, the results contained herein would tend to

support the conclusion that as long as hot sulfur paving mixtures do not exceed 300°F (149°C) all sulfur originating emissions (H₂S, SO₂, SO₃ and organic sulfur materials) levels will be below their respective Maximum Allowable Concentrations. Sulfur handling practices already established in the sulfur industry as well as those common to the hot asphaltic concrete community were sufficient to assure adequate personnel safety.

CONCLUSIONS

Two basic sulfur modified paving material concepts, Sand-Asphalt-Sulfur (SAS) and Sulfur-Extended Asphalt (SEA) were discussed. Mix design rationale, methods of preparation and construction procedures for each was presented. The state-of-the-art is such that both concepts can be considered available for general use should the relative cost and supply conditions of sulfur and asphalt require an immediate alternative to reduce asphalt demand. The extension of the two concepts to the recycling of old asphalt pavements and design of open-graded friction courses have also been demonstrated. More recent morphological studies have established that the long range stability of sulfur-asphalt blends needs to be examined to more firmly define the role of sulfur in the mix. Crystalline growth and sulfur-asphalt solubility changes with pavement age can be major considerations which will have an effect on future mix design procedures.

REFERENCES

1. "Sulfur; A Case of Delicate Balance", Chemical Week, November 19, 1980.
2. "Sulfur - Latest Victim of War", Houston Post, November 30, 1980.
3. "Sulfur Breakthrough", U. S. Department of Transportation, Federal Highway Administration, February, 1980.
4. Rennie, W. J., "Sulphur Asphalts", New Uses for Sulphur - SUDIC Technology Series No. 2 - Second Edition, 1979.
5. Metcalf, C. T., Canadian Patent 755,999, April, 1967.
6. Metcalf, C. T., U. S. Patent 1,076,886, July, 1967.
7. Kerr, J. E. D., Canadian Patent 781,353, March, 1968.
8. Kopvillem, O. and Maclean, J. W., U. S. Patent 3,738,853, June, 1973.
9. Kopvillem, O. and Maclean, F. W., Canadian Patent 945,411, April, 1974.
10. Kopvillem, O. and Deme, I. J., Canadian Patent 975,109, September, 1975.
11. Kopvillem, O. and Deme, I. J., Canadian Patent 994,059, August, 1976.
12. Deme, I. J., Canadian Patent 1,018,703, October, 1977.

13. Gaw, W., Canadian Patent 1,032,704, June 1978.
14. Hammond, R., Deme, I. J., and MacManus, D., "The Use of Sand-Asphalt-Sulphur Mixes for Road Base and Surface Applications", Proceedings Canadian Technical Asphalt Association, November, 1971, 16.
15. Burgess, R. A. and Deme, I. J., "Sulfur in Asphalt Paving Mines", Advanced In Chemistry Series, 1975, 140, pp. 85-101.
16. Deme, I. J., "Basic Properties of Sand-Asphalt-Sulfur Mixes", International Road Federation World Meeting, 7th, Munich, October, 1973.
17. Deme, I. J., "The Use of Sulphur in Asphalt Paving Mixes", Joint Chemical Engineering Conference, 4th, Vancouver, B. C., September, 1973.
18. Deme, I. J., "Processing of Sand-Asphalt-Sulphur Mixes", Annual Meeting of Association of Asphalt Paving Technologists, Williamsburg, Virginia, February, 1974.
19. Shane, G. and Burgess, R. A., "The Thermopave Process", Proceedings of the Symposium - New Uses for Sulphur and Pyrites, Madrid, Spain, May, 1976.
20. "Patching a Road with Sulphur", The Sulphur Institute Journal, Summer, 1975, p. 2.
21. Deme, I. J., et. al., "The Sulphur-Asphalt Mix Paver", Proceedings of the 25th Anniversary Conference, National Asphalt Pavement Association, Los Angeles, California, February, 1980.
22. Saylak, D. and Gallaway, B. M., "Beneficial Use of Sulphur in Sulphur-Asphalt Pavements", Final Report on Texas A&M Research Project RF 983, (Volumes I, II and III). For the U. S. Department of the Interior - Bureau of Mines and The Sulphur Institute, 1974.
23. Saylak, D., Gallaway, B. M. and Ahmaad, H., "Sulfur in Asphalt Paving Mixes", Advances In Chemistry Series, 140, pp. 102-129, 1975.
24. Saylak, D., et. al., "Sulphur-Asphalt Mixtures Using Poorly Graded Sands", Transportation Engineering Journal, ASCE, Volume 101, No. TE 1, Proc. Paper 11106, February, 1975, pp. 97-113.
25. Sullivan, T. A., McBee, W. C., and Rassmussen, K. L., "Studies of Sand-Asphalt Paving Materials", U. S. Bureau of Mines: Report of Investigations 8087, 1975, 19 pages.
26. "Airport Cracks Filled with Sulphur-Asphalt Materials", The Sulphur Institute Journal, Summer, 1976, p. 16.
27. Izatt, J. O., "Sulphur-Asphalt-Sand Paving Project - Construction Report", for The Sulphur Institute, January, 1977.
28. Izatt, J. O., Gallaway, B. M., and Saylak, D., "Sand-Asphalt-Sulphur (SAS) - Sand-Asphalt-Sulphur Pavement Field Trials", Highway U.S. 77, Kenedy County, Texas, April, 1977.
29. Elkins, H. B., The Chemistry of Industrial Toxicology, John Wiley and Sons, Inc., New York, pp. 95, 232, 1950.

30. Bencowitz, I. and Boe, E. S., "Effect of Sulphur Upon Some of the Properties of Asphalts", Proceedings of the American Society of Testing Materials, 39 (II), p. 539.
31. "Extension And Replacement Of Asphalt Cement With Asphalt Cement with Sulfur", FHWA Report No. FHWA-RD-78-95, March, 1978.
32. Kennepohl, G. J., Logan, A., and Bean, D. C., "Conventional Paving Mixes With Sulphur-Asphalt Binders", Proceedings of the Association of Asphalt Paving Technologists, 1975, 44.
33. McBee, W. C., Sullivan, T. C. and Saylak, D., "An Overview of Sulfur Extended Asphalt Usage", Asphalt Pavement Construction; New Materials and Technique, ASTM STP 724, J. R. Scherocman, Ed. ASTM, 1980, pp. 39-63.
34. Garrigues, C. and Vincent, P., "Sulfur/Asphalt Binders For Road Construction", Adv. in Chem. Series 140, American Chemical Society, 1975, pp. 130-153.
35. "Sulfur-Extended-Asphalt Field Trials-MH 153, Brazos County, Texas, "---A Detailed Construction Report", FHWA Report No. FHWA-TS-80-214, December, 1979.
36. Gallaway, B. M., and Saylak, D., "Sulphur Extended Asphalt (SEA) - Sulphur/Asphalt Mixture Design and Construction Details - Lufkin Field Trials", FHWA Report No. FHWA-TS-78-203.
37. Kennepohl, G. J. A. and Miller, L. J., "A Novel Method of Incorporating Sulphur in Conventional Paving", Energy Processing/Canada, July - August 1976, p. 24.
38. Societe Nationale des Petroles D Aquitaine, British Patent 1,303,318, January, 1973.
39. Saylak, D., Gallaway, B. M. and Noel, J. S., "Evaluation of a Sulfur-Asphalt Emulsion Binder Systems for Road Building Purposes", Final Report, Texas A&M Research Project - RF 3146, January, 1976.
40. Pronk, F. E., Soderberg, A. F. and Frizzell, R. T., "Sulphur-Modified Asphaltic Concrete", Proceedings of the Canadian Technology Asphalt Association, 20 p, 135, 1975.
41. McCullagh, F. R., "Sulfur-Extended Asphalt In Overview", Twenty-Ninth Annual Roads and Streets Conference, Arizona Transportation and Traffic Institute, Tucson, Arizona, (1980).
42. McBee, W. C., and Sullivan, T. A., "Direct Substitution of Sulfur For Asphalt in Paving Materials", U. S. Bureau of Mines, Report of Investigation 8303, 1978.
43. Deme, I. J., "Sulfur as an Asphalt Diluent and a Mix Filler". Advances In Chemistry Series, 1978, pp. 172-189.
44. McBee, W. C., Sullivan, T. A. and Izatt, J. O., "State-Of-The-Art Guidelines for Design, Quality Control and Construction of Sulfur-Extended Asphalt (SEA) Pavements".
45. Personal communication with Mr. Harold N. Weber, Demonstration Projects Division, Federal Highway Administration.

46. Saylak, D., Gallaway, B. M., and Epps, J. A., "Recycling Old Asphalt Concrete Pavements", Proceedings of the 5th Mineral Waste Utilization Symposium, Chicago, Ill., 13-14 April, 1976,
47. McBee, W. C., Saylak, D., Sullivan, T. A., and Barnett, R. W., "Sulfur As A Partial Replacement for Asphalt in Bituminous Pavements", New Horizons in Construction Materials: Vol. 1, H. Y. Fang Ed., 1976, pp. 345-361.
48. "The Asphalt Institute Handbook", Manual Series No. 4, (MS-4), March, 1970, p. 71
49. Personal communication with R. Olsen, Minnesota Highway Department.
50. Saylak, D., "Design of Open Friction Courses with Sulfur-Extended Asphalt Binders", Final Report on FHWA Contract No. DOT-FH-11-9588, May, 1981.
51. Personal communication with W. C. McBee, Boulder City Engineering Metallurgy Laboratory.
52. Personal communication with Dr. Claine Peterson, Laramie Energy Research Center.

RECEIVED October 5, 1981.

An Industrial Application of Sulfur Concrete

R. H. FUNKE, JR.

Asarco Incorporated, Baltimore, MD 21207

W. C. MCBEE

U.S. Department of the Interior, Bureau of Mines, Boulder City, NV 89005

In cooperation with the U. S. Department of the Interior Bureau of Mines and The Sulphur Institute, Asarco tested components of sulfur concrete, both precast and poured in place, in corrosive environments of sulfuric acid. Favorable endurance of these samples led to a full-scale cooperative demonstration project. The project selected was the rehabilitation of an electrolytic zinc cellhouse basement floor of approximately 21,000 square feet. Sulfur concrete utilizing an aggregate gradation of minus 3/8-inch and minus 1/8-inch materials was produced in a portable asphalt patch mix plant. Mixing and placing operations were conducted without problems. Economics of sulfur concrete versus portland cement concrete are highly variable. Total costs were approximately 15 pct higher than for portland concrete. Potential uses are electrolytic cells, holding tanks and vats, and floor and basin areas exposed to acidic environments.

Asarco, a major refiner of nonferrous metals and producer of byproduct sulfuric acid, has many areas where acidic damage to floor surfaces can occur. Even though different protective coating systems were used, routine replacement of concrete damaged by exposure to corrosive conditions has been accepted as the response to the problem. Accordingly, in 1977 Asarco welcomed an invitation from The Sulphur Institute, in conjunction with the Bureau of Mines, for field testing of sulfur concrete in a corrosive environment. The development of sulfur concrete materials was reported by McBee and Sullivan (1, 2). In early 1978, precast sulfur concrete slabs measuring 24- x 24- x 2½-inches, prepared by the Bureau of Mines at its Boulder City Engineering Laboratory, were laid at selected floor locations at the Corpus Christi, Tex. zinc refinery and the Amarillo, Tex. copper refinery. Table 1 indicates the sulfur concrete corrosion

0097-6156/82/0183-0195\$05.00/0

© 1982 American Chemical Society

Table I. Sulfur concrete corrosion test components in Asarco plants

Location	Installation date		Components and environment
Corpus Christi	Feb.	1978	Slabs, electrolytic zinc refinery floors.
	May	1978	Sump, catch basin under zinc electrolyte cooling tower.
	Nov.	1979	Sump, zinc electrolyte pumping circuit.
	June	1980	Floor, electrolytic zinc refinery.
Amarillo	March	1978	Slabs, electrolytic copper refinery sump.
	March	1980	Slabs, nickel sulfate plant floor.
Tacoma	Sept.	1980	Floor, nickel sulfate plant.
	May	1978	Floor patch, electrolytic copper refinery floor.
East Helena	May	1978	Pump foundation, sulfuric acid pump.
	June	1979	Slabs, sulfuric acid plant, lead smelter.
El Paso	Nov.	1979	Cylinders in acid plant complex.
Columbus	April	1980	Sump, sulfuric acid loading area in ZnO plant.
	Oct.	1980	Tile, liner for acid drain channel.

test components in Asarco plants. A few months later, several small on-site sulfur concrete pours utilizing equipment from the Bureau of Mines were made at the Tacoma, Wash. plant in both the electrolytic tankhouse basement and a pumping facility handling 93 pct sulfuric acid. In the spring of 1978, a precast sump prepared by the Bureau of Mines was installed in a drainage basin under the zinc electrolyte cooling towers erected as new construction in the ongoing modernization of the Corpus Christi zinc refinery. In June 1979, test slabs were placed in the sulfuric acid plant in the East Helena, Mont. lead smelter. In late 1979, an additional sulfur concrete sump, as shown in figure 1, was precast by the Bureau of Mines and installed in the zinc electrolyte pumping circuit at Corpus Christi. In November 1979, a series of test samples were put in the acid plant complex at the El Paso, Tex. plant. In 1980, a precast sump was placed in the sulfuric acid truck-loading area at the Columbus zinc oxide plant. All of the installations have exhibited essentially no deterioration in the sulfur concrete installations, except for one slab at East Helena. Examination of this sample showed that the sulfur binder had been melted. The replacement slab remains intact after more than a year's exposure.

After 1- $\frac{1}{2}$ years, the portland cement concrete control samples at Corpus Christi that were installed contiguous to and intermixed with the sulfur concrete test samples showed total disintegration, whereas the sulfur concrete exhibited no identifiable attack (figure 2). In the summer of 1979, the ongoing maintenance needs at the Corpus Christi plant placed rehabilitation of a cellhouse basement floor in a priority position. The opportunity to perform the repair work on a full-scale basis, utilizing Bureau of Mines technology for sulfur concrete in lieu of portland cement concrete, was accomplished by an agreement for a demonstration project executed between the Bureau of Mines and Asarco.

Demonstration Project

A modified Wylie Model PM-830 Patchmobile owned by the Bureau of Mines was assigned to the project. The Bureau of Mines had previously studied the available aggregates in the Corpus Christi area and designed a suitable mix. The Patchmobile is a small portable asphalt patch plant, propane-fired for heating and gasoline-powered for rotating motions and other auxiliaries. Because it is designed to be towed on the highway, its delivery point is at a conveniently low elevation for shoveling mixed patch material, but was too low for utilization on this project. The machine was cribbed up to a suitable elevation to permit handling of receptacle containers under the delivery point. This elevated position, in addition to a larger volume aggregate bin fitted to the machine by the Bureau of Mines, required the use of an elevating belt conveyor for delivery of aggregates to the bin.



Figure 1. Sulfur concrete sump for installation in the zinc electrolyte pumping circuit.



Figure 2. Sulfur concrete and control portland cement concrete (4-test sections each) in the floor area of the electrolytic zinc refinery. After 28 months, no corrosive attack is seen on the sulfur concrete sections, although the control samples were severely attacked.

An appropriate working platform was built adjacent to the elevated mixer to permit attendance.

The mixing operation was routine. Feeding of the drying drum was accomplished by an integral reciprocating feeder delivering both coarse and fine aggregate in correct proportions. The aggregate, heated to 400° F, was accumulated in a discharge hopper, periodically discharging to the pugmill when a predetermined volume was obtained. At the time of release of the aggregate to the mill, a previously measured volume of modified sulfur and silica flour was fed to the pugmill. The average delivery temperature of the sulfur concrete mixture was 280° F. Maintenance of the temperature in the pugmill was accomplished by the circulation of oil at 300° F through a jacket surrounding the pugmill. Delivery of sulfur concrete from the pugmill was continuous. The preparation of sulfur concrete is illustrated in figure 3.

Approximate proportions of the constituents of the mix were 83 pct aggregate and 17 pct modified sulfur. The aggregate fractions consisted of 46 pct minus 3/8-inch pea gravel, 46 pct minus 1/8-inch sand, and 8 pct minus 200-mesh silica flour. The fractions were blended as shown in figure 4 and gave a dense-graded aggregate requiring a minimum of sulfur to produce an acceptable sulfur concrete. The sulfur had been previously modified with a plasticizer consisting of dicyclopentadiene (DCPD) and oligomer in the amount of 5 wt pct of the total sulfur. DCPD-oligomer ratios of 65:35 and 50:50 were employed. The development of this formulation is described by McBee (3). The modified sulfur was prepared in a commercial plant and delivered in bags.

The coarse aggregate used was a siliceous river gravel and was sized by screening. The river gravel was relatively smooth and round. Resulting concrete strengths averaged 3,500 to 4,000 psi. The sharp edges of a crushed gravel would have given higher strength. Specific gravity of the sulfur concrete was approximately 2.4. Porosity on test samples indicated absorption of water of 0.0 pct to 0.2 pct. Corrosion testing of the sulfur concrete was done by immersing 3- x 6-inch compressive strength test cylinders in 10 and 20 wt pct sulfuric acid solutions for 6 months. The cylinders were periodically tested for corrosion, absorption, and compressive strength. A gradual increase in the compressive strength of approximately 8 pct was obtained during the test period. No corrosive attack on the material was found, and the absorption remained constant at 0.04 pct during the 6-month test period.

Transport of the mixed sulfur concrete was accomplished by motorized wheelbarrows with insulated buckets (figure 5). Covers would have assisted in retaining the heat of the mix, but were not necessary in the summer months in south Texas.

The approximate total area repaired was 21,000 square feet, with a nominal thickness of 4 inches. Site preparation for the repair required the establishment of a suitable grade, removal of



Figure 3. Sulfur concrete preparation at the Asarco Corpus Christi plant.

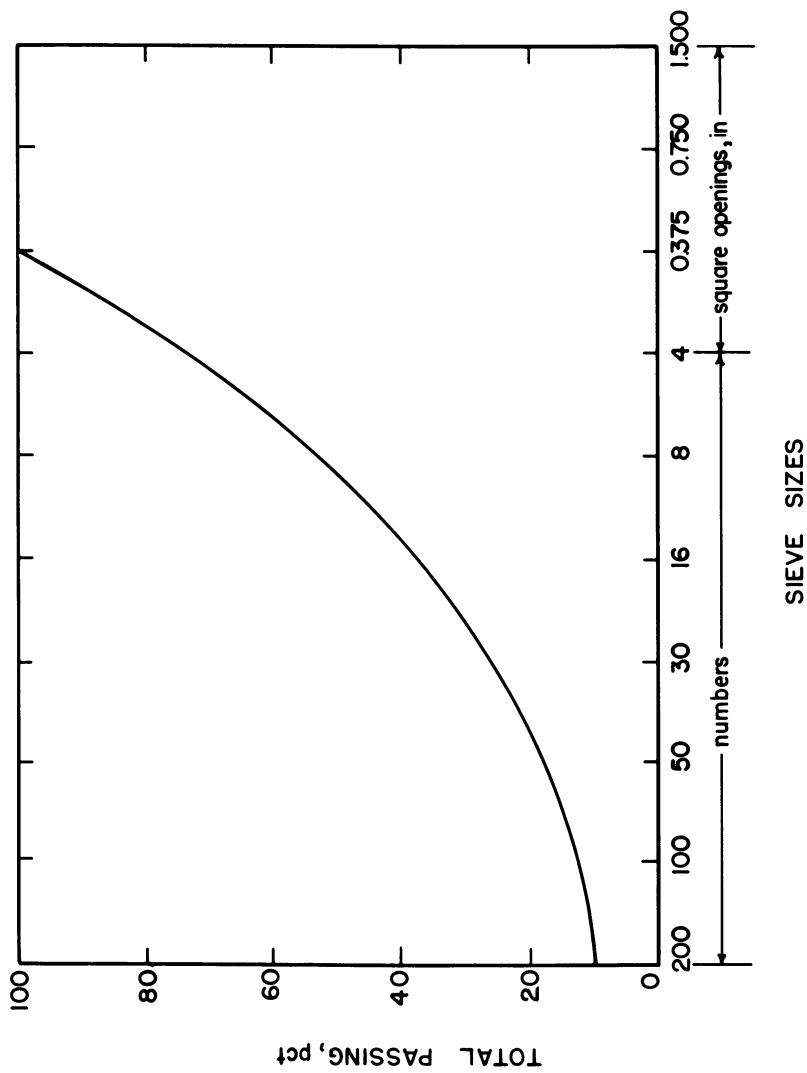


Figure 4. Aggregate gradation chart.



Figure 5. Transporting and pouring the hot sulfur concrete with an insulated motorized concrete buggy.

some deteriorated concrete, and preparation of subgrade. In addition to this routine work, a floor underdrain system utilizing PVC pipe and a cast-in-place sump was also installed. Elevation of subgrade was established by placement of washed sand. Finish grades were delineated by placement of screed boards. The procedure did not differ from the normal preparation for a portland cement pour. The structural pier pattern supporting the electrolytic cells and the tankhouse work floor presented an obstruction to straight-line work. Hence, the floor pattern was developed as a series of panels graded with appropriate pitches to drain to periodic swales intersecting the previously mentioned underdrain piping system.

At the initiation of the project in late June 1980, Bureau of Mines personnel were present to consult, assist, and advise. The Asarco Corpus Christi Plant Engineering Department organized and supervised the project at startup and assumed complete control after the departure of the Bureau of Mines personnel. The Bureau of Mines and The Sulphur Institute maintained periodic contact by telephone and visits throughout the work.

Panel widths ranged from 8 to 10 feet, lengths were 8 to 12 feet, and nominal thickness was 4 inches. The desirable approach is to deliver a full width of mixed material at the beginning to the panel and sustain a delivery rate to maintain full width ahead of the screed. Screeds used were wood equipped with a vibrator, either electrical or air-powered, the latter being preferred by these operators. Once the screed starts, it is preferable to continue in one single sweep to the completion of the panel. Figure 6 shows a floor section after screeding. Sulfur concrete freezes like a metal casting. The surface forms a skin first. Once the skin is formed, no further work can be accomplished. It can be reheated within limits by radiant heat and further worked. A single-sweep method is most effective. Some puddling can be done prior to the formation of the frozen skin. Finishes on the floors were screed finishes and were rougher than steel trowel finishes attained with portland cement concrete. The screed was adequate for the service installed. Finer finishes can be achieved by including external heat and correspondingly longer finishing operations. In addition to the floor panels poured, reinforcing and protective collars of sulfur concrete were poured around the support piers. Sulfur concrete can be vibrated with conventional concrete probes in forms, and reinforcing can be used as it was in these collars, but it was not used in the floor.

With respect to smoke and fumes, measurement of SO_2 in the mixing area showed no increase above background, and no hydrogen sulphide was detected. In the placement areas, there was some odor from the aromatics in the sulfur modifier. Pouring conditions were similar to those of an asphalt paving operation and included a similar odor. No special protective equipment was utilized or required. Operators at the mixer wore dust masks.



Figure 6. A section of the sulfur concrete floor after screeding.

Although the material is hot and worked hot, this was not a personnel problem factor in the placement.

There were some problems that were not viewed as being of great magnitude but are worthy of mention. Any moisture in the subgrade generated a small number of bubbles. This was corrected by pouring onto sheet polyethylene laid on the subgrade. Moisture in the aggregate also caused hangups in the feed hoppers. Vibrators were placed on the hopper shell side. Close attention must be paid to the temperature of the heated aggregate, because excessively moist aggregate will lower the delivery temperature, and correspondingly the temperature of the mix, rendering the mix potentially unusable.

The physical panel size used resulted in more joints between panels than would have been the case in a portland cement pour, owing to the surface finishing with a screed and the continuous obstruction of the existing support columns. Asphalt expansion strips were placed between panels and were provided with a removable top strip which was filled with a polyurethane compound. Shrinkage of pours in this work was negligible. Shrinkage in sulfur concrete was proportional to the amount of sulfur binder used.

Economics

Potentially every parameter of cost involved in sulfur concrete is a variable. The cost of sulfur and the cost to modify it, the availability and capacity of mixing equipment and the daily volume of material mixed, and the labor requirement at the mixing installation are variable factors for a specific project. Added to these variables are the normal parameters of a concrete jobsite preparation, form construction and grade delineation, transport, placement, finish, joint practice, and other items constituting the total concrete installation. Finally, a cost comparison must be made versus the local cost of portland cement concrete, which is highly variable in different locations.

Based on this experience and applied to a spread of ready-mix concrete cost of \$40 to \$80 a yard and extended to a range of quantity of sulfur concrete mixed per day, there is an indicated cubic yard comparison, materials only, of approximately 1½ to 6 times the cost of portland cement concrete for sulfur concrete. Greater volumes per day yield lower unit costs. Experience at Corpus Christi would put the premium cost of sulfur concrete approximately 15 pct more than the cost of portland cement concrete.

Limitations and Projected Future Use

The experience of Asarco was limited to exposures in different concentrations of sulfuric acid. Researchers studying sulfur concrete indicate that it is resistant to many organic and inorganic compounds, but not to aromatics, strong caustic

solutions, or oxidizing acids, and is not suitable at elevated temperatures because sulfur melts at about 240° F. Sulfur in the concrete can be flashed off when exposed to an open flame, but the concrete will not sustain combustion. Few data are published on its performance under sustained loads. The strength of the material ranges from 4,000 to 10,000 psi, depending on aggregate quality, gradations, and amount of sulfur binder used in the mix. For acidic environments at Asarco, silica gravel is the most suitable aggregate material. Crushed and graded metallurgical slags could be an acceptable aggregate; however, no investigation of this possibility has been made.

At the conclusion of the paving work at Corpus Christi, two electrolytic cells were cast of sulfur concrete for use in the zinc refinery. Subsequent to the work at Corpus Christi, a sulfur concrete floor was applied in the nickel plant at the Asarco Amarillo copper refinery. An isolating barrier of bituminous material was mopped on the concrete before the sulfur concrete pour. This floor, a substantially smaller area, was overlaid on a damaged existing floor. Similar techniques to those described were used in mixing and placement.

Sulfur concrete is not viewed as a substitute for portland cement concrete in general construction. A useful feature is achievement of strength within several hours after pouring. Placement can be made in a wider range of climatic conditions than can portland cement concrete. Sulfur concrete offers advantages in corrosive environments of the type tested and under testing at the Asarco plants and has advantages in floor areas, either as a structural material or as a protective overlay for structural concrete, with an isolating barrier between the concrete and the sulfur concrete. Precast slabs and sumps were prepared for installation at the Tacoma plant in an acid-truck-loading area. The slabs are overlaid on structural concrete. Sulfur concrete has potential as a material of construction for electrolytic cells, for leach vats, for other low temperature acidic containment vessels, and for general areas of floors and retention basins in acidic environments.

Acknowledgment

The review and comments on the text by Messrs. R. S. Jones, Plant Engineer, Asarco Corpus Christi; H. L. Fike, Vice President of The Sulphur Institute; and T. A. Sullivan, Research Chemist, U. S. Bureau of Mines, Boulder City, Nev. are greatly appreciated.

Literature Cited

1. Sullivan, T. A.; McBee, W. C. "Development and Testing of Superior Sulfur Concretes." BuMines RI 8160, 1976, 30 pp.
2. McBee, W. C.; Sullivan, T. A. "Development of Specialized Sulfur Concretes." BuMines RI 8346, 1979, 21 pp.
3. McBee, W. C.; Sullivan, T. A.; Jong, B. W. "Modified Sulfur Cements for Use in Concretes, Flexible Pavings, Coatings, and Grouts." BuMines RI 8545, 1981.

RECEIVED October 5, 1981.

Road Construction Using Sulfur

GERALD D. LOVE and EDWARD T. HARRIGAN

U.S. Department of Transportation, Federal Highway Administration,
Offices of Research and Development, Washington, D C 20590

Elemental sulfur has been modified in an exothermic reaction with commercially available hydrocarbon compounds to produce a pavement binder material that has been successfully utilized to construct several experimental pavement sections on public highways. The engineering properties, the formulation, and the methodology for producing and utilizing this chemically modified sulfur pavement binder, intended as a substitute for asphalt cement, are discussed.

The worldwide disruptions in crude oil supply in 1973-74, 1978-79 and 1980 have illustrated the tenuous nature of imported crude oil supplies. The United States annually consumes approximately 30 million tons (2.7×10^{10} kg) of asphalt cement refined from crude oil; 93 percent of the total mileage of surfaced highways and streets, or close to 1.6 million miles (2.6 million km), has been constructed with asphalt materials. Thus, the highway industry is very vulnerable to asphalt price and supply problems if crude oil imports again suffer severe disruptions.

Changing technology also promises to have a significant impact on asphalt production in the coming decade. First, modern refining technology is aimed at the processing of the residual fractions of crude oil to light products, to the detriment of asphalt production. Second, the government is committed to switching the nation's energy dependence from petroleum to a broader base in which coal, both as a boiler fuel and as a feedstock for synthetic fuels and chemicals, plays a principal role. The potential for bitumen production from synthetic fuel residuals is largely unassessed.

This chapter not subject to U.S. copyright.
Published 1982 American Chemical Society

Asphalt Extenders and Replacements

The oil embargo of 1973-74 caused the Federal Highway Administration (FHWA) to establish an R&D program to investigate the production of asphalt replacements and extenders from essentially non-petroleum sources. Since its inception, this program has examined in detail the use of: sulfur in elemental and chemically modified form; binders derived from cellulosic materials such as wood wastes and animal manure (1); and lignins produced as by products of the paper and pulp industries (2).

Both cellulosic wastes and lignins were found to have only limited applicability to the problem at hand. Sulfur, however, has been shown to be a very useful material for this purpose. Elemental sulfur may be used to extend asphalt, as in sulfur extended asphalt (SEA) binders, or chemically modified sulfurs may completely replace asphalt in paving mixtures.

Complementing the technical functionality of sulfur for pavement construction, U.S. sulfur production, while geographically localized, is favored with a nationwide distribution system. Sulfur is involuntarily produced from oil and natural gas, and the switch to coal promise to produce additional large U.S. surpluses of sulfur in the coming decades. Voluntary production is flexible so that the introduction of a major new sulfur use could be phased in without undue stress in the present supply and demand situation.

The development and evaluation of SEA binders has involved many public and private organizations including FHWA, and the wealth of information in this area will not be reviewed here (see, e.g. 3, 4, 5). FHWA has pursued the development of chemically modified (or plasticized) sulfur as a replacement for asphalt in flexible paving mixtures from a rudimentary level. This development program began in 1975 with the award of a contract to Southwest Research Institute to investigate materials and techniques to improve the engineering properties of elemental sulfur. From this contract has come the Sulphlex paving binders, a family of chemically modified sulfur binders designed as asphalt substitutes for highway pavement construction. These Sulphlex materials will be discussed in detail in this paper.

Development of Sulphlex Binders

The engineering properties of aggregate mixtures employing elemental sulfur as a binder are not suitable for highway pavement applications; such mixtures possess adequate compressive strength, but are extremely brittle and lack satisfactory fatigue behavior to resist repetitive traffic loading.

Rapidly quenched, pure elemental sulfur is extremely plastic (6). This plastic sulfur with its polymeric structure has tensile qualities lacking in the crystalline form, but

it quickly reverts back to the crystalline form which is thermodynamically favored under ordinary conditions. However, it may be stabilized by the addition of chemical modifiers, for example, hydrocarbons such as dicyclopentadiene. It has been demonstrated (7, 8) that such modifiers will apparently stabilize the polymeric, plastic sulfur indefinitely if they are present in sufficient quantities.

Southwest Research Institute (SWRI) undertook a program to screen a large number of potential chemical modifiers for their ability to produce asphalt-like modified sulfurs. Selection of the modifiers to be screened was based on several factors, most important being actual or potential availability from raw materials other than petroleum; as low a price as possible (no more than \$.40 a pound in 1976); and current availability in large quantities. The latter two factors dictated that the modifiers would be used in readily available, commercial grades of purity.

SWRI screened 80 different modifiers in its initial program, and produced more than 450 formulations in bench-scale batches (9). The formulations were screened by measurement of their physicochemical and rheological properties, and their stability.

Of the 450 formulations, 21 were considered promising enough for further testing. Properties of these materials in aggregate mixtures were determined, in particular stress-deformation behavior. Extensive testing was conducted on just three formulations, designated Sulphlex-233, -126, and -230 (Table I).

Table I
Initial Compositions - Sulphlex -233, -126, and -230

<u>Formulation</u>	<u>Component Percentage By Weight</u>				
	<u>Sulfur</u>	<u>Vinyl Toluene</u>	<u>Dipentene</u>	<u>Dicyclo- Pentadiene</u>	<u>Coal Tar</u>
233	70	8	10	12	-
126	61	13	-	13	13
230	70	-	15	15	-

Sulphlex-233 yields flexible mixtures with aggregates, similar in behavior to asphaltic concretes. Sulphlex-230 yields mixtures which are handled like asphaltic concretes, but which rapidly develop properties characteristic of rigid mixtures such as portland cement concrete. Sulphlex-126 has properties intermediate between the other two, though experience shows it tends more to the flexible end of the scale.

Sulphlex binders share certain physicochemical properties in common. Their temperature-viscosity curves are similar to asphalt, and very unlike the behavior of elemental sulfur. Their penetration decreases with age, but at a considerably faster rate than experienced with asphalt cements. Unlike asphalt, which hardens primarily through oxidation, Sulphlex binders can under certain circumstances be brought back to near their original penetrations by heating to approximately 120C.

Finally, due to their high sulfur content, Sulphlex binders have a specific gravity near 1.5 as compared to approximately 1.0 for asphalt cements. Therefore, if a Sulphlex binder is substituted by weight for asphalt in a paving mixture, the volume of Sulphlex binder present is only about two-thirds of the volume of asphalt it replaces. Based on original results (9), particularly Marshall stability and compressive strength data, it appeared that Sulphlex binders could replace asphalt in mixtures on an equal weight basis. This view has been tempered significantly by results discussed in the next section.

Detailed Testing of Sulphlex-233 Binder

The flexible binder, Sulphlex-233, was chosen for use in Sulphlex experimental pavement construction in 1980 and 1981. This choice entailed a comprehensive testing program by FHWA to develop tentative mixture design procedures for use with the Sulphlex-233 binder.

The results of this program are contained in reference (10). Table II presents a comparison of the selected physicochemical properties of Sulphlex-233 and an AC-20 grade asphalt cement used in the FHWA study. The table indicates that their properties are generally quite different, particularly the specific gravity, penetration, viscosities, and flash and fire points. However, from a practical standpoint, as the materials are used in the field, these differences are not highly significant.

The thin-film oven test (AASHTO T-179) is used to evaluate the susceptibility of asphalt to undesirable hardening during production of hot-mix. Table III compares the behavior of the Sulphlex-233 and the AC-20 asphalt cement after the thin-film oven test. The Sulphlex-233 binder suffers almost a fourfold loss of weight compared to the asphalt cement and this is reflected in the severe penetration loss. This test was conducted at 275F (135C) for the Sulphlex-233 (as opposed to 325F (163C) for the standard test) to avoid possible toxic gas generation. This penetration loss is irreversible, resulting for the most part as it does from a loss of volatilized material.

Table II
Comparison of Binder Properties

Tests	Sulphlex- _{1/} 233	Asphalt _{2/} Cement
Specific Gravity, 25/25C (77/77F) AASHTO T-228	1.538	1.032
Penetration, 25C(77F), 100g; 5 sec., AASHTO T-49	172	94
Viscosity, Absolute, 60C(140F), AASHTO T-202, poises	1042	2071
Viscosity, Kinematic, 135C(275F), AASHTO T-201, cSt	261	457
Flash Point, ^{3/} COC, F	355	505
Fire Point, ^{3/} COC, F	375	560
Solubility in Trichloroethylene, AASHTO T-44, Weight %	68.1	99.8

1. Produced by SWRI in 150 gallon (567.8 l) reaction vessel in October 1979; see reference 10, Appendix D.
2. Steam-reduced AMOCO AC-20 (Boscan).
3. Performed using AASHTO T-48, modified for the Sulphlex binder to use a hot-sand bath for heating. This modification prevented foaming of the Sulphlex material below the flash point.

1 poise = 0.1 pascal second 1 cSt = 10⁻⁶ metre²/second

$$^{\circ}\text{C} = (^{\circ}\text{F}-32)(5/9)$$

Table IIIComparison of Binder Properties After Thin-Film Oven Test
(AASHTO T-179)

Property	Sulphlex- <u>1</u> / 233	Asphalt <u>1</u> / Cement
	@275F	@325F
Loss, weight percent	2.64	0.73
Penetration, 25C(77F), 100g; 5 sec.,	51	50
% Penetration Retained	29.7	53.2
Viscosity, Absolute, 60C(140F), poise	5712	7428
Viscosity, Kinematic, 135C(275F), cSt	551	830

1. See Table II for sources of materials.

1 poise = 0.1 pascal second 1 cSt = 10^{-6} metre ²/second

$$^{\circ}\text{C} = (^{\circ}\text{F}-32)(5/9)$$

As noted above, Sulphlex-233 stored in bulk at ambient conditions gradually loses penetration, but this loss is essentially reversible upon heating. This penetration loss apparently involves crystallization of free sulfur in the material, and occurs regardless of whether the Sulphlex-233 is stored under air, nitrogen, oxygen or water.

These results accentuate the differences between Sulphlex-233 and the AC-20 asphalt cement, and the realization that Sulphlex-233 is not a strictly one-for-one replacement for asphalt. Failure to keep the differences in mind could have serious consequences in field use of the Sulphlex material.

Sulphlex-233 Mixture Properties

The Marshall design method (AASHTO T-245) in concert with the Immersion-Compression test (AASHTO T-165 and T-167) were selected by FHWA for the design of Sulphlex-233 paving mixtures (10). A traprock (diabase) aggregate used in Northern Virginia for road construction and having a past history of satisfactory service in asphaltic mixtures was chosen for study.

Table IV presents a comparison of the Marshall design parameters for mixtures of Sulphlex-233 and AC-20 asphalt cement under three conditions: 1) equal weight percents, 2) equal

Table IV
 Marshall Design Results: Sulphlex-233 and AC-20 Asphalt Cement

	Equal Weights Sulphlex		Equal Volumes Sulphlex		Equal (4%) Air Voids Sulphlex		Typical Marshall Criteria for Asphalt Concrete
	AC-20	233	AC-20	233	AC-20	233	
Wt. Percent ^{1/} Binder	6.1	6.1	6.1	9.09	6.1	9.6	-
Vol. Percent ^{2/} Binder	5.91	3.97	5.91	5.91	5.91	6.24	-
Unit Weight, pcf	161.5	156.0	161.5	162.6	161.5	163.8	-
Percent Air Voids	4.0	11.0	4.0	4.8	4.0	4.0	3 - 5 <u>3.4/</u>
Stability, Lbs.	2550	1450	2550	1825	2550	1850	500+ <u>3.4/</u>
Flow, 1/100"	10	10	10	12	10	13	8 - 18 <u>3.4/</u>
Percent VMA	17.4	20.0	17.4	19.1	17.4	18.7	16+ <u>3/</u>
Percent VMA- Filled	79.0	43.5	79.0	73.5	79.0	78.0	75-85 <u>4/</u>

Notes: ^{1/} By weight of total mixture
^{2/} Weight percent of binder divided by binder specific gravity
^{3/} Reference (11).
^{4/} Reference (12).
 1pcf = 16.018 kg/m³
 1 lb = 4.448 N
 1 in = 25.4 mm

volume percents, and 3) equal air void contents. The Sulphlex-233 mixtures meet all the typical Marshall design criteria for asphaltic concretes except in the case of equal weight replacement where the percent air void and percent VMA-filled criteria are unsatisfied.

Table V presents the "optimum" binder content for the Sulphlex-233 and the AC-20 asphalt cement and selected mixture properties obtained at these optimum values.

Table V

Optimum Marshall Binder Contents: Sulphlex-233 and AC-20 Asphalt Cement With a Well-Graded Diabase Aggregate

	<u>AC-20</u>	<u>Sulphlex-233</u>
Optimum (Wt. %)	6.4	10.3
Optimum (Vol %)	6.2	6.7

Mixtures Properties at These "Optimum"
Values

Percent Air Voids	3.1	3.0
Stability, lbs.	2600	1850
Flow, 1/100"	12	15
Percent VMA	17.0	18.6
Percent VMA-Filled	83.5	84.0

1 lb. = 4.448N

1 in. = 25.4mm

These data are derived from the Marshall design curves (10); the "optimum" contents meet all the criteria established for asphaltic mixtures. The optimum Sulphlex-233 content is at a slightly higher than equal volume replacement of the optimum AC-20 content. Reference (10) presents a fuller discussion of this topic.

The Marshall design method contains no provision for determining water damage susceptibility. The FHWA employs the Immersion-Compression test for this purpose. This test measures the retained unconfined compressive strength of a compacted mixture after soaking in a 140F (60C) water bath. The test data for the Sulphlex-233 and AC-20 asphalt cement are contained in Table VI. It is evident that with diabase aggregate, water damage is a potential problem with Sulphlex-233. The use of common anti-strip additives employed with asphalt, such as amines and tall oil, significantly improve the water damage resistance of the Sulphlex-233 mixtures.

Table VI
Immersion - Compression Data^{1,2/}

Volume Percent Binder ^{9/}	Weight Percent Binder ^{4/}	Additives	Compressive Strength psi @25C (77F)		Percent Retained	Percent Air		Percent Water Absorbed ^{3/}
			Dry ^{3/}	Wet ^{3/}		Strength	Voids	
Sulphlex - 233 ^{6/}								
3.97	6.10	None	744	NT ^{7/}	NT ^{7/}	12.4	12.4	NT ^{7/}
3.97	6.10	1% Amine ^{5/}	702	326	46.4	12.2	12.2	4.8
3.97	6.10	1% Tall Oil ^{5/}	708	301	42.5	11.2	11.2	2.0
5.91	9.09	None	657	NT ^{8/}	NT ^{8/}	6.4	6.4	NT ^{8/}
5.91	9.09	1% Tall Oil ^{5/}	681	478	70.2	4.4	4.4	0.7
AC-20 Asphalt Cement								
3.91	4.03	None	335	161	48.1	11.4	11.4	4.0
5.91	6.10	None	351	270	76.9	5.3	5.3	1.4
5.91	6.10	1% Amine ^{5/}	381	299	78.5	5.4	5.4	1.0

1/ AASHTO T-165, T-167
2/ Average of 4 specimens, except as noted.

3/ Average of 2 specimens

4/ Based on total mixture

5/ Added to the binder, percent by weight of binder.

6/ Aggregate temperature used was 300F, rather than 325F as specified.

7/ No test, specimens partially fell apart in water bath.

8/ No test, specimens completely fell apart in water bath.

9/ Weight percent binder divided by binder specific gravity.

^oC = (^oF-32)(5/9) 1 psi = 6895 pascal

No precise correlation is available between the immersion-compression test and results to be expected from pavements in the field. The test provides comparative guidance on water damage susceptibility. For the diabase aggregate, the Sulphlex-233 mixtures measured dry, and after immersion in the case of wet specimens, exceed the 300 psi (2.07×10^6 pascal) minimum compressive strength usually considered necessary for acceptable mixture performance in the field. Retained strengths generally fall below the 70 percent criterion considered acceptable for asphaltic mixtures.

Examination of Sulphlex-233 mixtures with other types of aggregates generally have confirmed the results presented here. Sulphlex-233 mixtures can meet or exceed most Marshall design and compressive strength criteria at either equal volume or equal weight replacement of asphalt cement, but "optimum" mixtures are obtained at or near the equal volume replacement level. The Sulphlex-233 mixtures are in many cases susceptible to water damage, and the use of tall oil as an anti-strip additive has been recommended where indicated.

Construction Operation with Sulphlex Binders

The success of SWRI in formulating Sulphlex binders with promising laboratory properties prompted FHWA to construct a small pavement section to evaluate the use of such materials with conventional asphalt construction equipment and practices. The goal was to determine if the Sulphlex binders might present unrecognized problems which would argue against their further development.

The construction was accomplished by SWRI on a low-volume road at its San Antonio facility in December, 1979. The total pavement is 645 feet (197 m) long, 24 feet (7.3m) wide, and includes ten Sulphlex sections in addition to portland cement concrete and an asphaltic concrete control sections. Three different Sulphlex binders, numbers -233, -126, and -230, were employed in the construction; besides the binder type, variables include the binder content, the pavement thickness, and the number of lifts used in the construction.

The construction required the production of 7.5 tons (6.8 tonnes) of each of the three Sulphlex binders. Scale-up to these quantities was required from laboratory batch size without benefit of investigating intermediate batch production. (Refer to (9) and (10) for discussion of Sulphlex manufacture in laboratory and pilot-scale batches.)

For the construction, the Sulphlex binders were produced in nominal 7500 lb (3400 kg) batches in rectangular metal vessels with loosely fitted plywood covers. Two batches of each formulation were required. Details of the production of the binders and of the pavement construction have been reported elsewhere (9).

The entire construction was accomplished without incident; the conventional equipment and techniques worked as well as with Sulphlex binders as with asphalt. After 2.5 years service, at a traffic volume of 1000 ADT (10 percent trucks), distress is evident in a number of sections. In general, the distress has been primarily attributed to poor subgrade drainage; placement of certain sections with mix at extremely low temperature (below 65C (150F)); ravelling of dry mixtures; and lateral shifting of lifts due to the absence of adequate tack between them. None of the distress is uniquely related to the use of Sulphlex binders in lieu of asphalt cement in the pavement.

The success of this pavement construction prompted development of a program to build larger Sulphlex pavement sections on public highways in a variety of climates and traffic loadings. Based on interest by the State highway agencies, seven sites were chosen for construction in 1980 and 1981. The goals of this program are to obtain limited data on the performance and durability of Sulphlex pavements and to further evaluate standard construction operations with Sulphlex.

The decision was made to limit the Sulphlex binder used in this program to Sulphlex-233. Arrangements were made with Chemical Enterprises, Inc. (CEI) of Houston, Texas for production of the Sulphlex-233 at its plant in Odessa, Texas. A total of 187 tons (170 tonnes) of Sulphlex-233/A binder were produced (NOTE: A shortage of one commercial grade of dipentene used previously necessitated its replacement by another source and minor reformulation of the Sulphlex-233 from the composition in Table I; the reformulated binder, having essentially the same physicochemical properties as noted in Table I, is designated Sulphlex-233/A).

CEI produced the Sulphlex-233/A in 7.5 ton (6.8 tonne) batches; the reaction vessel has a nominal 9 ton (8.2 tonne) capacity, is steam heated, and is equipped with a wet scrubber system to control potential hydrogen sulfide emissions. Since no cooling capability was available, the reaction exotherm was controlled by the rate at which the preblended chemical modifiers were added to the reaction mass.

The seven States selected for the Sulphlex construction projects and details of the projects are presented in Table VII. The San Antonio, Texas, construction is the largest job planned for the program, and its features will be discussed in some detail.

The Sulphlex-233/A binder material was shipped from the production point in Odessa, Texas to the McDonough Brothers hot-mix plant north of San Antonio, Texas, in three asphalt trailers containing approximately 20 tons (18.1 tonnes) each. The trailers were steam heated to allow the binder to be transferred into an empty asphalt storage tank.

Table VII
Sulphlex Construction Projects: 1980 and 1981

State	Location	Project Length ^{1/} (Approximate, Feet)	Sulphlex-233/A Requirement (tons)	Date Completed or Planned for Construction	Type of Construction
TEXAS	Loop 1604, San Antonio	7920 ^{3/}	60	8/26/80	1" thick overlay
NORTH DAKOTA	U.S. 2 and 52, Minot	1150	13	9/18/80	3.5" thick surface course
NEBRASKA	N-66, Valparaiso	1000	22	9/19/80	2" thick surface course
PENNSYLVANIA	TR 405, Montgomery	2000	22	10/27/80	1.5" thick wearing course
FLORIDA	I-75, Gainesville	900	22	11/20/80	5" thick surface course overlay
MICHIGAN	I-75 off ramp, Flint	--	22	Spring 1981	ND ^{2/}
ARIZONA	U.S. 70, Safford	--	22	Spring 1981	2.25" thick surface course

1 foot = 304.8 mm
1 inch = 25.4 mm
1 ton = .9072 tonne

- All projects are 12 feet in width.
- ND - not determined at this time.
- Approximately 3000 feet of 12 foot wide chip seal was also placed.

A mix design had been developed by the Texas State Department of Highways and Public Transportation (SDHPT) in conjunction with the FHWA. The aggregate proposed was composed of the following fractions: No. 10 limestone, 22.5 percent; limestone screenings, 7.0 percent; No. 4 sandstone, 43.0 percent; and silica sand, 27.5 percent.

This combination yields a well-graded blend, and is similar to the aggregate gradation used locally in asphaltic concrete and used in the 1978 SWRI construction. The mix design yielded a binder content of 7.3 percent by weight as most satisfactory. In order to assess the effect of binder content variation on performance, three sections with binder contents of 7.0, 7.5 and 8.0 percent were decided upon.

One and one-half miles (2.4 km) of existing asphaltic concrete pavement on Loop 1604 were overlaid with an inch (25.4 mm) thick Sulphlex mixture. The Sulphlex hot-mix was produced in a three ton (2.7 tonne) batch plant, and hauled approximately five miles (8.05 km) in open trucks to the construction site.

Weather conditions during the construction were hot and dry, with temperatures near 95F (35C). The construction operations proceeded without significant problems, and this project again demonstrated that the equipment and techniques used for asphalt pavement construction can be applied to Sulphlex pavement construction without modification. A view of the completed Sulphlex pavement is shown in figure 1.

In conjunction with the overlay construction, approximately 15 tons (13.6 tonnes) of the Sulphlex binder was used in a seal coat operation on Loop 1604 adjacent to the overlaid section. The binder was applied by a distributor truck at a rate of 0.4 gal./ yd.² (1.81 l/m²). Three hundred feet (91.4 meters) of 5/8 inch (15.87 mm) precoated rock asphalt were dropped on the binder followed by 2700 feet (823 meters) of 3/8 inch (9.5 mm) sandstone.

To date, the performance of both the Sulphlex overlay and sealcoat is satisfactory and completely comparable to the asphalt control sections constructed during the same period. Traffic volume on this section was measured at 5630 ADT; due to numerous heavy construction projects in the area, the percentage of heavy trucks is near 60 percent.

The Texas Air Control Board was responsible for monitoring emissions of hydrogen sulfide and sulfur dioxide during all phases of the Sulphlex construction. The measurements indicated that neither gas was present at levels near those which would pose a safety or environmental hazard during any phase of the operation.

The construction in Pennsylvania and Florida (see Table VII) also proceeded uneventfully. However, problems were encountered in North Dakota and Nebraska where drum mixers were used for the Sulphlex hot-mix production in contrast to the



Figure 1. Completed Sulphlex pavement (right-hand lane) on Loop 1604, August 1980.

other States where batch plants were employed. Difficulties were met in accurately metering the Sulphlex binders into the drum mixers, and the binder contents of the hot-mix were seriously deficient, particularly in Nebraska. This problem may be related to the higher specific gravity of the Sulphlex binder affecting the operation of the pumps which deliver the binder to the drum. The low binder contents have had deleterious effects on the integrity of the pavements. The situation is most acute in Nebraska. The outlook for adequate service in either State is problematical.

Future Developments

The use of Sulphlex in the future as an accepted alternative to asphalt is predicated on several factors, most importantly (1) a vigorous R&D program to optimize the engineering properties of the Sulphlex binders and characterize them for use in pavement construction, (2) evidence of adequate serviceability of the experimental Sulphlex pavements, (3) continuing rise in crude oil price and decline in assured foreign crude oil supplies, and (4) commercialization of Sulphlex production at a realistic unit price.

The FHWA has planned a comprehensive R&D program aimed at identifying a generation of Sulphlex binders ready for commercialization in the period 1985 to 1990. The program of pavement construction underway at the present time will be followed by a new round of projects using second or later generation Sulphlex binders and planned for a start in 1984 or 1985. This round would stress much larger pavement sections subjected to intensive evaluation of performance and durability. A necessary adjunct to this construction program will be production of the binder materials in a pilot plant specifically designed and constructed for maximum efficiency and minimum cost.

Literature Cited

1. Butte, W. A.; Kohn, E. M.; and Scheibel, E. G.; "Highway Binder Materials from Cellulose and Related Wastes"; Report FHWA/RD-80/031, May 1980.
2. Terrel, R. L.; "Evaluation of Wood Lignin as a Substitute or Extender of Asphalt"; Report FHWA/RD-80/125, November 1980.
3. Pickett, D. E.; Saylak, D.; Lytton, R. L.; Conger, W. E.; Newcomb, D.; Schapery, R. A.; "Extension and Replacement of Asphalt Cement with Sulfur."; Report FHWA-RD-78-96, March 1978.
4. Izatt, J. O.; "Sulfur-Extended-Asphalt Field Trials, M-153 Brazos County, Texas, A Detailed Construction Report"; Report FHWA-TS-80-214, December 1979.

5. Gallaway, B. M.; Saylak, D.; "Sulfur Extended Asphalt (SEA) Sulphur/Asphalt Mixture Design and Construction Details - Lufkin Field Trials"; Report FHWA-TS-78-203, January 1976 (reprint 1977).
6. Meyer, B. "Sulfur, Energy and Environment"; Elsevier Scientific Publishing Co.: New York, 1977; p. 41.
7. Blight, L.; Currell, B. R.; Xlash, B. J.; Scott, R. A. M.; Stillo, C.; "Preparation and Properties of Modified Sulfur Systems"; ADV. CHEM. SER. 1978, 165, 13.
8. Bordoloi, B. K.; Pearce, E. M.; "Plastic Sulfur Stabilization by Copolymerization of Sulfur with Dicyclopentadiene"; ADV. CHEM. SER. 1978, 165, 31.
9. Ludwig, A. D.; Gerhardt, B. B.; Dale, J. M.; "Materials and Techniques for Improving the Engineering Properties of Sulfur"; Report FHWA/RD-80/023, June 1980.
10. Lentz, H. L.; Harrigan, E. T.; "Laboratory Evaluation of Sulphlex-233: Binder Properties and Mix Design"; Report FHWA/RD-80/146, November 1980.
11. "Mix Design Methods for Asphalt Concrete"; Publication MS-2; The Asphalt Institute: College Park, MD, 1974.
12. "AASHO Interim Guide for Design of Pavement Structures"; American Association of State Highway Officials: Washington, D.C., 1972.

RECEIVED October 5, 1981.

The Potential for New Sulfur Products in the Middle East

RONALD L. TERREL¹

University of Washington, Seattle, WA 98195

In recent years, research into new uses for sulfur has centered in two areas: sulfur in agriculture and new industrial uses, primarily construction materials (1). Although sulfur in construction such as asphalt paving has been investigated for many years, increased interest since the 1973 oil crisis has spurred this interest into more practical realities. Significant progress in developing technology to utilize sulfur in construction has been made in North America through the sponsorship of such agencies as The Sulphur Institute, Sulphur Development Institute of Canada, Gulf Canada, Shell Canada, Federal Highway Administration, and other research agencies such as universities. Coupled with this rise in knowledge is the increasing supply of sulfur in some parts of the world, which may ultimately lead to widespread utilization of the new technology. For example, the Middle East is a source of sulfur that has not been utilized in the past. The recent rise in the rate of development in many countries provides new opportunities to utilize our new-found knowledge of sulfur's use in construction. A few of the more promising uses of sulfur in construction products are briefly described along with their application in the middle eastern society.

Sulfur Production (2)

Sulfur, one of the most important industrial raw materials, is distributed throughout the world in both elemental and combined forms. Sulfur has been used by mankind since antiquity and its consumption has increased at an annual growth of 4-4.5 percent. More than half of the world's sulfur output is in elemental form, nearly all of which is obtained from native sulfur deposits and natural gas. Fertilizer manufacture accounts for approximately 60 percent of all sulfur consumed, followed by chemicals, pig-

¹Current address: 1106 199th St. S.W., Lynnwood, WA 98036

0097-6156/82/0183-0225\$06.50/0
© 1982 American Chemical Society

ments, pulp, and paper. Construction products, as discussed in this paper are increasing in importance, but as yet are relatively insignificant.

Sulfur production is categorized as either voluntary or involuntary, depending on whether it is the primary, sought-after product or a by-product from other sources (3). Voluntary sources include massive pyrite, native sulfur, and gypsum. Native sulfur is usually recovered either by conventional mechanical mining or the Frasch process. Involuntary sulfur, as the term applies, is essentially a by-product arising from abatement of sulfurous emissions associated with processing or combustion of fossil fuels and the roasting and smelting of base metal ores. Involuntary sources include coal, oil shale, natural gas, petroleum, tar sands, and metal ore processing.

Until the 1960's, the majority of the world's sulfur supply was the direct result of the voluntary sulfur producers. However, the advent of sour gas production in Alberta, Canada in the 1960's resulted in the dumping of tremendous quantities of involuntary sulfur into the world marketplace. By 1968, a serious oversupply developed, sulfur prices were weakened, and a retrenchment in the fertilizer sector occurred. This led to a general collapse of the sulfur market, which continued through most of 1973.

By 1975, the sulfur market had become very tight in regards to supply and demand. Sulfur prices rose steadily as a result of the decline in involuntary sulfur production, the increase in Frasch production costs, logistic supply problems, an expansion in fertilizer manufacturing, and the ability of the fertilizer industry to pass increased sulfur prices on to their consumers.

The rapid shift from an apparent serious growing world oversupply situation, which had been considered permanent, to a very tight sulfur supply and demand situation, with indications of future sulfur supply shortages, resulted in the knowledgeable sulfur experts becoming very concerned and unable to agree on the future availability of sulfur. The lack of consensus continues to the present time.

Table 1 provides a forecast of the United States and world sulfur supply and demand for the years 1985 and 2000. Table 1 also includes estimates of the identified recoverable world sulfur reserves using 1978 technology at 1978 sulfur prices and at all price levels. A visual representation of the importance of price in determining the availability of sulfur is provided by Figure 1. Note that this figure is based on the assumption that these quantities of sulfur will be produced only if the sulfur price levels are maintained for a sufficient period of time.

Examination of Table 1 indicates that the United States cumulative domestic demand will exceed the recoverable sulfur reserves at 1978 prices by approximately 282 million metric tons and the recoverable sulfur reserves at all prices by 127 million metric tons. It is noted that the United States' future sulfur supply is better than these comparisons indicate, since the sul-

Table 1. Summary of Estimated Sulfur Supply and Demand
(Million tons)

Country	1978		1985		2000	
	Production	Reserves (a)	Supply	Demand	Supply	Demand
United States	11.2	330	20.0	21.0	28.0	31.5
Mexico	1.9	150	3.0	--	--	--
Canada	7.3	2,250	7.0	--	--	--
World	54.0	6,435	78.0	76.0	--	138.5

Source: Sulfur, U.S. Bureau of Mines, July 1979

(a) Recoverable sulfur at all price levels using 1978 technology

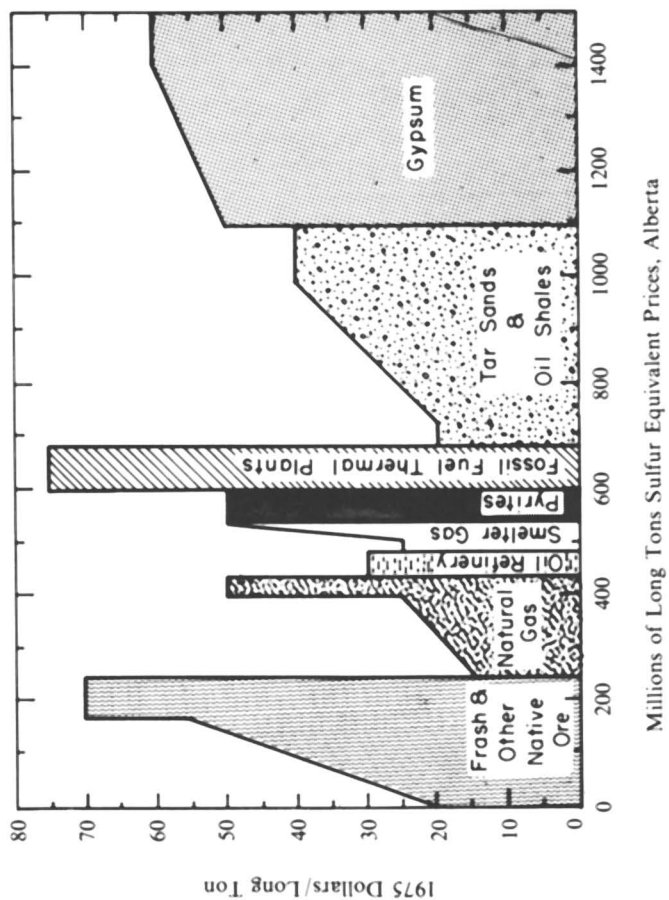


Figure 1. North American sulfur resources and supply prices.

fur reserve estimates are very conservative in that they do not account for improved sulfur recovery technology, new conventional reserves, and they exclude certain reserves and limit others. Improved technology and a basic change in the U.S. sulfur supply between now and the year 2000 will also significantly reduce the projected sulfur supply shortfall. These changes will be made by the market in response to the projected demand and the resultant higher price levels for sulfur will make the other sulfur sources, not identified in Table 1, very attractive and ensure their development. The exhaustion of domestic lower production-cost sulfur and the enforced production of coproduct sulfur for environmental reasons will also contribute to these changes.

Although the U.S. future sulfur supply will be better than Table 1 indicates, it is extremely difficult to estimate whether the above changes will result in a sufficient supply of sulfur to cover the cumulative demand to the year 2000. Accordingly, the possibility exists that the U.S. will be a net importer of sulfur until the year 2000.

Table 1 also indicates that if the price levels of sulfur are allowed to rise above 1978 price levels, the world's sulfur supply will cover world sulfur demand to the year 2000. The world will also experience the changes projected for the U.S. domestic sulfur supply and these changes will make the projected world sulfur supply look that much better. For example, Iraq, with its recent Frasch sulfur operations, is quickly developing into a strong competitor for Canada in India and the Far East. If the Arabian Gulf's rail system and rolling stock is upgraded, Canada could lose these one million metric ton markets. In addition, the Middle East is developing as a major sulfur producer due to its ongoing oil and gas field production. It has already begun to erode Canada's influence in Asia and the reopening of the Suez Canal would provide access to the markets in Europe. Also with the future development of extensive native sulfur reserves in Central America, South America, and Africa, Canada's off-shore markets could decline significantly.

The recent and future development of sulfur supplies in the Middle East tends to emphasize the resulting regional concept for sulfur supply/demand. However, as in North America, the rising production of involuntary sulfur has caused a drop in the amount of native pyrite sulfur produced. Table 2 shows recent past and estimated trends in several Middle Eastern countries. The future of by-product sulfur from oil and gas operations is very uncertain at the time of this writing (October 1980) because of the Iran-Iraq war and its effect on near-by countries.

However, by way of example, Saudi Arabia can be shown to have a rapidly changing sulfur outlook because of recent major programs (4). In addition, because of Saudi Arabian closer ties to the West, it may be a somewhat more stable source of major proportions.

The only source of sulfur in Saudi Arabia is involuntary

Table 2. Estimated Middle East sulfur production*

	1970	1975	1980	1985
<u>Native Sulfur</u>				
Iran	1	20	20	15
Iraq	--	600	700	100
<u>By-product sulfur</u>				
Egypt	8	9	12	15
Iran	412	474	100	500
Iraq	--	110	100	100
Israel	8	10	10	12
Kuwait	48	73	80	100
Saudi Arabia	5	3	792	1500
Syria	--	1	10	?

*Thousand metric tons

Table 3. Saudi Arabia's Sulfur Capacity

Plant	Total Design Capacity M tpd	Current Average Production M mpd
Berri	1,408	830
Shedgum	1,600	1,250
Uthmaniyah	1,200	none

production (5,6). This sulfur is a result of the Saudi Arabian Government's gas gathering and treatment program, launched in early 1975. The original scope of this program, which was 6 billion cfd and nine installations, has been reduced to three natural-gas-liquids (NGL) centers and two fractionation centers which will process a total of 3.5 billion cubic feet per day (cfd), including 0.6 billion cfd which is the capacity of the already existing Berri Plant.

Present Aramco facilities can handle around 0.6 billion cfd, hence Saudi Arabia gas capacity will grow to 4.1 billion cfd when the project is completed.

The new facilities will include a network of gathering lines, and compression and conditioning plants throughout Ghawar oil field, the world's largest, and two major gas plants in Shedgum and Uthmaniyah sectors of the field.

The 2.9 billion cfd fed from Ghawar field to Shedgum and Uthmaniyah Gas plants would yield 637,000 barrels per day (b/d) of NGL, 1.02 billion cfd of sweet residue gas and 2,790 metric tons/day of elemental sulfur.

Of these totals, the Shedgum plant would yield 311,000 b/d of NGL, 1650 tons/day of sulfur, and 570 MMcfd of sweet-residue gas from its design charge of 1,435 billion cfd of Ghawar gas. The Uthmaniyah plant would produce 326,000 b/d of NGL, 1,140 tons/day of sulfur, and 445 MM of residue gas from a 1,485 billion cfd feed stream.

The Shadgum NGL plant has been in production since January 1, 1980. Full production is planned for 1981. The Uthmaniyah NGL plant is planned for 1982 for full production. Table 3 shows how the country's NGL and sulfur capacity will grow.

The Berri Gas Plant, an Aramco facility, which came on stream in October 1977, has a current sulfur production rate of 1,200 tons/day. This would bring the sulfur production by the end of 1982 to 3,990 tons/day or nearly 1.5 million tons per year. Expansion of the program is probable, but timing depends on crude-production rate and demand for gas.

In conclusion, the United States, the Middle East and the world will be able to obtain adequate sulfur supplies at reasonable prices to satisfy their demand requirements well beyond the year 2000 (2). Improved sulfur recovery technology, expected basic changes in sulfur sources, and the supply benefits resulting from expected increased sulfur price levels will relax the world's present tight sulfur market and ensure adequate future supplies. The world's increasing dependence on involuntary sulfur sources will drastically restructure existing markets and have important implications for both sulfur producers and consumers. In addition the existence of regional sulfur surplus and deficit areas throughout the world will become more pronounced, and both the U.S. and the world sulfur-producing and sulfur-consuming industries will undergo continual regionalization and each will develop supply/demand relationships that will be largely independent of other regions.

A Special Environment

During the 1970's the Middle Eastern countries which belong to OPEC have experienced a very rapid increase in construction activity. The increase was due to their desire to build housing, industry and other infrastructure features that were virtually nonexistent twenty years ago. Hundreds of kilometers of roads have already been constructed with many more to come. Three major international airports and 20 plus smaller ones are to be built in Saudi Arabia alone. Other countries are following suit in proportion to their own population and needs. Housing for citizens as well as expatriate workers is a first priority item. Industrial and commercial construction as well as military facilities continue to be a large proportion of the construction budget. In summary, there is an unprecedented amount of construction underway in the Middle East, and demand for construction materials is at an all-time high.

The climate in the Middle East in general and the Arabian Gulf area in particular is extremely arid, but the temperatures can range over a wide spectrum. Although little rainfall may occur, high humidity is the rule near the Gulf and other large bodies of water. This environment has proven to be harsh to buildings, portland cement concrete, asphalt concrete pavements as well as other constructed facilities.

In the early stages of development, Saudi Arabia and other countries relied entirely on imported products. While this is still largely the case, there is a trend toward self-sufficiency. For example, rather than simply export crude oil, there is a marked drive toward the development of a petrochemical industry that will be aimed at products for export (6,7). This will not only increase potential income from oil, but will provide employment for indigenous populations. Other industry and materials for construction are also being developed by Saudi Arabian engineers in order to reduce dependence on imports.

The construction industry in Saudi Arabia has grown rapidly in the last two decades from simple local industry that relied for centuries on limited local materials and craftsmanship to a complex modern industry with the capability of processing construction materials available in the country (4).

In the second Five-Year Development Plan of Saudi Arabia (1975-1980) it was estimated that construction expenditure will reach about SR 300 billion (8). This boom in construction expenditure was due to the urgent need for housing, highways, airports, hospitals, schools, industrial plants, and many other needs to meet the desire of the country to build itself into a developed nation. As a result of the huge projects, shortages in the main locally produced construction materials have occurred.

One example of a potential material shortage is asphalt cem-

ent for road building in Saudi Arabia. Asphalt is largely the residue from several processes of distillation. Asphalt is produced from three main refineries; Ras Tanura, in the eastern province, Riyadh in the center, and Jeddah in the western province. In 1978 the total production of asphalt was 5.8 million barrels while the consumption exceeded 7.7 million barrels (9,10). Table 4 shows the production and consumption of asphalt, the difference being imported.

Most of the asphalt produced is used in roads and airfield pavements. Nearly all roads and airstrips built in Saudi Arabia since 1950 have been paved with Ras Tanura asphalt.

During 1978 and 1979, 2,200 kilometers and 1,896 kilometers, respectively, of asphalt roads were built in Saudi Arabia (Table 5) (10). During the first four years of the Second Five-Year Development Plan (1975-1979), a total of 7,965 kilometers of asphalt roads were constructed as against 3,732 kilometers in the entire First Five-Year Development Plan period. Another 1,277 kilometers are expected to be completed during 1980. Moreover, a total of 5,760 kilometers of roads is under construction while studies and design of 9,904 kilometers of roads have been completed.

With Saudi Arabia now in its Third Plan, the demand on asphalt cement will be a very serious problem unless other measures or solutions are taken, such as utilization of sulfur extended asphalt.

Another example of an important construction material in the Middle East is portland cement. For example, all-purpose Type I and sulfate-resisting Type V portland cements are manufactured in Saudi Arabia in three plants at Hofuf, Jeddah, and Riyadh. The cement production from the three plants totaled 1,790,000 tons in 1978 which is about a 38.5 percent rise over 1977. Portland cement is a basic construction material, and is primarily consumed by the construction industry. In Saudi Arabia cement does not seem to be encountering competition from any other building materials which are capable of endangering its present level of demand. Today the cement industry in Saudi Arabia is in one of the most crucial periods of its history. After many years of stable demand the industry faced a tremendous increase in demand. Table 6 shows the consumption of cement. The alternatives being considered by the government and the cement industry are either to continue depending on imports, expand existing plants or build new ones, or do all of these, to meet the present and future demand.

The nation's cement forecasts based on the analysis of Al-Turki and McCoullough (11) are shown in Table 7. The forecast shows that the country will suffer, for at least up to 1981, from insufficient domestic supplies of cement. However, the Saudi Arabian Government has decided to encourage the expansion of the present 1.79 million tons annual capacity to 10 million tons. The expansion will be in two forms, expanding the three existing cement plants and adding new plants. Until these expansions are

Table 4. Production and Consumption of Asphalt (10)

Year	Total Production	Total Consumption
1970	1,662	1,031
1971	1,099	1,120
1972	1,142	1,009
1973	1,482	1,653
1974	1,987	2,003
1975	2,465	2,811
1976	5,081	4,948
1977	6,793	10,283
1978	5,763	7,704

Thousand barrels

Table 5. Road Network in Saudi Arabia (10)

Asphalt Paved Roads					
Year	Main	Secondary	Feeder	Total	Rural Roads
1975	6,141	5,556	473	12,170	8,510
1976	7,182	5,798	1,125	14,105	11,193
1977	8,362	5,897	1,779	16,038	13,307
1978	9,618	5,959	2,660	18,238	16,948
1979	10,834	6,030	8,270	20,132	20,119

Cumulative length in kilometers

Table 6. Cement Consumption in the Kingdom (10).
(Thousand tons)

Year	Local Production	Imports	Total	Production % of total
1378	30.3	346.5	376.8	8.0
1379	78.8	229.5	308.3	26.6
1380	89.6	270.8	360.4	24.9
1381	120.2	234.0	354.2	33.9
1382	196.2	275.7	471.9	41.6
1383	217.0	201.5	418.5	51.8
1384	258.5	339.7	598.2	43.2
1385	250.2	491.8	742.0	33.7
1386	323.2	456.0	779.2	41.5
1387	417.6	291.6	709.1	58.9
1388	510.8	490.3	1,001.1	51.0
1389	574.1	685.7	1,259.8	45.6
1970*	666.9	463.7	1,130.6	50.0
1971	703.4	549.9	1,253.3	55.1
1972	911.1	299.5	1,210.6	75.3
1973	1,008.3	280.5	1,288.8	78.2
1974	1,056.6	1,510.7	2,567.3	41.2
1975	1,125.7	1,825.8	2,951.2	38.2
1967	1,143.0	2,795.0	3,938.0	20.0
1977	1,292.5	5,356.0	6,648.4	19.4
1978	1,790.7	6,679.0	8,469.7	21.1

*Beginning 1390(1970) years on the basis of Gregorian Calendar.

Table 7. National forecasts for cement supply and demand in
thousand metric tons (11).

Year	Supply	Demand
1977	1,408	4,860
1978	2,176	5,623
1979	3,040	6,579
1980	3,904	7,793
1981	5,216	9,228

in operation the balance of the country's cement requirements must be covered by imports, or other alternatives such as sulfur concrete.

Coupled with the shortages in asphalt and portland cement is the general problem of shortages in quality mineral aggregates. For example, crushed stone and dune sand are normally used as concrete aggregates throughout the Eastern province of Saudi Arabia. These materials are similar to those throughout the Arabian Gulf area. Crushed limestone coarse aggregates are produced by local crushing plants at various locations to serve the demands of the locality. Over 50 percent of the coarse aggregates do not meet the requirement of Saudi Arabian Ministry of Communications for base course and wearing course in terms of hardness, toughness, durability and soundness (12).

Dune sand is the primary source of fine aggregates. No particular preparation or processing is normally performed on the sand before its use. It is available everywhere and the only cost involved in using it is, normally, the cost of transportation. The dune sand generally consists of fine well-rounded grains shaped by the action of the wind. It is composed mostly of quartz with small percentages of soft calcareous shell fragments and gypsum pellets (12).

The dune sand by itself does not meet the requirements of ASTM C-33 for fine aggregates. However, such deficiency is sometimes corrected by compensating with screened aggregate obtained from crushing of limestone. A typical dune sand sieve analysis is shown below (12).

Sieve No.	% Passing	
	ASTM C-33	Dune Sand
3/8"	100	100
#4	95-100	100
#8	80-100	100
16	50- 85	100
30	25- 60	91
50	10- 30	41
100	2- 10	7

Based on the previous discussion, it can be seen that there is a high demand for basic construction materials such as asphalt and portland cement. This demand cannot be fulfilled by existing local supplies. Moreover, the primary source of sand, which is usually obtained from existing sand dunes, does not meet the usual requirements, leading to poor quality end products. This poor quality can be upgraded but at higher cost.

In order to meet the demand and reduce extra cost for upgrading poor quality of construction materials used, the utilization of an existing alternative material such as sulfur is highly recommended.

Promising Sulfur Products (13, 14, 15)

The chemical properties of sulfur and its compounds are being widely utilized by the chemical industry. Sulfuric acid, in particular, has been regarded as the workhorse of the industry. By contrast, the mechanical properties of sulfur are largely unexploited, although it has been known for many years that sulfur does possess a number of interesting and potentially useful mechanical characteristics.

Since the 1960's, when the need to create new uses became apparent, utilizing the mechanical properties of sulfur has become the subject of an increasing amount of research and development. A number of those that appear to have particular application in the Middle East are outlined below, while several are highlighted in later sections.

Sulfur-Asphalt Paving Materials (16, 17). Two different technologies are used to combine asphalt and sulfur into a binder that exhibits unique properties and often enhance the pavement performance as well as extend the supply of available asphalt.

Sulfur Concretes (15, 18). A range of different approaches are emerging to fabricate numerous products from a mixture of elemental or modified sulfur and mineral aggregates. These include cast-in-place as well as preformed or precast items which were previously made from portland cement.

Sulfur Impregnation (14). Stronger and more durable products such as portland cement concrete, ceramic tile and even wood and paper products have been shown to be feasible. In addition, sulfur as an impregnant for fabric liner systems would have application in ponds, holding tanks, etc.

Sulfur Coatings (15, 18). Molten sulfur, often mixed with fibers or modifiers can be used to spray coatings on unbonded block or brick buildings, linings for ponds, portland cement concrete, and other applications where a durable coating is required or useful.

Foamed Sulfur (15, 18). By using additives and simple machinery, sulfur can be turned into a foam that has very useful properties. Lighter than water, foamed sulfur can be used for building insulation, subbases for pavements, and perhaps lightweight structural members for housing and other small structures.

Sulfur-Asphalt Paving Materials (15)

The current sulfur-asphalt technologies are the result of research and development carried out since the late 1960's, but the sulfur-asphalt concept is far from new. The foundation was laid in the 1930's by Bencowitz (19) and his co-workers who produced and patented sulfur-asphalt mixtures which had several advantages over regular asphalt.

However, it was the availability of large quantities of by-product sulfur combined with the energy crisis of the early 1970's which stimulated the research and development needed to make sulfur-asphalt technology a commercial reality. The need to dispose of large potential tonnages of sulfur and the need to find alternative new materials to increasingly expensive petroleum-based asphalt spurred interest and research by many organizations. Major companies like Shell Oil Canada, Societe Nationale Elf Aquitaine, France, and Gulf Oil of Canada and the Sulfur Development Institute of Canada, initiated major research and development programs.

The acceptance of sulfur-asphalt technology (generally called sulfur-extended asphalt or SEA) by highway departments and contractors has been due not only to the desire to replace asphalt by readily available sulfur, but also to the fact that the sulfur-asphalt materials have shown improved properties compared to asphalt, and the potentially even more interesting fact that sulfur-asphalt permits the use of aggregates which would be unsuitable for use with asphalt. With good quality aggregate becoming increasingly scarce in many locations, many highway departments are interested in processes which allow the use of low-grade, low-cost aggregates. Several major technologies have developed in North America and abroad, each of which may have application in the Middle East. In recent years, many field trials have been conducted to demonstrate the feasibility of sulfur-asphalt construction. Several of these have been constructed in the Middle East as noted in Table 8.

Gulf Canada Limited (20, 21). The process developed by Gulf consists of a pumping system which continuously delivers measured volumes of sulfur and asphalt to a mixing device which disperses the molten sulfur in the liquid asphalt. The composition of the emulsion is typically in the range 25-60 parts sulfur to 75-40 parts asphalt. The temperatures of the sulfur, asphalt and S/A emulsion are maintained in the ranges 121-154°C, 121-177°C, and 121-154°C, respectively.

The emulsification is carried out in such a manner that part of the sulfur is dissolved in the asphalt and the remainder is dispersed in the continuous asphalt phase as molten sulfur droplets with a particle size range of 1-50 μm .

The emulsion should be used within one hour after preparation to coat aggregate particles to yield a hot-mix paving material.

This paving material is transported, placed and compacted in the normal manner using conventional paving equipment.

Early field trials were conducted in Saudi Arabia using this technology (22, 23). Considerable interest in sulfur asphalt pavements has been generated, but not projects of significance have been completed. Considerable research and development as well as demonstrations are continuing under the guidance of the Sulphur Development Institute of Canada.

Pronk (24, 17). The Pronk patents deal with stabilized sulfur in asphalt emulsions for use as binders for pavement construction. Small amounts of organosiloxane polymers are used as stabilizing agents. A typical composition contains 60-70% asphalt, 30-40% sulfur and 0.001% siloxane polymer based on the weight of the asphalt. The preferred mixing temperature is in the range 130-145°C and the emulsified binder may be stored with gentle agitation.

There is evidence that the Pronk additive reduces the evolution of sulfur vapors and gases. Air monitoring data are routinely collected during field trials.

A Pronk paving mixture can be prepared by mixing the asphalt (containing the stabilizing additive), sulfur and aggregate in an asphalt plant pugmill. However, in order to simplify plant operations and not increase the total batch-to-batch cycle time, it is easier to blend and emulsify the sulfur and asphalt using an in-line mixer just prior to the asphalt plant weight bucket. Numerous field trials as well as substantial paving projects have been completed in North America as well as Europe.

S.N.E.A. (Societe Nationale Elf-Aquitaine). S.N.E.A. was the first of the three groups to publish any details of its research in 1973. The S.N.E.A. patents and applications claim a procedure to manufacture an emulsion of sulfur in asphalt such that the sulfur particle size does not exceed 10 μm , and averages 0.5-5.0 μm . A turbine with a preferred gas setting in the range 0.5-1.15 mm is used to produce the emulsions. The mixture may be recycled a number of times through the turbine or a series of turbines. Alternatively, a coarse dispersion may be produced and subsequently homogenized in the turbine. Although the patents cover emulsion compositions of 13-50% sulfur, 16.5-39% is the preferred range. The optimal temperature range for manufacture of the emulsion is 130-170°C. These S/A emulsions are claimed to be particularly suitable as binders for pavement construction.

The emulsifying equipment has been set up as a self-contained trailer-mounted unit. The unit used at the 1975 field trial in Lufkin, Texas is designed to accept molten sulfur and hot asphalt from road tankers. The sulfur and asphalt flow rates are controlled by two proportioning pumps driven by a sprocket and chain arrangement from a common shaft. This arrangement enables the sulfur content of the binder to be varied from 20% to 50%.

The metered sulfur and asphalt streams are combined and fed through a baffle-containing pipe to generate some premixing, to a turbine mill powered by an electric motor. The S/A emulsion is discharged to a surge tank from which it is pumped to the weight bucket as required. The mobile unit contains a complete stream generation system used to maintain the desired sulfur temperature in the road tanker. A circulating hot-oil system controls the temperature of the pipes, valves and pumps.

In addition to the numerous projects completed in Europe, one U.S. trial and several in the Middle East have also been demonstrated (Table 8). Saudi Arabia constructed one in 1979 to com-

Table 8. Sulfur-Asphalt Road Paving
Trials in the Middle East
(7) (15) (23)

Location	Length (miles)	Type of Test	Year	Process
Iraq	0.6	Full depth	1977	SNEA
Kuwait	1.0	Full depth	1977	SNEA
United Arab Emirates	0.6	Full depth	1978	SNEA
Saudi Arabia	0.6	Resurfacing	1979	SNEA
Saudi Arabia	0.6	Full depth	1979	Gulf

pare with that done by Gulf (22,23). During 1977, two other projects, one in Kuwait and one in Iraq (25) have shown that S/A technology has considerable promise in hot climates.

Shell Canada Limited (26,27,28,29). Shell Canada Limited has been investigating mixes produced with low grade aggregate. The Shell patents broadly cover a bituminous paving composition in which the aggregate is coated with bituminous binder and the excess undissolved sulfur acts as a filler in the void spaces between the aggregate. The process is particularly adaptable for use with inexpensive, ungraded sands which are not suitable for use as an aggregate in a conventional hot mix asphalt concrete; this mix class has often been called sulfur-asphalt-sand (SAS), but Shell's product is currently tradenamed THERMOPAVE.

A number of compositions have been designed for specialty applications such as road patching (i.e., THERMOPATCH).

The asphalt content of THERMOPAVE mixes is similar to that of conventional asphalt paving mixes for base and wearing courses; mixes containing 4-7% asphalt are generally most suitable. In general, the ratio of sulfur to bitumen is at least 1:1 and pre-

ferably not more than 5:1. Hence, in comparison to a conventional hot mix which is 4-7% asphalt and 93-96% aggregate, sulfur replaces a portion of the aggregate in the THERMOPAVE formulation.

Mixes with an S:A ratio of 1.0-2.5:1 are recommended for use in the construction of flexible paving structures, while those with an S:A ratio greater than 5:1 make suitable rigid pavements. It is claimed that mixes with an intermediate ratio of 2.5-5.0:1 form very strong pavements which retain some degree of flexibility.

A typical formulation for a flexible pavement application is 82 parts sand, 12 parts sulfur and 6 parts asphalt. In the hot mix the sulfur increases fluidity to an extent where the mix is essentially self-compacting, and requires no rolling. Upon cooling, the sulfur solidifies, filling the void spaces between the aggregate particles and makes a significant contribution to the mechanical stability of the pavement. As well, the addition of sulfur provides a third variable for mix design purposes. The asphalt acts as the binder for the aggregate particles in a manner similar to the conventional mixes, and imparts the visco-elastic properties to the pavement structure.

The Shell approach may have considerable application in the Middle East where many areas have very poor aggregates and must rely upon dune sand, as discussed earlier. A drawback, however, is the specialized insulated trucks and other features that may detract from its ready acceptance.

Other Work. In addition to the work conducted by Shell Canada Limited, a number of studies with similar materials have been conducted by the Texas Transportation Institute (29), the U.S. Bureau of Mines (30) and the National Research Council of Canada, Dept. of Building Research (31).

Utilization of sulfur asphalt pavements in the Middle East appears to have an excellent chance of success. For example, in Saudi Arabia, the production of asphalt in-country has not increased much during the rapid rise of construction activities in recent years. Figure 2 shows the recent and expected production of both asphalt and sulfur in Saudi Arabia. As discussed earlier, demand for asphalt has surpassed the supply. Use of sulfur in pavements may provide the needed binder material and thereby preclude the need for added imports or increased sulfur production(7).

Sulfur Concrete

Sulfur concretes (SC) are basically simple materials, made by mixing sulfur plus certain additives with heated mineral aggregates. On cooling, SC sets to give a high-strength material with superb corrosion resistance.

Early attempts to make and use SC date back more than a hundred years. However, current SC technology is a product of the 1960's and 1970's following the discovery and development of suit-

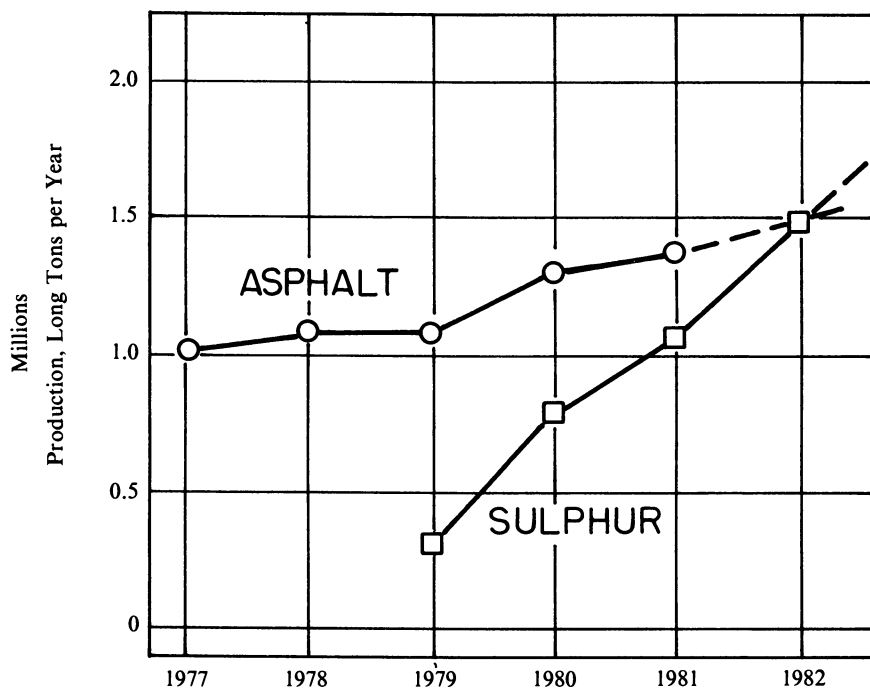


Figure 2. Projected production data for asphalt and sulfur in Saudi Arabia (7).

able additives or "plasticizers" for the sulfur which impart durability to SC. A considerable number of compounds have been screened as additives. Currently, the most popular ones are dicyclopentadiene (DCPD), dipentene (DP), certain proprietary polymeric unsaturated hydrocarbons, and combinations of these materials. Much of the current research work is concentrated on finding additives or combination of additives which will further improve the durability and performance of SC.

Sulfur concretes can be designed to have compressive and tensile strengths twice or more those of comparable portland cement concretes (PCC), and full strength is reached in hours rather than weeks. Sulfur concretes are extremely corrosion resistant to many chemicals, including most acids and salts. The metallurgical and fertilizer industries have shown interest in using SC in corrosive environments where PCC has a very short lifetime.

As with other new products, commercial acceptance of SC will depend not only on the technological advantages of the material, but to an equal or greater degree on the economics. The inherent and potential economic advantages of SC are determined chiefly by:

1. The relative cost and availability of portland cement and sulfur.
2. The importance of the improved properties of SC in any particular situation.
3. Whether SC can permit the use of locally available aggregate which for some reason is unsuitable for PCC.

The improved performance of SC over PCC is of importance not only in the applications such as corrosive industrial situations, but also in certain regular construction applications. In some areas of the world, the mineral aggregates available locally do not produce a PCC capable of withstanding the climate conditions. However, those aggregates may be used in SC to give durable building materials. Examples of this aspect of the use of sulfur concretes are sulfur concrete block projects developed by Ortega (32) and Terrel (33).

Ortega (32). Under the sponsorship of the United Nations Mission on Housing, Building and Planning to the United Arab Emirates, Alvaro Ortega participated in a three-year project to evaluate the suitability of sulfur concretes in these countries.

In addition to the advantages mentioned earlier, SC has other characteristics that favor its use under the prevailing conditions in the Emirates.

1. Unlike portland cement, sulfur can be stored in the open for indefinite periods without deterioration.
2. SC can be recycled by remelting, with only minor input of energy.
3. SC mixing, and casting techniques are suitable for self-help construction.
4. SC can be cast to produce building components with pre-

cise dimensions and sharp edges. This permits the manufacture of interlocking blocks that can be assembled without the use of mortar or special skills. The smooth, nonabsorbing surfaces of the blocks are essentially maintenance-free and eliminate the need for plastering or painting the interior or exterior surfaces.

The concept of interlocking SC blocks was originally developed at McGill University as part of the "Ecol Operation". The blocks used in the Emirates were based on a sand-cement block designed by Professor Bruce Etherington for use in the Philippines and adapted to SC by Bernard Lefebvre.

The molds for casting the blocks are made of 6mm thick steel plates, and designed to produce blocks of 40 cm X 20 cm X 20 cm, weighing 20 kg. Other steel molds were used to produce 20 cm X 20 cm interlocking paving blocks weighing 8 kg for patios, sidewalks, and driveways. This design was developed by the UN "Project Experimental de Vivienda" in Lima, Peru, in 1970.

To prepare the SC mix, sulfur was heated in a one-bag capacity concrete mixer fitted with two 3,000 BTU propane burners. Two percent by weight of dicyclopentadiene (DCPD) was added to the sulfur, followed by the aggregate, which was 75% of the SC. The mixing temperature was kept in the range 130-150°C. Unmolding can be done approximately ten minutes after pouring, but the blocks are then still fragile and should be handled with care. Full strength is reached in about one hour, and the block is then ready for use.

Because of the short curing time, only a small number of molds are needed. Continuous production can be achieved with four molds. The pouring takes about two minutes, and by the time the last mold is poured, the first is ready to be disassembled and refilled. Any broken blocks are remelted and recycled.

The SC technology was demonstrated by constructing an addition to an existing office building in Dubai, U.A.E. The SC interlocking blocks were laid on a foundation of reinforced concrete. The first course of blocks was laid on cement mortar to make sure it was level. Once this mortar was set, the remaining 450 interlocking mortarless blocks were laid in 15 man-hours, using unskilled workers. The resulting walls which have good thermal insulation properties, are water-proof and need no mortar, plastering or painting. The blocks come out of the mold with a polished, marble-like surface. They do not absorb moisture, repel dirt, and are easily kept clean by washing. The need for regular maintenance is practically eliminated.

Terrel, et al (33,34,35). Another approach uses SC to fabricate various block shapes and is aimed at a variety of uses particularly suited for the Middle East. Until recently, all attempts to develop a cold, press-mold sulfur-based technology have been unsuccessful. However, this barrier appears to have been broken with the promising technology being developed at the University of Washington, Seattle. Through careful formulation,

Terrel has been able to produce a sulfur-based composition which can be press-molded under those conditions currently used for portland cement concrete block. The aggregate and dry sulfur along with a small amount of water and binding agent are placed in the mold and press-molded at room temperature. The product has sufficient cohesion that it can be immediately demolded and handled. Heating the product in an oven melts the sulfur to permanently bind the material and the cooled product is a strong, homogeneous well-shaped block.

Preliminary testing has shown these blocks to have strength and durability properties equal to or better than portland cement block standards. The viability of the process has been demonstrated on a small scale and mix designs and process conditions have been optimized. Ongoing work will involve scaled-up production along with extensive product testing.

The major markets for this technology are expected to be those developing countries, such as Mexico, Venezuela and the Middle East, which have traditionally used much block construction. There should be a ready market for sulfur blocks in these countries because many suffer from shortages of conventional block raw materials but have large supplies of sulfur.

U.S. Bureau of Mines (36,37). The industrial use of sulfur concretes in corrosive environments has been pioneered by the U.S. Bureau of Mines. In cooperation with metal smelting and fertilizer industries USBM has installed test sections of SC in several locations where PCC deteriorates in a matter of a few months.

The inherent flammability and low melting point of sulfur impose some limitations of SC use. Flammability can be controlled to some extent by the use of additives, and it is fortunate that the DCPD types of additives used to improve the durability of SC also impart a degree of fire resistance. Sulfur concretes are in any case considerably less of a fire hazard than wood. Because of the low thermal conductivity, heat penetration is slow, and SC can survive short exposures to fire without serious damage. Sulfur concretes do not support combustion, and flame spread is essentially zero.

The low melting point of sulfur limits the use of SC in applications where loss of structural strength in event of a fire could be catastrophic. Thus, high-rise buildings intended for human occupation will probably not use SC for load-bearing structures. However, the properties of SC appear to make it fully acceptable for single-story dwellings, as well as for utility buildings and a wide range of pre-fabricated structures.

A major application now under very active research is the use of SC as a road paving material. This technology is considerably different from the use of sulfur as a potential substitute for asphalt which was discussed earlier. Paving with SC can be regarded as a total substitution of sulfur for asphalt, or as an

alternative to PCC paving. In any case, SC may provide a high quality paving material without the use of petroleum-based asphalt. It also attains full strength in a matter of hours rather than the days or weeks needed with PCC.

Preliminary road trials with SC paving have taken place in Canada and the U.S. In Canada, Sulphur Innovations Lts., carried out paving tests with Sulfurcrete (15), and in the U.S. the Southwest Research Institute has done research and development work on Sulphlex paving under contract to the Federal Highway Administration (15, 38, 39).

Using SC as a road repair material may be attractive in many situations. In this application the advantages of short cure time and high strength may be enough to offset any additional cost of the material.

Sulphurcrete (18). Sulphur Innovations Ltd. (S.I.L.) of Calgary, Alberta, has developed and produced considerable tonnage of SC under the tradename SULPHURCRETE. S.I.L. technology is based on work originally carried out at the National Research Council of Canada on the durability of SC which showed that an unsaturated resinous hydrocarbon polymer (CTLA) was effective in improving the freeze-thaw durability of sulfur composites. In a joint project with SUDIC, the physical properties of these materials were characterized, mix designs refined, and durability studies initiated.

A patented process involves pre-reacting the hydrocarbon plasticizer with a small amount of molten sulfur at the manufacturing plant to form a concentrate which is shipped to the work site. At the site it is mixed with the heated aggregate and additional sulfur to reach the desired binder level; fine filler is added, if necessary, and the molten mass is mixed and ready for casting. The concentrate process avoids reacting all of the sulfur with the plasticizer, thus minimizing the reactor size that is needed, but pre-reaction of the plasticizer under controlled conditions prior to the concrete manufacturing step is still required.

S.I.L. uses standard concrete transit mixer trucks modified to provide gas or propane heat to the mix drum to prepare mixes for both precast and poured-in-place work. Since 1977 several poured-in-place field trials have been completed and numerous projects in the Calgary area have now been constructed. Precast products that have been marketed include parking curbs, pipeline weights, sewer pipe, median barriers, and sidewalk slabs.

In most cases the material is performing well and has shown to be much more resistant to salt and acid attack than regular concrete. The material still suffers from brittle failure at the ultimate stress, thus requiring different design considerations.

SUDICRETE (40). All sulfur concrete technologies involve an additive or modifier to increase durability by reducing the pro-

ducts susceptibility to thermal and mechanical shock. In general these additives react with and plasticize the sulfur. This temporarily increases the strain capacity of the sulfur binder so the product is capable of absorbing the otherwise potentially damaging shocks. However, chemical plasticization of sulfur reverses with time, with the result that the material loses its strain capacity and embrittles.

SUDICRETE, the trade name of a new material developed by the Sulphur Development Institute of Canada (SUDIC) possesses two important properties that are not found in other sulfur concretes:

1. The SUDICRETE additive modifies the whole concrete system, not just the sulfur binder, so the effect of the SUDICRETE additive is permanent and does not show the embrittling effects observed in other modifier technologies.
2. Because the effect of the SUDICRETE additive increases with concentration, SUDICRETE can be formulated with a very wide range of strength/flexibility combinations. Depending on the formulation, SUDICRETE products can possess the rigid high compressive strength characteristics of portland cement concrete or the semi-flexible lower strength properties of asphalt concrete. Cost differential over the whole range of formulations is small.

SC manufacture using the SUDIC technology is simple, and existing conventional equipment can be used with few, if any, modifications. The preferred method of manufacture involves mixing molten sulfur with preheated graded aggregates, fine filler and the proprietary additive at temperatures typically in the 125-150°C range; no prereaction of the sulfur and additive is necessary. Conventional asphalt plants are ideally suited to this technique. Alternatively, solid sulfur, fine filler and additive may be mixed with super-heated aggregate 190-220°C, in any suitable mixing unit. Mixing time can vary from 45 seconds to 3 minutes, depending on mixer efficiency.

Once mixed, the material can be handled using any equipment suitable for asphalt mixtures. As consistency can be varied from the equivalent of zero slump concrete to that of a sloppy mortar, the molten mix can be used for precast, slip-formed, extended or poured-in-place applications.

In addition to features similar to those for conventional materials, SUDICRETE products are remeltable without degradation or change in properties and thus waste and unused materials can be recycled by crushing and feeding back to the mix cycle.

A wide range of applications for sulfur concrete such as SUDICRETE provide many advantages. Included are industrial flooring, electrolytic vats, sumps, catch basins, tanks, sewage and waste impoundment ponds, bridge decks, pipes, etc., all of which can benefit from its extreme corrosion resistance. Rapid

**American Chemical
Society Library
1155 16th St., N.W.
Washington, D.C. 20036**

In Sulfur: New Sources and Uses; Raymont, M.;

ACS Symposium Series; American Chemical Society: Washington, DC, 1982.

repair of floors, roads, airstrips, and others can be made with out-of-service time kept to a minimum.

Semi-flexible SUDICRETE formulations have strong potential for road paving applications. Though still in the development phase, the materials have shown very high resistance to fatigue damage.

Sulphlex (15,38,39). Under a contract with the Federal Highway Administration (FHWA), the Southwest Research Institute (SWRI) has developed a series of plasticized sulfur binders referred to as Sulphlex binders. These binders are basically a range of materials that have been formulated to give engineering properties ranging from asphalt to portland cement. They are composed of 60-80 percent by weight of elemental sulfur and 40-20 percent of a mixture of plasticizers. The plasticizers currently used are derived from petroleum, but future formulations may be derived from coal, agricultural wastes, or other materials. Typical compositions of these binders are shown in Table 9.

Table 9. Compositions of Sulphlex Binders

	Binder No.		
	126	230	233
Sulfur	61%	70%	70%
Cyclodiene concentrate	13%	15%	12%
Dipentene	-	15%	10%
Vinyl toluene	13%	-	8%
Coal tar	13%	-	-

The engineering properties of Sulphlex binders when combined with mineral aggregates are similar to those for paving materials. As such, the principal application may be in pavements, either semi-flexible or rigid, depending on the formulation used.

FHWA has given considerable push to further development of Sulphlex by sponsoring a relatively large research effort as well as demonstration projects throughout the U.S.

Conclusions

In the previous pages, the author has attempted to outline the emerging technologies for construction products that are coupled with new sources of sulfur throughout the world. The Middle East is a particularly good candidate for implementation of this technology. Large quantities of sulfur are rapidly becoming available, while at the same time traditional construction materials such as asphalt cement and portland cement are continuing to be in short supply. In addition, many Arabian Gulf

countries, for example, have very poor aggregates and many of the sulfur technologies can alleviate this problem by utilizing materials unsuitable for conventional construction methodologies.

The rapid development of housing, roads, and airports will continue to require large quantities of construction materials. In housing, for example, masonry type of construction is traditional and the sulfur concrete developments lend themselves well to meeting the local needs. The problems in asphalt pavements associated with high temperatures may be overcome by the use of SEA or SC pavements.

In conclusion, it would appear that sulfur construction materials technology developed largely in North America and is ideally suited for rapid implementation in the Middle Eastern construction industry.

Literature Cited

1. Muir, D. R.; Proc. Int. Conf. on Sulphur in Const., 1978, 2.
2. Loose, Michael K. CEMP Report No.600-80-5. Dept. Civil Engr., Univ. Wash. 1980.
3. Chalmers, William W. Conf. of Am. Paper Inst. 1979.
4. Al-Mana, Saleh A. CEMP Report No.600-80-4. Dept. Civil Engr., Univ. Wash. 1980.
5. Anon. The Oil and Gas J. 1978, 76, 122.
6. Anon. The Oil and Gas J. 1979, 77, 63.
7. Terrel, R. L.; Epps, J. A.; Al-Otaishan, A. T. "Utilization of Sulphur in Pavements", Dept. Civil Engr., Univ. Wash., Seattle, 1978, 4.
8. Kingdom Saudi Arabia, Cent. Planning Organ., "Dev. Plan, 1975".
9. Ministry Petrol. Min. Res., Petroleum Statis. Bul., Saudi Arabia.
10. Saudi Arab. Monetary Agency. "Annual Rep. 1399, (1979)", Research and Statis. Dept.
11. Al-Turki, A.; McCullough, J. Proc. IAHS Int. Conf. 1978, 2, 594.
12. Shilstone Test Lab., Inc., "Rep. Conc. Mix Studies for Coll. Petrol. and Min., Saudi Arab.", Houston, 1967.
13. Anon. "New Markets for Tommorrow's Sulfur", 1978.
14. West, J. R., ed. "New Uses of Sulfur", Advances in Chemistry Series 140, Am. Chem. Soc., Wash. D.C. 1975.
15. Sulphur Research and Development, Sulphur Inst., 1978, 1, 2; 1979, 2; 1980, 3.
16. Rennie, W. J., "Sulphur Asphalts", SUDIC New Uses of Sulphur, 1977, 2.
17. Rennie, W. J., "Sulphur Asphalts: The Pronk S/A Emulsion Binder System", SUDIC, New Uses for Sulphur, 1978, 3.
18. Raymont, M. E. D., "Sulphur Concretes and Coatings", SUDIC, New Uses for Sulphur, 1979, 3.
19. Bencowitz, I., and Boe, E. Proceedings, Amer. Soc. Test. and Materials, 1938, 38, 2, 539.

20. Kennepohl, G. J.; Miller, L. J. New Uses of Sulphur - II, Advances in Chem. Series 165, Am. Chem. Soc., Wash. D.C.
21. Kennepohl, G. J.; Logan, A.; Bean, D. C. Proceedings, Assoc. Asphalt Paving Tech., 1975, 44.
22. Akili, W., "Preliminary Investigation of Sulphur-Asphalt Mixtures Using Local Materials", Research Inst., Univ. Pet. and Min., Saudi Arabia, 1979.
23. Akili, W.; Sayyari, A. "Sulphur/Asphalt for Pavements in Saudi Arabia", unpub., Pres. at Int. Road Fed. Conf. 1980.
24. Pronk, F. E.; Soderberg, A. F.; Frizzell, R. T. Proceedings, Can. Tech. Asph. Assoc., 1975.
25. Samarai, M. A. Proc. Int. Conf. on Sulphur in Construction, Ottawa, Can., 1978, 2.
26. Deme, I. Proc. Assoc. Asph. Paving Tech., 1974, 43.
27. Burgess, R.; Deme, I. New Uses of Sulphur, Amer. Chem. Soc. Adv. in Chemistry Series 140, 1975.
28. Anon., Sulphur Research and Dev., Sulphur Inst., 1978, 1.
29. Saylak, D.; Gallaway, B. M.; Epps, J. A.; Ahmad, H. ASCE Transp. Engr. J., 1975, 101, 97.
30. Sullivan, T. A.; McBee, W. C.; Rasmussen, K. L. "Studies of Sand-Sulfur-Asphalt Paving Materials", U.S. Bur. Mines, Rep. Inv., 1975, 8087.
31. Garrigues, C.; Vincent, P. New Uses of Sulphur, Amer. Chem. Soc., Adv. in Chemistry Series 140, 1975.
32. Ortega, Alvaro, Sulphur Research and Dev., Sulphur Inst., 1979, 2.
33. Terrel, Ronald L.; Babaei, Khossrow. Proc. Int. Conf. on Sulphur in Const., Ottawa, Can., 1978, 2.
34. Ehsani, C. S. "Evaluation of Physical Properties of Sulfur-Concrete Blocks", MSCE thesis, Univ. Wash., Seattle, 1979.
35. Babaei, K. "Fabrication and Evaluation of Physical Properties of Mortarless Sulphur-Concrete Units", MSCE thesis, Univ. Wash., Seattle, 1979.
36. Anon. "BuMines Develops Improved Sulphur Concretes", Sulphur Inst. J., 1976, 12, 6.
37. Sullivan, T. A.; McBee, W. C.; Blue, D. D. New Uses of Sulphur, Amer. Chem. Soc., Advances in Chem, Series 140, 1975.
38. "Sulphur May Pave Way for Yellow Brick Road", Chemical Week 1979, 125, 18.
39. Sulphur Paving Material Begins Road Test. Chem and Engr. News, 1979, 57, 30.
40. Sulphur Development Institute of Canada, "SUDICRETE: A Versatile New Sulphur Concrete", Brochure, 1980.

RECEIVED October 5, 1981.

INDEX

A

- Absorption, selective, in sweetening process 42-43
 AC (*see* Asphalt cement)
 Acid gas
 enrichment 60
 high CO₂ 59-60
 removal followed by Claus 59
 removal systems 28-29
 separated, sulfur processes 61*f*
 streams, Claus processing 57-68
 Acid rain, effects 50
 Acid, smelter 8-9
 Active site in alumina catalyst 46
 Additives in sulfur concrete 243
 Aggregate
 blends from Beiseker Pit 148*t*
 blends, gradation curves 148, 149*f*
 gradation chart 202*f*
 gradation, sulfur concrete 200
 source, dune sand 236
 Agriculture, sulfur 135
 Air monitoring stations, syncrude's
 ambient 80, 81*f*
 Air void content, SAS mixtures 160, 164
 Alberta
 Clean Air regulations 69
 environment regulations 79
 oil sands deposits, location 71*f*
 Alloy materials development 41
 Alumina catalyst, active site 46
 Alumite 104
 Ambient concentrations
 H₂S 80*t*
 SO₂ 80*t*
 Amine(s)
 -based processes 28-29
 rate of H₂S and CO₂ reaction 43
 sweetening solution 42
 Ammonia 62, 66
 Ammonium sulfate formation 66
 Applications, Sudicrete 247
 Aramco facilities 231
 Arizona copper mines 103
 Asarco demonstration project 196*t*, 197-206
 Asphalt
 concrete paving mixes 129
 extenders and replacements 210
 pavement, recycled, using S/A
 emulsion binder 182

- Asphalt (*continued*)
 pavement use in Middle East 241
 paving mixes, sulfur-extended 128-130
 -sulfur paving materials 155-193,
 237-238
 viscosity-temperature properties 168
 Asphalt cement (AC) 128
 immersion-compression data 216-218
 Marshall design parameters 215*t*
 Sulphlex-233 binder comparison 212,
 213*t*, 214*t*
 for road building in Saudi
 Arabia 233, 234*t*
 Asphaltic concretes, relationship
 between air voids content and
 permeability 160, 163*f*
 Athabasca deposit, geological
 stratification 70, 72*f*, 78*f*

B

- Barrels/day of fuel-oil equivalent
 (BPDFOE) 22
 Beavon Sulfur Removal (BSR) 51, 62,
 63*f*, 64*f*, 67
 Beiseker pit, blends of aggregate 148*t*
 Binder(s)
 content
 equivalent SEA, calculation 177, 178
 variation on performance 221
 vs. strength 150*t*
 polymerization 142, 143*f*
 properties, comparison 213*t*, 214*t*
 SEA, use 167
 Sulphlex
 compositions 248*t*
 construction operation 218-223
 development 210-212
 transportation 219, 221
 Bitumen 69, 73
 upgrading processes comparison 79*t*
 upgrading schematic 74*f*
 Bituminous paving composition 240
 Blockage of condenser tubes and
 sulfur piping 66
 Blocks, molded sulfur 134
 Blocks, sulfur-based 244, 245
 Bond behavior, sulfur
 concrete 145, 146*f*, 147*f*
 BPDFOE (*see* Barrels/day of fuel-oil
 equivalent)

- Demonstration project, Asarco 197
 Deposition of sulfur40-41
 Desulfurization
 direct, of gas58-59
 distillate oil 5
 gas-phase 27
 processes, tail-gas50-51
 Diabase aggregate216-218
 Dicyclopentadiene (DCPD) 200
 Dicyclopentadiene polymerized
 sulfur142, 143f
 Dipentene (DP) 243
 Direct
 desulfurization of gas58-59
 liquefaction14, 87
 liquefaction, coal gasification93, 94f
 oxidation processes27, 28
 substitution173, 176f
 Distillate oil desulfurization 5
 Dune sand sieve analysis 236
 Durability of sulfur concrete138, 246
 Duval Corporation, Tucson 102
 Duval's CLEAR process 103
- E**
- Economics of sulfur concrete vs.
 portland cement 206
 Efficiency, Claus reactions50-51
 Electric utilities 9, 12t
 Elemental sulfur 52
 markets 11
 quantities produced 97
 Emission
 levels 51
 monitoring 79
 during SAS field trials 187
 H₂S 221
 SO₂ 221
 compositions of sulfur, SNEA
 process 239
- Energy
 conversion facilities problems32-33
 conversion processing conditions
 of sulfur25, 26
 sources, new, from sulfur recovery 21-35
 sources, new, sulfur supply and
 demand109-125
 Environment49-50, 52
 Environmental regulations22, 67, 79
 Environmental and safety impact,
 sulfur use in highway paving
 mixtures187-190
- F**
- Fatigue life, sand-asphalt-sulfur
 mixtures164, 165f
 Fatigue of sulfur concrete 145
 Federal Highway Administration
 (FHWA)210, 223
- Feedstock
 occurrence of, sulfur23-24
 shale composition 95
 variability 32
 Ferric chloride 102
 β -Ferric hydroxide 104
 Fertilization with sulfur 135
 Fertilizer industry 112
 Fertilizer manufacture 225
 Field construction of SEA mixes178-186
 Field Evaluation Document 189
 Field trials of sulfur concretes 151
 Fischer-Tropsch technology 87
 Flexible pavement application
 formulation 241
 Flexicoking 76
 Flooding rainfall intensity 186
 Floor section after screeding 204
 Flooring in corrosive environments,
 relative costs 133t
 Flotation process104-105
 Flue gas desulfurization1, 9, 11, 118t
 Foamed sulfur 237
 France, sour gas development 38
 Frasch sulfur2-4, 114, 118t
 Iraq 229
 major producers 123
 production costs121, 123
 U.S.123, 124f, 125f
 Front end reaction furnace43-45
 Fuel(s)
 consumption, asphalt paving mixes 129
 cost increase11-12
 development, alternative 12
 synthetic
 availability 98t
 use in sulfur production 98t
 use in United States97-98
 Fuller curves148, 149f, 150
- G**
- Galena 102
 Gas chromatography, use 45
 Gas
 direct desulfurization58-59
 plants, Shedgum 231
 streams, acid, Claus processing57-68
 streams, sulfur removal27-30
 Gases stripped from process water66, 67
 Gasification, Lurgi 97
 Gasification processes 25
 Gasifier products 58
 Geographic location, natural gas
 sources 7
 Geological stratification of Athabasca
 deposit70, 72f
 Gulf Canada Limited process, SEA .. 238
 Gulf portable sulfur-asphalt module .. 180f

H	
H ₂ S (see Hydrogen sulfide)	
Handling characteristics	52
Hastelloy G	41
H-Coal process	93, 94f
Heat balance technique	30
Heat soak technique	47
Heated dump bodied trucks	164, 166f
Heavy crude oils	16
Heavy oil	15-16
Hematite	104
Highway construction using Sulphlex binders	218-223
Hydraulic block machine	134
Hydrocracking	76
Hydrogen polysulfide formation	40, 48
Hydrogen sulfide (H ₂ S)	
ambient concentrations	7, 26
-containing gases, sulfur production	37-56
emissions monitoring	188f, 221
hydrolysis to COS and CS ₂	46
removal	28
-rich sour gas fields	39t
thermal decomposition	49
Hydrolysis	
of COS to H ₂ S	46
of CS ₂ to H ₂ S	46
systems, COS	34
Hydrometallurgical processing of sulfide materials, sulfur	101-108
Hydrotreated shale oil	96-97
Hydrotreated shale oil plant, Colony ..	96f
I	
Immersion-compression test	216, 217t
Incoloy 825	41
Indirect liquefaction	87, 89-93
Industrial application of sulfur concrete	195-208
Inhibitors use	42
Inorganic sulfur feedstock	23
Installations, sulfur concrete	197
Interlocking sulfur concrete blocks ..	244
Iraq Frasch sulfur operations	229
Iron pyrite (FeS ₂)	23
Iron sulfide (FeS)	23
Iron sulfide stability	23
K	
Kenedy County construction report	158
Kerogen	89
L	
Lead sulfide (PbS)	102
Lead via hydrometallurgical process ..	102
Lingen plant, West Germany	62
Liquefaction	
direct	14, 87
direct, coal gasification	93, 94f
indirect	87, 91f
indirect, coal gasification	89-93
processes, single-stage	25
technology, indirect vs. direct	88f
Liquid sulfur product temperature, control	46
Location of Alberta oil sands deposit	71f
Locations for coal conversion	13
Location of H ₂ S-rich sour gas fields ..	39
Long bypass scheme	59
Lurgi gasification	97
Lurgi Rectisol process	90
M	
Marshall	
binder contents, optimum	216t
design parameters comparison	215t
Method	160, 162f
MDEA (see Methyl-diethanolamine)	
Mechanisms of sulfur-forming processes	53t
Melting point of sulfur	207, 245
Methane	52, 87
Methyl-diethanolamine solutions (MDEA)	43
Mexico sulfur demand outlook	121, 122t
Mexico sulfur production	119, 122t
Middle East	
construction material demand	236
potential for new sulfur products	225-250
sulfur asphalt pavements use	241
sulfur production	229, 230t
Mineral constituents, shale oil	95t
Mineral matter characteristics, sulfur in feedstock	24-25
MITRE synfuels scenario	98
Mix design	221, 241
Gulf Canada Limited	238
methods for SAS mixtures	158
methods for sulfur-extended asphalt mixtures	173
sulfur concrete	145-151
Mixer heat-transfer method	184
Molybdenite	105
Monitoring, emission	79
N	
Naphtha removal	73
National Petroleum Council (NPC)	5, 6t
Natural gas	
demand	100
processing	5-8

- Natural gas (*continued*)
 sour114-116
 forecast sulfur production 7*t*
 and refineries 4
 sources, geographic location 7
 Nitrogen oxide formation 66
 North American
 sulfur prices123, 125*f*
 demand outlook 120
 supply/demand summary121, 122*t*
 supply outlook 114-119
 NPC (*see* National Petroleum Council)
- O**
- OGFC (*see* Open graded friction courses)
- Oil
 desulfurization capacity 5
 heavy crude15-16
 import price figures per barrel 97
 sands deposit, Athabasca 70
 sands, sulfur recovery69-82
 shale13-14
 composition 95*t*
 organic material 89
 Olefin reaction with SO₂ 59
 OPEC, construction activity 232
 Open graded friction courses (OGFC) 182
 Optimum sulfur recovery efficiency 45
 Organic sulfur, feedstock 23
 Organic sulfur, temperature dependence 24
 Organosilozane polymers 239
 Ortega, Alvaro243, 244
 Orthorhombic sulfur, use as binder 142
 Output capacity, Frasch sulfur 2
 Overthrust Belt7, 116
 Oxidation processes, direct27, 28
- P**
- PAD (*see* Petroleum Administration for Defense districts)
- Paraffin hydrocarbons 62
 Paraffinic feeds 24
 Particle size, sulfur 239
 Patchmobile 197
 Pavement
 construction, Sulphlex binders
 use218-223
 flexible, application formulation 241
 performance129-130
 Paving
 materials, sulfur-asphalt238-248
 mixes, SEA128-130
 technology, sulfur-asphalt155-193
 trials, Shell Canada156-157
 Percent sulfur recovery, Selectox
 process 67
 Permeability to moisture, sulfur
 concretes 139
 Permeability test results for limestone
 SEA mixes 186*t*
 Petroleum refining114-116
 Petroleum Administration for Defense
 districts 2
 Phosphates 112
 Plasticization, chemical 132
 Plasticization of sulfur 247
 Polish Air Prills53-54
 Polymerization of binder142, 143*f*
 Polysulfide equilibrium 40
 Polythio S₈ chain 48
 Portland cement (PC)
 concrete(s)131, 133*t*, 138
 at Corpus Christi 197
 fatigue 145
 vs. sulfur concrete, economics 206
 production, Saudi Arabia 233
 with acid-resistant coating 133*t*
 Potassium jarosite 104
 Preblending concepts 178
 Preblending method, schematic mixing
 station for preparing SEA
 mixes175*f*-176*f*
 Premium products53-54
 Price
 figures per barrel, oil import 97
 North America, sulfur123, 125*f*
 outlook121, 123
 Problems in energy conversion
 facilities32, 33
 Process combinations60, 62
 Processes, comparison of bitumen
 upgrading 79*t*
 Processing conditions, sulfur in energy
 conversion25, 26
 Processing, natural gas 5-8
 Proctor GX granules53-54
 Product(s) 52
 gasifier 58
 opportunities for sulfur127-136
 specifications, Canadian industry .. 53
 upgrading, sulfur compounds26, 27
 Production42-49
 asphalt in Saudi Arabia 234*t*
 costs, Frasch 121, 123
 refinery sulfur 4-5
 sulfur225, 232
 Pronk additive 239
 Pronk static in-line static mixer 181*f*
 Prussian blue formation 32
 Purification of gases 90
 Pyrite 105
 sulfur 23
 use 110
 Pyrolysis processes 25
 Pyrolysis retort, TOSCO II93, 95

R	
Rate of H ₂ S and CO ₂ reactions with amines	43
Reaction furnace, front end	43-45
Recovery	
capacity, refinery sulfur	5, 6 <i>t</i>
efficiency, optimum sulfur	45
hydrogen and sulfur from H ₂ S	49
SO ₂	10 <i>t</i>
Recovery systems, sulfur	21-35
Redox reaction of H ₂ S with SO ₂	48
Reductive tail-gas treatments	51-52
Refineries and sour natural gas	4
Refinery	
operating scenarios	114
sulfur production	4-5, 115 <i>f</i>
sulfur recovery capacity	5, 6 <i>t</i>
Regeneration of sulfated catalyst	47
Regenerative burn-off	47
Rehabilitation of electrolytic zinc	
cellhouse basement floor	197-206
Removal, sulfur from gas streams	27-30
Retorting of shale	93-97
Richard Process	47-49
Road building in Saudi Arabia, asphalt	
cement use	233, 234 <i>t</i>
Road construction using sulfur	209-224
Road network in Saudi Arabia	235 <i>t</i>
Road patching mixes, SAS	130-131
Road paving trials in Middle East, sulfur-asphalt	240 <i>t</i>
Road paving material, sulfur	
concrete use	245
S	
S/A (sulfur asphalt) emulsions	239
SAS (<i>see</i> Sand-asphalt-sulfur)	
SO ₂ (<i>see</i> Sulfur dioxide)	
Safety and environmental impact, sulfur use in highway paving	
mixture	187-190
Sand-asphalt-sulfur (SAS)	156-167
coefficient of permeability as a function of air voids	
content	160, 163 <i>f</i>
development in United States	158
matrix, photomicrograph	161 <i>f</i>
mix, fatigue life as a function of sulfur content	165 <i>f</i>
mixes, Bureau of Mines studies	158
mixes, Marshall Stability as function of sulfur and asphalt contents	160, 162 <i>f</i>
mixtures	
coefficients of permeability	164
preparation and mix design	
methods	158-164
Sand-asphalt-sulfur (<i>continued</i>)	
relationship between sulfur content and fatigue life	164
paving materials, field studies	158
paving mixtures, heated dump	
body truck	166 <i>f</i>
paving trials, number	167 <i>t</i>
road patching mixes	130-131
status, summary	164
SASOL, sulfur distribution from coal conversion plant	90
Saudi Arabia	
asphalt cement use for road	
building	233, 234 <i>t</i>
cement supply and demand	233, 235 <i>t</i>
construction expenditure	232
portland cement production	233
road network	235 <i>t</i>
sulfur by-product production	229, 231
sulfur capacity	230 <i>t</i>
Screed temperature control	157
Screeding, sulfur concrete floor	204, 205 <i>f</i>
SEA (<i>see</i> Sulfur-extended asphalt)	
Selectox process	62-67
Settling of sulfur from sulfur asphalt	
emulsion	169 <i>f</i>
Shale oil	13-14
composition	89, 95 <i>t</i>
plant, Colony hydrotreated	93, 96 <i>f</i>
production estimates	13
Shale retorting	93-97
Shedgum gas plant	231
Shell Canada Limited	240-241
Shell Canada paving trials	156, 157
Shell Claus Off-Gas Treatment (SCOT)	51
Shrinkage in sulfur concrete	206
Silica gravel	207
Sulfur Innovations Ltd. (S.I.L.)	246
Slated sulfur	52
Slump characteristics	156
Smelter acid	8-9
capacity	8
recovery	10 <i>t</i>
Smelting of metal sulfide	101
Smelting nonferrous metals	116
Societe Nationale Elf-Aquitaine (S.N.E.A.)	239-240
Sphalerite	102-103
Spectrophotometric detectors, use	45
Solid sulfur	52
Solid sulfur, new forms	52-53
Solvent-based processes	29
Solvent systems	41
Sour gas	52, 114-116
and refineries	4
development, France	38

Sour gas (*continued*)
 fields, H₂S-rich 39*t*
 production 37
 forecast sulfur production 7*t*
 U.S. Frasch vs. Canadian 123, 125*f*
 Sources of recovered sulfur from H₂S-
 containing natural gas 38, 39
 South Africa's coal gasification
 process 89–90
 Southwest Research Institute (SWRI) 211
 Static mixer, Pronk static in-line 181*f*
 Steam stripping 66
 Stress–strain behavior
 change with time 142, 143*f*, 144*f*
 mortar and concrete with varying
 percentages of additives 146*f*
 Sudicrete as function of age 147*f*
 sulfur concrete 140–144
 Stretford process 58
 Stripping, steam 66
 Substitution, direct 173
 Sudicrete 146*f*–147*f*, 151, 246–248
 Sulfate formation 23
 Sulfation reaction 47
 Sulfide(s) of calcium 25
 Sulfide materials, sulfur from hydro-
 metallurgical processing 101–108
 Sulfur
 in agriculture 135
 asphalt
 emulsion binder, properties of
 recycled asphalt pavement .. 182*t*
 emulsion, settling of sulfur 169*f*
 module (SAM), Gulf portable 180*f*
 pavements in Middle East use 240*t*, 241
 paving materials 237, 238–248
 paving technology 155–193
 ratio effects 168, 171*f*
 emulsifier, Texas Gulf portable .. 181*f*
 blocks, molded 134
 by-product production, Middle
 East 229, 230*t*
 capacity, Saudi Arabia 230*t*
 from coal-based synthetics 15*t*
 coatings 237
 commercial new uses 128–133
 compounds product upgrading 26, 27
 concrete(s) 106, 131, 133*t*, 237,
 241–248
 advantages 207
 aggregate gradation 200
 applications 132, 152, 247
 blocks, interlocking 244
 bond behavior 145, 146*f*, 147*f*
 compared with portland cement
 concrete 197, 199*f*
 corrosion test components in
 Asarco plants 196*t*

Sulfur (*continued*)
 concrete(s) (*continued*)
 DCPD additives 243
 DP additives 243
 durability 132, 138, 246
 economic advantages 243
 fatigue 145
 field trails 151
 floor after screeding 205*f*
 hot, transporting and pouring 203*f*
 industrial application 195–208
 limitations and projected
 future use 206
 mix design 145–151
 peak stress 142
 permeability to moisture 139
 potential and properties 137–154
 preparation 200, 201*f*
 resistance to corrosive materials 206
 shrinkage 206
 stress–strain behavior 140–144
 sump for installation in zinc
 electrolyte pumping circuit .. 198*f*
 tensile strength 243
 transport 200
 use as road paving material 245
 from various blends of aggregate
 vs. portland cement concrete,
 economics 206
 consumption in U.S. 83
 content(s)
 compaction temperature effect on
 SEA mixtures stability at
 different 172*f*
 for SAS mix, fatigue life as a
 function 165*f*
 in SEA binders, temperature-
 viscosity chart indicating
 influence 183*f*
 demand 84
 projected 99*f*
 U.S. forecast 84*t*
 elemental 52, 97, 210
 in energy conversion processing 25, 26
 –extended asphalt (SEA) 167–173,
 238–248
 binders 167–168, 171*f*,
 174*f*, 177, 182
 blends with different S/A ratios,
 relative sulfur settling 170*f*
 blends, dissolved and crystallized
 sulfur 169*f*
 concrete mixtures, determination
 of optimum binder concrete 178
 projected to year 2000 98, 99*f*
 outlook Canada 120, 122*t*
 outlook Mexico 121, 122*t*
 deposition 40–41

Sulfur (*continued*)

dicyclopentadiene polymerized	142, 143f
dioxide	
ambient concentrations	79, 80t
emission(s)	76, 77f, 78f, 79, 221
formation	50
recovery	10t
stack gas removal processes	9
disposition diagram	76
distribution	73-79, 90
Gulf Canada Limited process	238
justification test data	179f
mix(es)	
plant and construction site, H ₂ S	
emissions	188f
field construction	178-186
permeability test results for	
limestone	186t
Preblending Method, schematic	
of mixing station	175f-176f
preparation and mix design	
methods	173-187
open graded friction courses	
(OGFC)	182-184
paving mixes	128-130
paving projects, number	186t
status, summary	186
in feedstock, mineral matter	
characteristics	24-25
in feedstock occurrence	23-24
foamed	237
forming processes, mechanisms	53t
Frasch	2-4
from hydrometallurgical processing	
of sulfide materials	101-108
imports in 1979	3
impregnation	237
industry, potential impact of	
synthetic fuels	83-100
Innovations Ltd. (S.I.L.)	246
liquid phase, Richard Process	48
markets	11, 85, 86f
melting point	207, 245
Middle East new uses	225-250
-modified paving materials, tempera-	
ture limit for continuous	
handling	189
new forms, solid	52-53
new product opportunities	127-136
North American prices	123, 125f
output	5, 97
oxidation catalyst	31
particle size	239
pavement material, ignition test	189
plant tail-gas treatment	31
price levels	227t, 229
processes for separated acid gas	61f
product(s)	237, 241
contamination	33

Sulfur (*continued*)

product(s) (<i>continued</i>)	
in Middle East, potential	225-250
temperature, control of liquid	46
production	225, 232
Canada	117-119, 122t
from coal conversion processes	14
from H ₂ S-containing gases	37-56
Mexico	119, 122t
Middle East	230t
potential	12t
refinery	4-5
from sour natural gas, forecast	7t
from synthetic fuel use	98t
in U.S., refinery	115f
world	111t
properties	245
recoverable world reserves	226, 227t
recovered as by-product	98, 99f
recovery	
capacity, refinery	5, 6t
from new energy sources	21-35
from oil sands	69-82
systems	30-31
recycling of old asphalt pavement,	
schematic of central plant	185f
removal from gas streams	27-30
road construction using	209-224
settling rate in SEA binder	168
slated	52
solid	52
solidification temperature	168
sources	
by-product	114-116
existing	2-9
future	9-16
in U.S.	1-19
supply and demand, world trend	109-127
technologies	128
U.S. Frasch	123, 124f
use(s)	
asphalt paving mixes	128-130
binder, orthorhombic	142
potential products	237
fertilization	135
highway paving mixture	187-190, 237
hydrometallurgical	105
sulfur concrete	131
value capacity projection	17t
Sulfurcrete	142, 151, 246
Sulfreen Process	50
Sulfuric acid	237
plant design	33
production	117
use	85
Sulphlex	105, 151, 248
binders	
comparison with asphalt	
cements	212-216

- Sulphlex (continued)**
 binders (continued)
 compositions 248*t*
 development 210–212
 pavement construction use 218–223
 problems in use 223
 transportation 219, 221
 formulations, compositions 211
 pavement 222*f*
 pavement construction, traffic
 volume 221
 use, future developments 223
- Sulphlex-233**
 binder, testing 212–214
 with diabase aggregate 216*t*
 Marshall design parameters 215*t*
 mixture properties 214–218
- Suncor Incorporated** 70
- Supply and demand in Saudi Arabia,**
 for cement 233, 235*t*
- Supply and demand summary, North**
 American 121, 122*t*
- Supply outlook, North American** 114–119
- Surface mining techniques** 73
- Surface tearing problem** 164
- Sweetening process, selective**
 absorption 42–43
- SWRI (see Southwest Research**
 Institute)
- Syncrude Canada Limited** 70
- Syncrude, ambient air monitoring**
 stations 80, 81*f*
- Syncrude, sulfur balance** 77*f*
- Synthetic fuels**
 availability 98*t*
 coal-based 14–15
 industry development 21, 33–34
 potential impact on sulfur
 industry 83–100
 scenario, MITRE 98
 technology 85–89
 U.S. use 97–98
- Synthetic natural gas (SNG)** 85–87, 91*f*
- Systems analysis** 31–32
- T**
- Tail-gas**
 desulfurization processes 50–51
 processing, Claus 67
 treatment
 Claus plant with BSR/Selectox .. 63*f*
 reductive 51–52
 sulfur plant 31
- Tar sands** 15–16
- Temperature**
 compaction 172*f*
 control of liquid sulfur product 46
 control, Screed 157
- Temperature (continued)**
 limit for handling of sulfur-modified
 paving materials 189
- Tensile strength, sulfur concrete** 243
- Terrel, Ronald** 244, 245
- Texas Air Control Board** 221
- Texas Gulf portable sulfur asphalt**
 emulsifier 181*f*
- Texas State Department of Highways**
 and Public Transportation
 (SDHPT) 221
- Texas Transportation Institute**
 (TTI) 158, 187
- Thermal decomposition of H₂S** 49
- Thermopatch, Thermopave** 156, 240
- Thin-film oven test (AASHTO**
 T-179) 212, 214*t*
- Thiosulfate formation** 58–59
- TOSCO II pyrolysis retort** 93, 95
- Transporting hot sulfur concrete** 203*f*
- TTI (see Texas Transportation**
 Institute)
- U**
- Unisulf process** 59
- United States**
 Bureau of Mines 144*f*, 245
 Frasch sulfur 123, 124*f*
 Frasch vs. Canadian sour gas 123, 125*f*
 resources of natural gas 7
 SAS development 158
 sulfur
 consumption 83
 demand forecast 84*t*, 120, 122*t*
 sources 1–19
 supply outlook 114–117, 118*t*
 synthetic fuel use 97, 98
- University of Calgary** 142, 143*f*,
 145, 146*f*
- Upgrading of sulfur compounds** 26
- Utilities, electric** 9
- W**
- Water**
 –gas shift reaction 59
 process, gases stripped 66–67
- West Germany, Lingen plant** 62
- World reserves, recoverable**
 sulfur 226, 227*t*
- World supply and demand outlook,**
 sulfur 110–112
- Z**
- Zinc**
 electrolyte pumping circuit 198*f*
 sulfide 103
 sulfate 103