

Review of Metals and Binary Oxides as Sorbents for Removing Sulfur from Coal-Derived Gases

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Effective methods for removing sulfur from hot, coal-derived gases are being developed for both coal gasification and coal combustion processes. A comprehensive literature review and analysis on this subject was carried out because there appears to be a lack of familiarity among recent investigators with work done prior to the 1980s and work done in other countries. Presented here is information on the historical background and properties of metals and binary oxide compounds. Included are sorbents that contain Ca, Fe, Zn, Cu, Ni, and Mn. The results of thermodynamic calculations and a review of mixed oxide compounds will be covered in future publications.

1. Introduction

THERE has been interest and active research on desulfurization of coal-derived combustible gases since they were first produced by coal carbonization more than a century ago. Approximately 19 metals and their compounds have been evaluated for their desulfurizing abilities, and the compounds of iron, zinc, and calcium have been studied almost continuously over this period. There has even been research done on eggshells^[1] and sugar^[2] as desulfurizing agents.

The published literature on sulfur sorbents is so extensive that both new and experienced investigators should profit from a comprehensive review of past work. It is clear from the bibliographies of some recent articles that the investigators were unaware of closely related research done many years ago or in other countries. During the past few years, Hederer^[3] and Newby^[4] have reviewed the need for sulfur sorbents to meet the requirements of developing technologies, such as fluidized bed coal combustion and the tie of coal gasification to combined cycle electric power generation. In both articles, it is stated that an efficiency gain can be obtained if satisfactory sulfur sorbents can be found with operating temperatures in the range of 500 to 800 °C. The approach taken here is to summarize the complete evolution of sulfur sorbent technology and to present the information by classes of sorbent materials. In collecting information on this subject, a computer search of *Chemical Abstracts* and of *Energy Research Abstracts* was conducted.

2. Historical Background

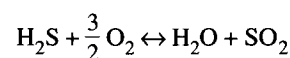
The earliest attempts to produce gaseous products from coal were made in Europe in the latter part of the 18th century.^[5] Minckelers, for example, showed in 1784 that coal dust could be converted into gas that was four times lighter than air, a result that led to the development of hot air balloons. In 1792, a Scottish engineer distilled coal in an iron retort and used the gas produced to light his home.^[6] Shortly thereafter, companies

were formed to distribute coal gas for lighting in London (1812) and in Baltimore (1816). It wasn't until the Bunsen burner was invented in 1855 that the use of coal gas became widespread. Most towns built their own plants, so the gas they distributed was commonly called "town gas."

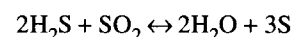
Even in these early days of coal carbonization and coal gasification, there was a requirement that sulfur be removed from the raw gas prior to distribution.^[7] The raw gas typically contained 0.7 to 1.0% H₂S and lesser amounts of other sulfur compounds. Regulations in most states in the United States required that the product gas contain less than 0.0005% H₂S. The reasons for purification were prevention of corrosion of piping and removal of the disagreeable odor caused by H₂S. Both then and now, the cost of gas cleanup was approximately half of the entire cost of producing gaseous fuel.

Calcium hydroxide was used as a sulfur sorbent in England as early as 1809, 2 years after the first use of gas for street lighting.^[8] A few years later, solid lime scrubbers were used. The disposal of spent lime was reported to be a problem because CO₂ from the air reacted with the spent lime and released H₂S. Partly for this reason, iron oxide purifiers were developed and patented in 1849. After this new technology was reduced to practice, a law was passed in England, called the "Sulfur Act of 1860" to set controls on the use of lime scrubbers. Thus, recyclability was the main reason iron oxide replaced lime as a sulfur sorbent. Hydrated Fe₂O₃ was the form of iron used. It reacted with H₂S in the raw gas and air injected into the reactor to form iron oxysulfide. The temperature of the reactor was controlled at 40 to 45 °C. During regeneration in air, care had to be taken to prevent the exothermic heat of reaction from fusing the contents of the reactor.

Claus and Hill began their pioneering work on recovery of sulfur as a by-product in 1880,^[8] and a description of Claus' kiln was published in 1909.^[9] The basic reactions in the Claus process are



and



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Thus, gaseous H_2S was converted to solid sulfur. To increase sulfur recovery, the kilns or reactors contained several stages for the second reaction. The incentive for developing the Claus process was that iron oxide purifiers required more ground area than was often available in the urban areas where the gas plants were constructed. The Claus process is still used today with nearly the same design features developed 100 years ago.

In the early 1900s, interest in fuel gas production extended from coal carbonization to complete conversion of coal to pipeline gas. In 1922, the first Winkler coal gasification plant was built.^[5] A Lurgi plant was built in 1931, followed by a Kopper Totsek plant in 1941. These plants never became replacements for the original town gas plants because the capital costs of the newer plants were very high and were too expensive for individual towns.

The other relevant topic whose history dates back to the 19th and early 20th century is the possible use of coal-derived gases in fuel cells.^[10] Papers and patents on this topic started appearing in 1855, and solid electrolytes of yttria and zirconia were studied by Nernst in 1899. The opinions of experts at the time were that the idea had merit, but slowness of electrode reactions was believed to be a major obstacle. No mention was made of the poisoning of electrode reactions by sulfur, but poisoning may have been one of the reasons for concern over electrode kinetics.

The pioneering work described above provided both the foundation and the stimulation for continuing research and development from the early 1900s to the present. Until recently, it was assumed that the fuel gas would be supplied at ambient temperature; consequently, hot desulfurization processes were studied only if there was an advantage in having the sorption reactions occur at high temperature. Interest in zinc oxide as a sorbent developed in the early 1900s in this manner.^[11] When added to sodium sulfite solutions and heated with steam, the zinc oxide was converted to zinc sulfite. Regeneration of the zinc oxide was accomplished by calcining to release sulfur as SO_2 . Interest in mixed oxides as sorbents developed in the same time period. Nachod^[12] obtained a patent in 1948 on the use of mixed oxides of copper, zinc, and lead as sulfur sorbents. Sorption occurred at temperatures up to 550 °C, and regeneration in air-steam mixtures was possible in the 370 to 540 °C temperature range. Another interesting activity during this period was research on promoters to improve the effectiveness of lime as a sorbent. Sodium chloride was studied as a promoter in 1943,^[8] and it was still being studied in 1988.^[13]

A number of other examples could be given of areas of desulfurization research initiated prior to 1950 that are still active today. Pioneering workers in this field deserve a great deal of credit because of the longevity of their contributions and because their accomplishments were made without computers, modern instrumentation, or the databases that are now available.

3. Present Technical and Economic Status

The events of the past 40 or 50 years in the development and commercialization of pipeline gaseous fuels from coal have been rather typical of new energy technologies. Improvements in the technology have been made steadily, but commercializa-

tion has been slow. Cost effectiveness has fluctuated between poor and good as the prices of conventional fuels, particularly oil, have fluctuated. For capital-intensive facilities like coal gasification plants, investors understandably have been reluctant to commit funds. Countries throughout the world have become more concerned about air quality and other environmental issues. The result is that engineers have additional requirements to meet, and cost effectiveness has become more difficult.

In 1988, it was reported that there were four large coal gasification plants in operation.^[14] None of the literature references found discussed coal gasification plants in China. However, it is known that thousands of small plants were built many years ago to produce ammonia for fertilizer by coal gasification. Some larger plants have been built in recent years as well.^[15] The plants described in Ref 14 were: the Synthese-Anlage Ruhr in Oberhausen, Germany; the Tennessee-Eastman plant; a lignite plant in North Dakota; and the Cool Water plant in California. The first two plants produce acetic acid and acetic anhydride, respectively. The last two were designed to produce fuel gas.

It is interesting to discuss details of the Cool Water plant in more detail. The gasification technology is from the well-established Texaco process, which is also used in the Synthese-Anlage Ruhr and Tennessee-Eastman plants. There are now three additional plants based on the Texaco process either in operation or under construction.^[16] The unique feature of the Cool Water plant is that it contains both a high-temperature gas turbine, driven by the combustion of fuel gas, and a lower temperature steam turbine. This so-called combined cycle plant has a 15% higher efficiency and comparable investment cost compared to a single-cycle plant. In the Cool Water plant, the fuel gas is cooled to ambient temperature, purified, then burned in the gas turbine. Desulfurization and sulfur recovery are accomplished with a combination of the Claus and other conventional processes.^[17] There is a consensus opinion that, if the fuel gas were desulfurized without cooling to ambient temperature, there would be major benefits in both process efficiency and capital cost.

Many companies and research organizations have now become interested in combined cycle technology and the related topic of high-temperature desulfurization processes. There is also considerable interest in the development of high-temperature fuel cells for electric power generation.^[18] The coal gas to be used in the fuel cells must be as clean or perhaps cleaner than that needed for gas turbines.

Gasification is not the only developing coal technology for which desulfurization at high temperature is important. Another example is fluidized bed coal combustion.^[19,20] Because of the variety of types of coal that can be burned, high thermal efficiency, and low emissions of sulfur and nitrogen oxides, use of fluidized bed combustion is becoming widespread for producing industrial process heat. For electric power generation, it is believed to have great potential, and the first large plants are in various stages of construction. Desulfurization is accomplished by charging lime or other calcium compounds into the combustion chamber. Even with older coal-fired boilers, lime or limestone injection into a hot part of the system is considered

a promising alternative to downstream scrubbing of the flue gas.^[4,21,22]

In the following sections, the literature is reviewed on various categories of sorbent materials individually.

4. Calcium Compounds

There has been more interest in calcium compounds as sulfur sorbents than any other class of materials, because they are inexpensive and because they are effective under both reducing and oxidizing conditions. CaS forms readily under reducing conditions, and CaSO₄ forms under oxidizing conditions. The principal limitations of Ca-base sorbents are that they react slowly at low temperatures, regeneration of spent sorbents is difficult, and there is a wide variability of properties of materials obtained from different sources.

As evidence of the high level of interest in calcium compounds, more than a thousand literature citations were found for the 1975 to 1990 time interval. Because it was not feasible to review all of these articles, it was decided to concentrate on citations from 1988 to 1990, which still amounted to more than 200 articles. The emphasis in these articles covered a wide spectrum from basic research on single particles to engineering evaluation of sorbents in commercial plants. Although CaO is a key constituent for sulfur uptake in steelmaking slags, there is another body of literature on this topic that will not be reviewed.

A good summary of the performance of Ca-base and other sorbents in commercial practice and large-scale tests is given by Newby.^[4] For sorbent injection into conventional furnaces, 50% of the sulfur can be removed, with the amount of sorbent used corresponding to Ca/S=2. For all other applications considered, which include various types of coal combustion and gasification, 90% of the sulfur can be removed with Ca/S loadings ranging from 1 to 4. In all of these tests, once-through use of the sorbents and no regeneration applies. Two specific examples of experience with retrofit sorbent injection into existing plants were mentioned earlier.^[20,21]

In both plant tests and in research, the advantages and disadvantages of using different calcium compounds have been studied. The compounds of greatest interest are limestone (CaCO₃), lime (CaO), calcium hydroxide [Ca(OH)₂], and dolomite (CaCO₃·MgCO₃). Schwarten *et al.*^[21] added CaCO₃ and Ca(OH)₂ to brown coal briquettes and found that Ca(OH)₂ was more effective in removing SO₂, but was more difficult to handle. Kübler and Gutberlet^[23] studied the use of dry sorbents in flue gas desulfurization and concluded that CaCO₃ is more economic than either CaO or Ca(OH)₂. Newton *et al.*^[24] reported that dolomite sorbents were better than calcite sorbents on an equivalent Ca basis. They and others found that little or none of the Mg in dolomite reacted with sulfur, for reasons that are not mentioned. They also found that hydrated sorbents, in general, were more reactive than carbonates. Another example of a study in which various calcium compounds were compared is research by Newby.^[25] The intended application is coal-fired turbine engines. The article was a progress report on continuing work, and no conclusions were drawn on a preferred sorbent. The available literature on this subject creates the impression

that the choice of a preferred sorbent should vary with the temperature of use and other systems parameters.

It should not be implied that in all systems sorption of sulfur is a better approach than recovery of sulfur by the Claus or another low-temperature process. There are abundant sources of limestone in many areas, which make it an attractive option. However, the high cost of transporting limestone to plant locations far removed from its sources could make it noncompetitive as a sulfur control material. Another factor is the market for elemental sulfur and sulfuric acid that is produced in sulfur recovery processes.

Turning now to developmental projects in which sulfur sorption is desired, calcium compounds are being evaluated in competition with and in conjunction with other types of sorbents. In adapting the Texaco gasification process to the requirements of combined-cycle electric power generation, consideration was given to adding limestone or dolomite to the coal-water slurries charged to the gasifier.^[16] This idea was later abandoned because it was thought that lime would react preferentially with silica in the coal slag. Now a combination of iron oxide and sodium carbonate is being considered instead.

In another project,^[26] sorbent technology is being developed for the Kellogg-Rust-Westinghouse (KRW) coal gasification process. The approach being taken is to remove most of the sulfur with limestone or dolomite and remove sulfur to the low ppm level with an external bed of zinc ferrite. The calcium compounds react in a fluidized bed at approximately 1400 K to form CaS, which combines with the ash. Test data show that 70 to 95% of the sulfur can be removed in this way.

In a third example, Gudenau *et al.*^[27] evaluated materials for use with the high-temperature Winkler (HTW) gasification process. A comparison was made between Ca(OH)₂ and ZnCO₃ for two types of coal in the 640 to 861 °C temperature range. For brown coal containing 0.94% S, more complete desulfurization was obtained with ZnCO₃. For another coal that contained 4.90% S, neither sorbent reduced the sulfur level to a sufficiently low value to meet the project objective.

The experience gained in the engineering evaluation and developmental activities just discussed leads to the conclusion that calcium compounds as sorbents perform quite well in general, but are marginal in some instances. To extend the possible range of applications and to obtain a better fundamental understanding of reaction rates, an extensive amount of bench-scale laboratory work has been done. By far, the majority of this research has been focused on the relationship between pore characteristics in the materials and reactivity. Recent research on this subject was undoubtedly stimulated by a classic paper published in 1970 by Borgwardt.^[28] Because the molar volume of CaSO₄ is much larger than that of CaO, the pores in calcined limestone become smaller as sulfidation proceeds, and the sulfidation rate decreases as a result. References 29 through 33 are examples of recent papers in which data are presented and analyzed with models that relate pore closure to reaction rates.

As an outgrowth of this extensive knowledge of pore closure behavior, it is encouraging to see attempts made to take advantage of this knowledge for improving sorption processes. An example is the research of Anderson *et al.*^[34] Their approach is to expose limestone and dolomite particles to sulfur-bearing gases for very short (millisecond range) times at 1200

°C. The idea is based on the knowledge that there is a lag time between calcining reactions and sintering of the particles. Thus, the desulfurization reactions occur to the extent of 20% utilization of the sorbent before pore closure becomes important.

Another example is the research of Weisweiler and Stein.^[35] They showed that different calcining and pelletizing procedures can be used to optimize the reactivities in SO₂-H₂O gas mixtures at various temperatures in the range from 300 to 1000 °C. At higher temperatures, sorbents with small surface areas and large pores were best, whereas at low temperatures high surface area was important. Below 500 °C, lime reacted mainly to form CaSO₃·0.5H₂O, and above 600 °C, the reaction product was CaSO₄.

An approach to improve the reactivity of Ca-base sorbents that has received limited attention is the use of additives. Shadman and Dombek^[36] added kaolin (Al₂O₃·2SiO₂·2H₂O), silica (SiO₂), and bauxite (Al₂O₃·2H₂O) to lime as structure modifiers. Such additions have a physical rather than a chemical effect in that they tend to increase macroporosity. The degree of enhancement in performance was nearly the same for all three additions. Adding 50% kaolin tripled the initial reaction rate and produced twice the amount of CaO converted to CaSO₄ after a reaction time of 2 hr at 500 and 700 °C.

Other investigators have added alkali salts as promoters. Boni *et al.*^[37] believed that alkali salts form eutectic liquid layers on the lime surface, which facilitates the transport of SO₂ through the pore structure. They contend that other promoters, like chromium and vanadium compounds, catalyze the formation of SO₃ from SO₂. Diffenbach *et al.*^[13] evaluated a large number of halides, silicates, nitrates, and hydroxides as additives to Ca(OH)₂. It was found that the alkali halides worked best and that the procedure used for incorporating the promoter was important. They speculated that chemical reactions between the additives and Ca(OH)₂ modified the nature of the surfaces in contact with SO₂.

Many of the basic studies in this field suffered because the investigators were not able to make direct measurements on the species formed on a microscale in their materials. This gap in the information base is being filled in a series of publications by Cook and Siriwardane.^[38,39] X-ray photoelectron spectroscopy (XPS) is being used to study sulfidation on surfaces of single crystals of CaO. They found that SO₂ reacts initially with CaO at 700 and 800 °C to form sulfite ions, SO₃²⁻, if no O₂ is present. At longer times, most of the SO₃²⁻ decomposes, releasing SO₂ and forming both CaS and CaSO₄. When O₂ is present with SO₂, the SO₃²⁻ ions produced initially react with O₂ to form CaSO₄ as the only product.

Generally, in the projects discussed above, calcium compounds were assumed to be once-through sorbents, because the materials are readily available and inexpensive. However, space for disposal of solid wastes in landfills is becoming an increasingly serious problem, so regeneration is being considered more actively. As discussed by Turkdogan,^[40] it is possible to regenerate CaO from CaS and CaSO₄ thermochemically. For CaS, CaO can be recovered by reacting with a mixture of CO₂, H₂O, and up to 3% O₂ at 1000 to 1100 °C. Under these conditions, CaSO₄ does not form, and the CaO can be reused seven to ten times. Recovery of CaO from CaSO₄ can be ac-

complished by using either CO or carbon as a reducing agent under carefully controlled conditions.

The CO₂-H₂O method of reclaiming CaO from CaS is now being tied to fluidized bed coal gasification technology.^[41] An alternate process for accomplishing the same purpose was developed by Schwerdtfeger.^[42] CaS is reacted with a controlled amount of air in the first step until some of the CaS is converted to CaSO₄. In the second step, the mixture of CaS and CaSO₄ is heated in an inert gas to produce CaO and SO₂.

Even if the spent sorbents are not regenerated, a technology problem still remains. When the spent sorbent contains CaS, it reacts slowly in the landfill with CO₂ from the air to form H₂S. No information was found on laws and regulations that address the problem, but it is generally accepted that such sorbents must be treated prior to disposal.^[8,40,41] Oxidation of the CaS to CaSO₄ is an acceptable approach, and it was studied by Pham.^[41] The same challenge is faced in this process as in sorption; at low temperatures, the chemical reaction is slow, and at high temperatures, sintering results in slow mass transport of reactants and products.

5. Iron and Iron Oxides

Desulfurization with iron oxide (Fe₂O₃) offers some of the same advantages as desulfurization with lime. Fe₂O₃ is the common form of iron oxide present in iron ore; consequently, it is inexpensive and no chemical processing is needed before using it as a sorbent. With the sorption products produced, disposal of spent sorbent material is not a serious problem. Desulfurization of hot gases to a level of hundreds of parts per million of H₂S is possible, but it must be used in combination with another sorbent to reach a level of less than 10 ppm, which is needed for gas turbine or fuel cell systems. A thermodynamic calculation showed that 10 ppm H₂S is possible, but only at a temperature of 350 °C or less.

Recent efforts are not able to draw on the technology used a century ago,^[8] because the temperatures of interest are much higher. Brooks^[43] reviews research done in the 1950s, 1960s, and 1970s on iron oxide sorbents. There was difficulty in solving problems with sorbent degradation, but when Fe₂O₃ was mixed with silica fly ash, H₂S levels as low as 200 ppm were obtained in the temperature range of 400 to 750 °C. Successful regeneration in air or steam at 950 °C was demonstrated. In Brooks' research, iron was infiltrated into zeolite pellets by an ion exchange reaction. Calcining in air then produced iron oxide in the pores of the zeolite. With this sorbent, desulfurization to a level of 100 ppm H₂S was achieved at 650 °C. Regeneration was possible at the same temperature with simulated fuel cell exhaust gas containing 11% O₂. Essentially the same experiments were conducted with zinc oxide substituted for iron oxide in the zeolite. The results with zinc oxide were better in that desulfurization to less than 5 ppm H₂S was possible at 500 °C.

In a larger scale project, iron oxide was evaluated as a once-through sorbent in a slagging gasifier.^[16,44] It was stated that the reaction product was "iron oxysulfide," and it formed as a dispersed phase in the coal slag, but its structure was not identified. Because the gasifier operates at temperatures in the range from 1100 to 1650 °C, it is likely that the oxysulfide

formed as a liquid and solidified as a glass. This conclusion is based in part on the fact that eutectic liquid can form in the Fe-O-S system at a temperature of approximately 920 °C, and a wide range of liquid compositions is possible at temperatures above 1100 °C [43].

In Ref 44, scanning electron micrographs and energy dispersive X-ray (EDX) data on oxysulfide particles were presented. For a medium-sulfur coal, the Fe/S atom ratio in the oxysulfide, as determined by EDX, was 2.83. For a high-sulfur coal, the corresponding ratio was 1.45. The particles appeared to be single phase in the scanning electron micrographs, which is further evidence that the particles formed as liquid droplets and solidified as glass. Had crystallization occurred on cooling, one would expect to see a two-phase mixture of FeS and FeO or Fe₃O₄, because there are no stable solid oxysulfides other than iron sulfates, and there is no mutual solubility between FeS and the oxides of iron. In principle, it should be possible to compare the compositions obtained with compositions derived from thermodynamic calculations^[45], but insufficient information was provided in Ref 16 and 44 to carry out the calculations. The authors state that their thermodynamic calculations indicate it should be possible to increase the sulfur capture beyond 50% and additional tests are planned.

A completely different approach to sulfur capture in a slag has been taken by Okamura *et al.*^[46] The gasification process consists of blowing pulverized coal onto the top of a molten iron bath. Data were obtained in a pilot plant with a capacity of 60 tons of coal per day. It was stated that both the molten iron and the slag contribute to desulfurization. Depending on test conditions, the sum of the H₂S and COS concentrations in the product gas ranged from 10 to 310 ppm. The sulfur concentration in the slag reached a level of 0.5% by weight.

Courcier and Rist were awarded a patent for developing a similar molten iron gasification process.^[47] Their process differed from the one mentioned above in that ferromanganese, manganese, or zinc was added in the process to enhance desulfurization.

Concerning work in Brazil, Ferrei described a multi-faceted R & D program on coal combustion and gasification in which sponge iron is one of the sorbents of interest.^[48] The only detail provided is that an external sponge iron bed is being developed for use in a fluidized bed gasification system.

Finally, Hasatani and Wen conducted a basic study on sorption of sulfur by iron oxide and iron.^[49] Single particles were reacted in a thermogravimetric apparatus at temperatures in the range from 600 to 900 °C. They found that sponge iron produced by reducing Fe₂O₃ pellets was much more reactive than when Fe₂O₃ was the starting material. Depending on experimental conditions, the product of the reaction was found to vary from FeS_{1.1} to FeS_{1.2}.

6. Zinc Oxide

The attractive features of zinc oxide as a sorbent are that it can reduce H₂S concentrations in gas mixtures to very low levels and its reactivity is high, particularly for fine particles. The principal limitation of ZnO is that loss of Zn by vaporization can be high at the temperatures of current interest. If it is assumed that a Zn pressure greater than 10⁻³ mm Hg is unaccept-

able for sorbent applications, then calculations show that ZnO should not be used above a temperature of 900 K. This value agrees with the upper limit mentioned in several of the publications reviewed on Zn compounds.

An escalation in interest in ZnO as a sorbent began in 1977 with a study by Westmoreland, Gibson, and Harrison.^[50] From an initial thermodynamic screening, they selected MnO, ZnO, CaO, and V₂O₃ as the most promising compounds for experimental research. In their experiments, they only considered initial rates of sulfur absorption and found CaO and MnO react faster than ZnO and V₂O₃. However, CaO, MnO, and ZnO are all susceptible to pore closure at longer reaction times, a factor they did not consider.

Jalan^[51] evaluated ZnO along with some other sorbents in a packed bed reactor. Pore closure was found to be a serious problem with ZnO when 5.5% of the material was converted to ZnS at 650 °C. Regeneration in steam-air mixtures worked better than air alone because of higher sulfur removal efficiency and less structural degradation. Additional thermal treatments in N₂ were used to decompose zinc sulfates that formed during regeneration.

In a project dedicated to the study of pore closure in ZnO when it reacts with H₂S, Ranade and Harrison^[52] developed a model to explain the behavior. As in studies discussed earlier on calcium compounds, specific surface area was used as an experimental parameter to evaluate the combined effects of sintering and the sulfidation reaction. Although no tie was made to sorbent technology, Rao and Kumar^[53] conducted a similar study to model the reverse process of oxidation of ZnS to form ZnO.

There is still active research on ZnO pellets and small particles. Sotirchos has published a series of articles on this subject, the most recent being Ref 54. He found the reactivity varied dramatically with particle size, but the pore diffusion rate was a controlling factor even for small particles. As mentioned earlier,^[27] when Zn was injected into a coal gasification apparatus as ZnCO₃, its performance was better than Ca(OH)₂ for brown coal. However, neither sorbent was very effective for a coal that contained 4.9% S.

An alternative to using monolithic ZnO particles is to infiltrate a Zn salt into a zeolite, then to calcine the material and form fully dispersed ZnO in the pores. Gasper-Galvin *et al.*,^[55] as well as Brooks,^[43] took this approach. The materials performed well at temperatures between 500 and 650 °C, but poor results were obtained at 870 °C. At this temperature, it was reported that loss of Zn by vaporization was excessive, and loss of Al from the zeolite occurred.^[55]

7. Copper and Copper Oxide

Like lime, copper and copper oxide react readily with sulfur under both oxidizing and reducing conditions to form either CuSO₄ or Cu₂S. Regeneration is rather easy at moderate temperatures in an appropriate gas mixture. The limitation of copper in the newer coal gasification applications, for example combined-cycle power generation, is that it cannot reduce the H₂S concentration to very low levels. A calculation showed that a maximum temperature of about 400 °C would be needed to reduce the H₂S concentration to below 10 ppm, and it is a dis-

advantage to cool the gas to such a low temperature. Thus, copper may be most useful as one of the sorbents in a two-step desulfurization process.

Jalan^[51] conducted one of the first investigations in which Cu was evaluated in simulated coal gas. Pellets were made by pressing and sintering CuO powder. The pellets reacted readily with H₂S in the coal gas, but some sulfate formed when regeneration was attempted at 650 °C in air. It was found that the sulfate decomposed when the pellets were heated in N₂ and that sulfate formation occurred to a lesser extent when regeneration was carried out in an air-steam gas mixture.

A more comprehensive investigation of Cu as a sorbent in reducing atmospheres was carried out by Sick and Schwerdtfeger.^[56-58] The first phase of the project was a fundamental study of the behavior of solid Cu spherical specimens in a gas mixture containing H₂ and H₂S at 800 °C. The initial rate of sulfidation was linear and controlled partly by the rate of the chemical reaction and partly by mass transport in the gas phase. For longer reaction times, the sulfidation process became more complicated because concentric shells of Cu₂S formed with gaps between them.

In the second phase of the project, Cu particles were dispersed in an Al₂O₃ matrix. The material was prepared by sintering a mixture of CuO and Al₂O₃, then reducing the CuO to Cu in H₂. For a loading of 20% Cu, all of the Cu was converted to Cu₂S in 30 min at 800 °C. Regeneration was carried out both in air and in an 8.5% O₂-91.5% N₂ mixture at 900 °C. No changes in properties occurred after ten sulfidation-regeneration cycles in a packed bed reactor.

Kyotani *et al.*,^[59] who were apparently unaware of the Sick and Schwerdtfeger investigation, carried out similar experiments with Cu dispersed in SiO₂ and a commercial zeolite. Although the Cu was present as CuO when the specimens were exposed to H₂-H₂S gas mixtures, it was found that reduction of CuO to Cu occurred in the first few minutes, followed by the conversion of Cu to Cu₂S.

Two publications were found in the recent literature that relate to desulfurization of combustion gases. Cho and Lee^[60] studied sulfur sorption in CuO-Al₂O₃ pellets in a gas mixture containing 0.3% SO₂, 5% O₂, and the balance N₂. In a packed bed reactor controlled at temperatures between 250 and 450 °C, the CuO in the pellets reacted to form CuSO₄. They compared their results with prior investigations of a similar nature and concluded that Cu is a better sorbent under oxidizing conditions than Mn, Fe, Co, Ni, and Zn.

The second publication on combustion gas cleanup involved simultaneous removal of SO₂ and nitrogen oxides. Yeh *et al.*^[61] conducted similar experiments to those of Cho and Lee,^[60] except that they used a fluidized bed rather than a fixed bed reactor. It was demonstrated that the sorbent could be regenerated in either H₂, CO, or CH₄ gases. Both CuO and CuSO₄ present in the sorbents acted as catalysts for the reduction of NO and NO₂ to N₂.

8. Nickel and Nickel Oxide

There has been less research on nickel and nickel oxide than on many other sorbent materials, in part because the reaction product is a liquid at temperatures above 645 °C. However, as

discussed below, this property can be used to advantage if the liquid product is contained. Otherwise, Ni has properties similar to those of Cu. Both react readily with H₂S. Their sulfides can be converted to oxides by heating in air, and their oxides and sulfides can be reduced to metal by heating in hydrogen or another reducing atmosphere. Thermodynamic calculations show that neither metal should be able to reduce H₂S levels below 10 ppm, except at temperatures below about 450 °C.

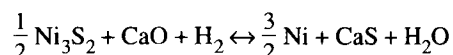
A precaution that is needed with Ni, but not with Cu, is that harmful amounts of Ni carbonyl may form at temperatures below 300 °C if CO is present.^[62] The same precaution applies for Fe-containing sorbents.

Patel *et al.*^[63] obtained data on Ni sorbents in the very low H₂S concentration range. Ten commercial catalysts containing dispersed Ni were evaluated in a fixed bed reactor in the temperature range of 500 to 700 °C. Their objectives were to remove both sulfur and arsenic from hot gas streams to levels needed for molten carbonate fuel cells. Success was claimed in reducing sulfur species concentrations from 10 ppm to 20 ppb. Some of the catalysts contained Mo and other additives that also react with sulfur. However, the best results were obtained with catalysts containing only Ni in a porous Al₂O₃ support structure. The explanation for the low levels of sulfur reached in the sorbent beds lies not in the conversion of Ni to Ni sulfides, but in the chemisorption of sulfur on the nickel surfaces. Regeneration tests were conducted also. Good results were obtained at 600 and 700 °C with a gas mixture of 70% steam and 30% H₂.

Steiner and Gutterman^[64] conducted tests on Ni and NiO pellets in which a Ni-S liquid product was formed deliberately. Simulated coal gas was passed through a fixed bed of pellets at 740 °C. The liquid sulfide flowed away from the pellets, exposing fresh surfaces to react with the coal gas. Thus, there was no solid sulfide present to curtail the reaction by serving as a diffusion barrier. The concept included a provision to collect the sulfide formed and regenerate it in a separate reactor.

The authors of this review are investigating dispersed Ni as a sorbent in Cu and Al₂O₃ matrices.^[65] With the Cu matrix, the reaction product is a Ni-Cu-S eutectic liquid that can form at temperatures above 575 °C.^[66] At this temperature, the composition of the liquid is 70% Ni, 6% Cu, and 24% S (weight basis). With the Al₂O₃ matrix, the Al₂O₃ is inert, so that the reaction product is a Ni-S liquid above 645 °C and Ni₃S₂ below 645 °C. The results show that dispersed Ni reacts with H₂S at approximately the same rate as found by Sick and Schwerdtfeger for dispersed Cu.^[58] The best procedure for regeneration of the Ni appears to be reduction of the sulfide in H₂ or an H₂-N₂ gas mixture in the temperature range of 800 to 1000 °C.

Tan and Ford^[67] conducted a study on reduction of Ni₃S₂ with H₂ which could be of value in sorbent technology. To obtain more complete reduction of the sulfide, CaO was blended with the Ni₃S₂. Thus, the reaction studied was



This procedure was found to be effective in obtaining complete reduction of the Ni₃S₂ at temperatures of 500 to 700 °C, but a large excess of CaO over the stoichiometric requirement was needed.

No information was found in the literature on the performance of Ni-base sorbents under oxidizing conditions. It is well known that alloys containing Ni corrode in oxidizing, sulfur-bearing gas mixtures at high temperatures by forming liquid sulfide as one of the reaction products. Sarrazin and Skalli^[68] demonstrated that very rigorous calculations must be carried out to reconcile this experience with thermodynamic principles. More specifically, it is necessary to consider not only SO₂ and H₂S as sulfur species, but also SO₃, S₂O, and SO as minor constituents. Therefore, both thermodynamic calculations and experience show it should be possible to remove SO₂ from combustion gases with Ni, but it might not be competitive with other sorbent materials under oxidizing conditions.

9. Additional Materials

No attempt has been made in this review to mention every metal and binary oxide that have been studied as desulfurizing agents. There are a few others that deserve mention, the first being sodium compounds. Sodium forms both a stable sulfide and a stable sulfate. Soda ash, or Na₂CO₃, is widely used in low-temperature flue gas desulfurization processes and was thought to have potential in the Texaco coal gasification process.^[69] Serious handling problems were encountered when it was tried as an *in situ* sorbent. For example, the slag containing the sulfur as a reaction product was unstable and oxidized when exposed to air.

Sodium oxide was one of the sorbents evaluated by Swisher *et al.*^[70,71] in a study of thermochemical processes for removing sulfur from solid coal. At a temperature of 500 °C, Na₂O was superior to Mn, CaO, and Zn as a desulfurizing agent.

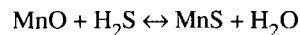
Sodium carbonate in mixtures with the carbonates of Si, K, and Ca was studied by Lyke *et al.*^[72] The mixtures were contained in a porous Li aluminate support and were liquids at the temperatures of interest. Molten salts and sodium compounds have one important advantage over other sorbents in that they remove chlorine in addition to sulfur from coal gas.

Another category of materials that deserves mention includes manganese, ferromanganese, and manganese oxide. Because Mn is the principle element added to steels to control the harmful effects of sulfur on mechanical properties, it was sensible to consider it also for sulfur removal from hot gas streams. In steelmaking practice, Mn is added in the form of ferromanganese, which contains up to 90% Mn. It is commercially available in large quantities, and spent ferromanganese sorbents could probably be reclaimed by the steel industry.

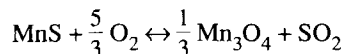
Swisher *et al.*^[70,71] demonstrated that manganese and ferromanganese can be used for the desulfurization of solid coal, but they are less effective than sodium oxide. As discussed by Danielewski,^[73] Mn tends to form an adherent layer of MnS on its surface during sulfidation at 600 to 1100 °C, which acts as a diffusion barrier as the reaction proceeds.

In research on MnO as a sorbent, Westmoreland *et al.*^[50] found that its initial reaction rate with H₂S was faster than the corresponding rates for CaO, ZnO, and V₂O₃ at temperatures up to 800 °C. Turkdogan and Olsson^[40] carried out a comprehensive study of the sulfidation and regeneration of pellets containing 75% MnO and 25% Al₂O₃. In a packed bed reactor at

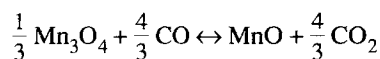
1000 °C, the H₂S concentration was reduced from 3% to 159 ppm, which is close to the equilibrium value for the reaction:



At equilibrium, the H₂O content of the gas would be 30 ppm. The best reaction sequence for regeneration was

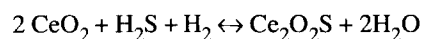


and

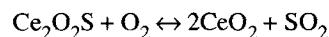


It was concluded that MnO is a better sorbent than CaO because of the ease of regeneration.

The last publication to be discussed is a description of research on cerium oxide by Meng and Kay.^[74] It deserves mention not because cerium oxide has exceptional promise as a sorbent, but because the publication is a good example of research in which a careful and rigorous thermodynamic analysis was carried out to guide experiments. The sulfidation reaction studied at 800 to 1200 °C was



and the regeneration reaction was



The H₂S concentration in the hot gas was reduced from 12,000 to 3 ppm, but pore closure in their pellets resulted in low sorbent utilization.

10. Conclusions

The information presented above makes it clear that the number of metals and binary oxides that have been evaluated for sulfur sorption characteristics at high temperature is quite large. This breadth for effort is desirable because commercial exploitation is not proceeding rapidly, and there is time for exploratory work.

Calcium compounds are expected to continue to be of interest because of their utility under both oxidizing and reducing conditions and because of their low cost. Their limitations are poor reactivity at low temperature, pore closure during sulfidation, and difficult regenerability. There is also a growing need to convert spent sorbents into a form that is chemically stable after disposal in landfills.

The other metals and binary oxides reviewed are generally effective only in reducing atmospheres. Sorbents containing Fe, Cu, and Ni are relatively easy to regenerate, but may not reduce H₂S levels to low enough values for critical applications. Zn and ZnO are good in this respect, but suffer from excessive Zn loss due to vaporization at temperatures of 600 °C and higher.

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