Thermochimica Acta, 26 (1978) 229–239
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USE OF OIL SHALE FOR CONTROL OF SULFUR DIOXIDE EMISSIONS FROM THE COMBUSTION OF COAL*

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ABSTRACT

Experimental results have been obtained which indicate that oil shale from the Mahogany ledge of the Green River formation (28 gal oil/ton) has short-term (≤ 3 h) sulfation properties superior to those of 1337 dolomite and consequently could be used more effectively to control SO_2 emissions from the combustion of coal. In a gas mixture containing 0.27% SO_2, the initial sulfation reaction rate at 750°C for the half-calcined shale is nearly six times that for the half-calcined dolomite. After 3 h, all of the $CaCO_3$ in the half-calcined shale is sulfated, compared with only 37% in an equal amount of half-calcined dolomite.

Although the results were obtained on spent shale (kerogen removed), they suggest that raw shale might be used for emission control in fluidized-bed combustors to derive an added benefit from the heat content of the shale.

INTRODUCTION

A potential energy resource receiving considerable attention is oil shale. The most important oil shale deposits within the United States occur in the Green River formation. These deposits are reported to contain total reserves equivalent of 4050 billion barrels; of this total, the equivalent of 620 billion barrels, present at concentrations ranging from 25 to 65 gal/ton, is considered to be recoverable[1]. The processing of this vast energy resource by retorting will yield a substantial quantity of spent shale.

Approximately half of the mineral content for an average shale (25 gal/ton) consists of dolomite and calcite; thus, the Green River oil shales are not true shales but marlstones[2]. These two carbonates (dolomite and calcite) are the essential components of calcareous rocks used in the emission control of SO_2 evolved from the combustion of coal. Furthermore, these carbonates in oil shale are fine-grained, with grain sizes ranging from 1 to 10 μm; this property is desirable because fine-grained calcareous rocks, in general, are better SO_2 sorbents than the coarse-grained varieties[3]. These two favorable properties, namely, mineral content and fine grain size, warranted

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* Work performed under the auspices of the Division of Basic Energy Sciences of the U. S. Energy Research and Development Administration.
Presented at the 7th North American Thermal Analysis Society Conference, St. Louis, Missouri, September 25–28, 1977.

an investigation of the feasibility of using oil shale as an SO_2 sorbent. Accordingly, the oil shale study was undertaken as part of a program to investigate the kinetics and mechanism of the sulfation of calcareous minerals. The preliminary results presented in this paper indicate that the oil shale has some distinct advantages, as will be shown. These advantages indicate the feasibility of using oil shale to control SO_2 emissions from coal combustion. Such a process would provide a practical use for spent shale. Moreover, the combustion of raw shale should be considered as a method for controlling coal-related SO_2 emissions while simultaneously utilizing the shale's energy content.

STARTING MATERIALS

The oil shale used in this study was from the Mahogany ledge of the Green River formation and was supplied by Dr. John W. Smith of the Laramie Energy Research Center of the U.S. Energy Research and Development Administration. Assays showed the oil content to be about 28 gal/ton. As reported by Smith[4], approximately 85% of the oil shale is mineral matter; the average composition of these minerals is (in wt.%): ferrous dolomite, 32; calcite, 16; quartz, 15; illite (a clay mineral), 19; Na and K feldspars (aluminnm silicates), 16; pyrite, 1; and analcite (hydrous aluminum silicate), 1. These concentrations can vary considerably both laterally and vertically in the formation. Moreover, other minerals may occur locally in amounts up to several weight percent; these include siderite ($FeCO_3$), magnesite ($MgCO_3$), shortite [$Na_2Ca_2(CO_3)_3$], dawsonite [$NaAl(OH)_2CO_3$], nordstrandite [$Al(OH)_3$] and nahcolite ($NaHCO_3$).

The dolomite, known as BCR 1337, was obtained from the Pfizer Co., Gibsonburg, Ohio, and is quarried from the Guelph member of the Niagaran dolomite which is Silurian in age. It is very pure, contains less than one percent impurities, and, according to our chemical analysis (which verified that of the supplier), has an empirical formula of $Ca_{1.01}Mg_{0.99}(CO_3)_2$. This dolomite had one of the highest sulfation capacities among several surveyed by Harvey and Steinmetz[3].

TABLE 1

CONCENTRATIONS OF MAJOR CARBONATE MINERAL COMPOSITION OF GREEN RIVER OIL SHALE AND 1337 DOLOMITE

	Dolomite (wt.%)	*Calcite (wt.%)*	*$CaCO_3$ (wt.%)*	*MgO (wt.%)*
Raw shale	27[a]	14	28.0	
1337 Dolomite	100	0	54.3	
Half-calcined spent shale			34.4	6.0
Half-calcined dolomite		71.3	71.3	28.7

[a] Assuming ferrous dolomite, $Ca_{1.0}Mg_{0.85}Fe_{0.15}(CO_3)_2$, as reported by Smith and Robb[5].

Typical concentrations of the major carbonate minerals in the oil shale and 1337 dolomite are given in Table 1.

EXPERIMENTAL

The experimental approach parallels that used in a current program which deals with the sulfation properties of dolomite. The specific conditions selected are those most typical of pressurized fluidized-bed combustion of coal. However, to ensure adequate control of conditions, experiments were conducted in laboratory apparatus rather than in coal-fired equipment. The processes involved in the dolomite program are half-calcination, sulfation, and regeneration. An additional process was required for the oil shale, namely, the removal of organic fraction (no organic material is present in the dolomite with which the shale was being compared).

Stones of $-16 +18$ U.S. standard screen size (about 1.1 mm) were used. Isothermal kinetic experiments were performed in a thermal gravimetric apparatus described elsewhere[5, 6]. These experiments employed approximately 200 mg samples under gas flow rates of 300 cm^3/min at 1 atm pressure and certified standard gas mixtures obtained from a commercial vendor were used. Treated samples were examined by optical microscopy, X-ray diffraction and scanning electron microscopy (SEM) techniques.

The raw shale was preheated at 400°C in air to eliminate the organic fraction (kerogen). The spent shale was then half-calcined at 800°C for 3 h in 100% CO_2 at 1 atm pressure. Mineral dolomite decomposed by the reaction

$$CaMg(CO_3)_2 \rightarrow CaCO_3 + MgO + CO_2 \quad (1)$$

The half-calcined shale was then sulfated at 750°C for 3 h in 1 atm of a gas mixture consisting of approximately 5% O_2, 40% CO_2, and 50–55% He and SO_2 (either 0.27 or 3.78%). The half-calcined products may sulfate according to the reactions

$$CaCO_3 + MgO + SO_2 + \tfrac{1}{2} O_2 \rightarrow CaSO_4 + MgO + CO_2 \quad (2)$$

$$CaCO_3 + 3\,MgO + 4\,SO_2 + 2\,O_2 \rightarrow Mg_3Ca(SO_4)_4 + CO_2 \quad (3)$$

A significant point here concerns the relative importance of reactions (2) and (3) for half-calcined 1337 dolomite and oil shale. For dolomite, reaction (2) is major and (3) is minor[7] as evidenced by the presence of MgO which remains as a major phase in the X-ray powder pattern of the sulfated material. In contrast, the patterns of the sulfated oil shale showed that the amounts of MgO decrease with increasing SO_2 concentration and MgO is not detectable after the 3.78% SO_2 treatment; these results indicate a trend at higher SO_2 concentrations toward complete reaction according to reaction (3). In addition, the binary sulfate, $Mg_3Ca(SO_4)_4$, becomes more prominent in the patterns for the sulfated oil shale.

RESULTS

Half-calcination

As mentioned previously, the mineral composition of the Green River formation is variable and this variability is particularly pronounced for the 1–2 mm particles used in this study. Some particles may be 100% dolomite and calcite, whereas others may be carbonate-free. For those particles rich in these two minerals, the two phases are intimately mixed; the coherence between Ca and Mg in a raw shale particle is evident in Fig. 1(a) and (a′), and that in a half-calcined particle, in Fig. 1(b) and (b′). The continued coherence in the half-calcined material indicates that the MgO resulting from the decomposition of dolomite does not diffuse but remains uniformly dispersed within the newly formed calcite. In this respect, half-calcination of the shale parallels that of 1337 dolomite.

An X-ray pattern taken of a sample of powder obtained by crushing 30 particles of half-calcined shale shows that the main decomposition products are calcite, MgO, and iron oxide (Fe_3O_4). Except for the iron oxide, the main products are the same as those resulting from the decomposition of 1337 dolomite. The silicate minerals in the

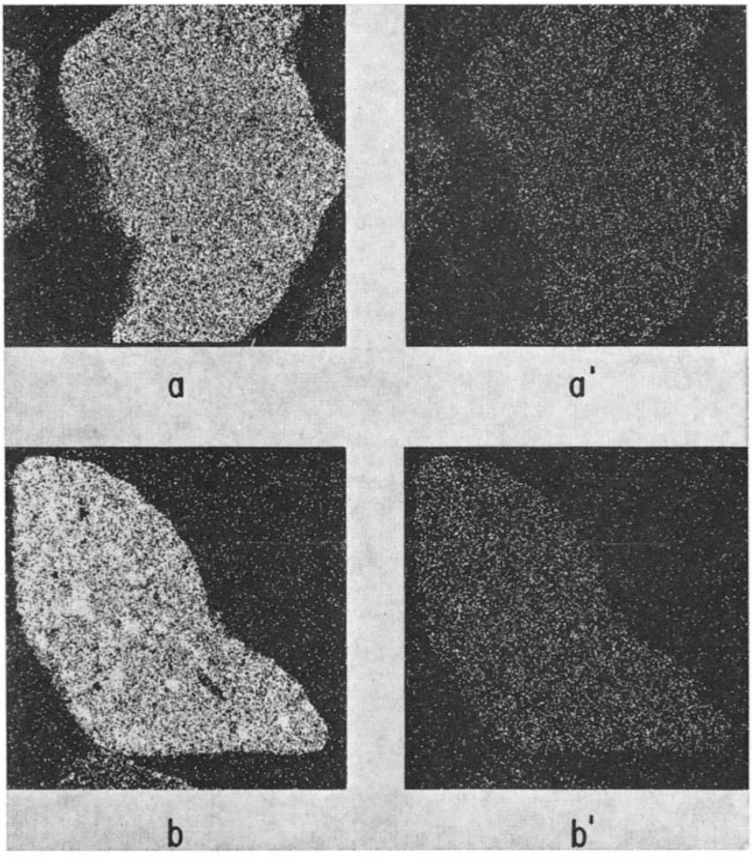


Fig. 1. SEM photographs of Ca (left) and Mg (right) X-ray scans for a raw shale particle (a, a′) and for a half-calcined shale partical (b, b′). Both are high-carbonate particles about 2 mm long.

shale are relatively inert to the heat treatment except for some loss of water from the hydrated varieties. Pyrite is oxidized to iron oxide, but the total amount of iron oxide in the heated sample appears to be greater than that expected from the oxidation of pyrite. The additional source could be the ferrous component of the dolomite which, according to Smith and Robb[8], amounts to 15 mole % ferrous iron that substitutes isomorphously for magnesium. Some of the heated shale particles contained several percent of amorphous Al_2O_3 grains from 10 to 20 μm in diameter which were devoid of SiO_2 and Na_2O. The source mineral was either dawsonite [$NaAl(OH)_2CO_3$] or nordstrandite [$Al(OH)_3$]. Huggins and Green[9] have observed that dawsonite decomposes in a two-step process to form amorphous alumina and Na_2CO_3 from 300 to 375°C; in the interval from 375 to 650°C, CO_2 is driven off and Na_2O combines with the alumina to form crystalline sodium aluminate. The nature of such a reaction or reactions will, of course, influence the capacity of the resulting Na-bearing phase or phases to undergo sulfation. Sulfation of a Na-containing silicate glass, for example, would not be expected, whereas sulfation of a Na-containing oxide would. The other possible mineral source for the alumina could be nordstrandite, but this mineral is not known to exhibit local enrichments like dawsonite.

The major difference between the dolomite and oil shale, after half-calcination, is the marked increase in porosity of the shale. This effect is shown in Fig. 2, which relates pore volume measurements of 1337 dolomite and oil shale before and after half-calcination. Not only does the half-calcined oil shale have a greater pore volume (0.4686 cm^3/g versus 0.2132 cm^3/g for the half-calcined dolomite), but the distribution of pore sizes in the shale is shifted toward larger pores. For example, in half-calcined shale 83% of the pores have diameters larger than 0.1 μm, whereas only 34% of the pores in the half-calcined dolomite have diameters larger than 0.1 μm. The enhanced porosity of the shale is undoubtedly due to the removal of kerogen, which produces a multitude of submicrometer intergranular voids. Larger voids ($\geq$ 5 μm) are apparent in polished sections of shale particles impregnated with epoxy resin. Some particles

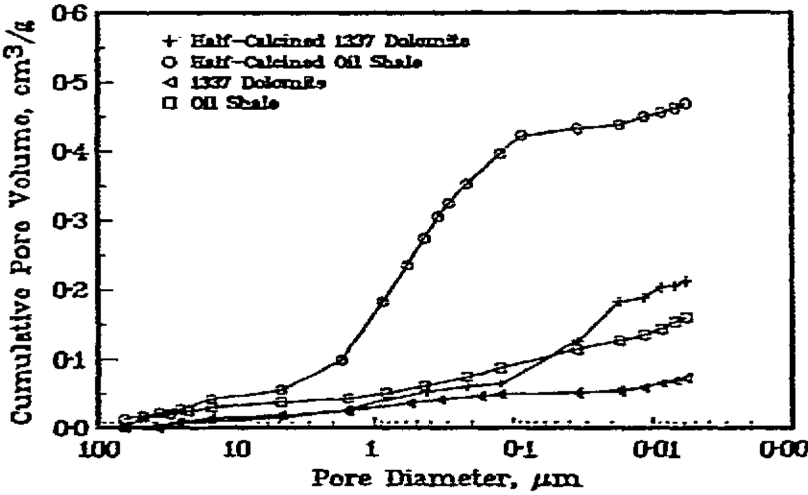


Fig. 2. Pore size distribution in untreated and half-calcined forms of oil shale and 1337 dolomite.

were even reduced to hollow shells. To the extent that increased porosity results in increased permeability, the half-calcined oil shale would be expected to undergo sulfation more readily.

Sulfation

If reactivity toward sulfation were based solely on the amount of $CaCO_3$ present, a comparison of the relative amounts in the dolomite and oil shale (bottom two rows of Table 1) would indicate that 2.1 times more shale would be required to react with equal amounts of SO_2. This relationship holds true for complete sulfation involving long residence times; however, higher reaction rates for the shale make it more favorable for shorter sulfation periods of 3 h or less, which might be encountered in fluidized-bed combustion. The experimental results are given in Figs. 3 and 4 for concentrations of 0.27 and 3.78% SO_2, respectively. Weight gains are proportional to the quantities of SO_2 reacted to form sulfates.

The initial reaction rates (i.e. at time = 0) computed from the results with 0.27% SO_2 given in Fig. 3 are 0.45 mg weight gain/(100 mg half-calcined shale) (minute) and 0.08 mg weight gain/(100 mg half-calcined 1337 dolomite) (minute). Thus, the initial reaction rate of shale is nearly six times that of 1337 dolomite. Based on the amount of SO_2 captured per unit mass of sorbent after 3 h, the oil shale captured 14.5/9.5 or 1.5 times more than the dolomite (or, stated differently, 0.7 as much shale captured the same amount of SO_2 as a unit mass of 1337 dolomite). This value is certainly more favorable than that expected from the amounts of $CaCO_3$ in

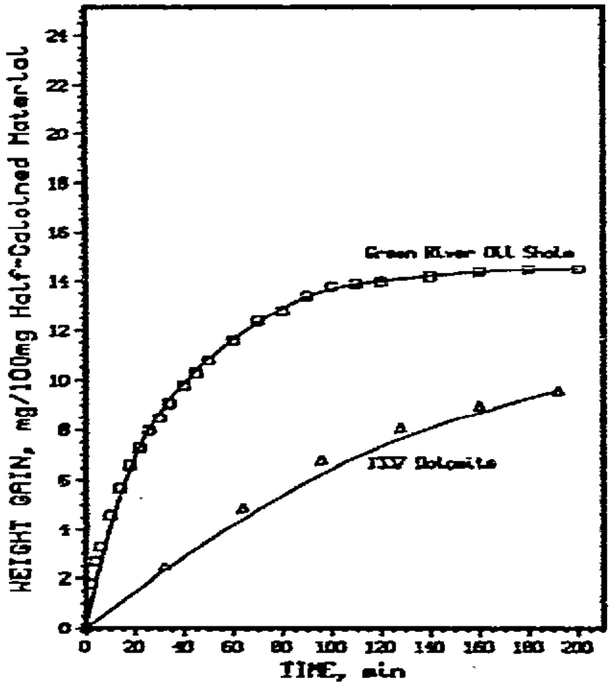


Fig. 3. Sulfation kinetics for half-calcined oil shale and half-calcined 1337 dolomite reacting with 0.27% SO_2, 4.85% O_2, 39.77% CO_2 balance He at 1 atm and 750°C.

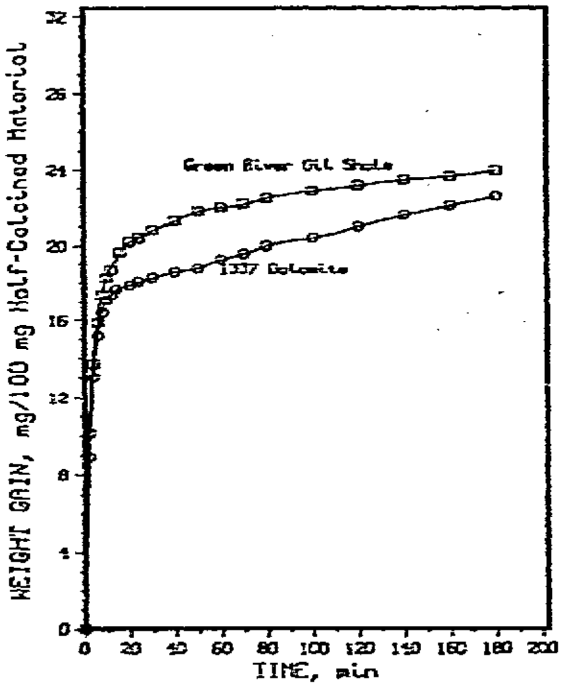


Fig. 4. Sulfation kinetics for half-calcined oil shale and half-calcined 1337 dolomite reacting with 3.78% SO_2, 4.23% O_2, 38.22% CO_2, and balance He at 1 atm and 750°C.

each and from the assumption that dolomite and shale have similar reaction properties. The weight gain after 3 h for dolomite represents 37% conversion of $CaCO_3$ to $CaSO_4$, whereas that for the shale represents approximately 120% conversion of $CaCO_3$ (based on the data in Table 1). Thus, it is evident that other phases in the half-calcined shale in addition to $CaCO_3$ are being sulfated. X-Ray and petrographic analyses indicate that some MgO is reacting to form the binary sulfate, $Mg_3Ca(SO_4)_4$. If the assumption is made that all of the $CaCO_3$ in the shale has been sulfated, then the observed weight gain indicates that approximately 20% of the MgO has been converted to $Mg_3Ca(SO_4)_4$. Thus, the increased sorbent capacity of the shale compared with dolomite is, in part, related to its ability to form larger amounts of $Mg_3Ca(SO_4)_4$.

The initial reaction rates computed from the 3.78% SO_2 results given in Fig. 4 are 3.03 mg weight gain/(100 mg half-calcined shale) (minute) and 2.89 mg weight gain/(100 mg half-calcined dolomite) (minute). Thus, the initial reaction rates, at this higher SO_2 concentration, are approximately equivalent, but after 3 h the shale had captured 1.1 times more SO_2 than the dolomite. The weight gain of the 1337 dolomite after 3 h represents a maximum of 87% conversion of available $CaCO_3$ to $CaSO_4$ [a small fraction of this weight gain is associated with the formation of a minor amount of $Mg_3Ca(SO_4)_4$]. The weight gain for the shale indicates that essentially all of the $CaCO_3$ and MgO have been converted to $CaSO_4$ and $Mg_3Ca(SO_4)_4$. These results were supported by X-ray and chemical analyses of the products. Thus, it is still evident that, for short reaction periods of 3 h or less, the shale has more favorable

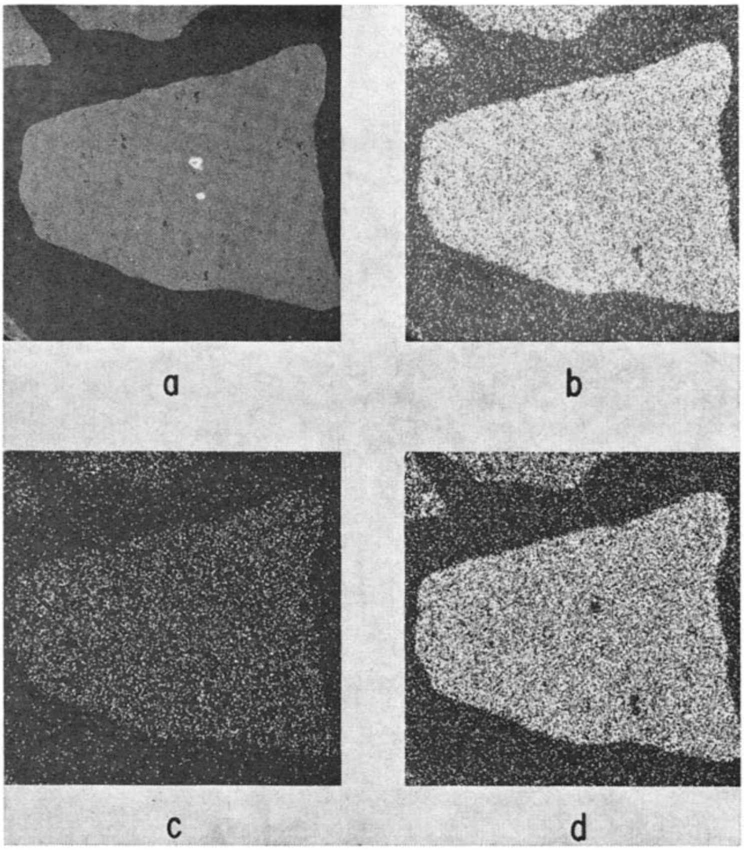


Fig. 5. SEM photographs of a high-carbonate shale particle (1.0 mm long) sulfated for 3 h with 0.27% SO_2. (a) Specimen current image; (b) Ca X-ray scan; (c) Mg X-ray scan, (d) S X-ray scan.

sulfation properties. This effect is more pronounced under the lower SO_2 concentration, which is closer to that encountered in fluidized-bed combustion.

Scanning electron microscopy photographs of a typical shale particle at the end of the 3 h sulfation with 0.27% SO_2 are shown in Fig. 5. A comparison of the Ca, Mg and S X-ray scans demonstrates that these elements are coherent and are uniformly distributed throughout the particle; thus, the sulfated areas are not confined to exterior surfaces. This result is in sharp contrast to the sulfation behavior of half-calcined 1337 dolomite reported earlier, namely, sulfation with 0.39% SO_2 at 750°C for nearly 3 h resulted in a sulfate distribution that was primarily on the particle periphery[10]. The difference in sulfate distribution can probably be related to the difference in porosity mentioned earlier. The X-ray powder pattern of the sulfated shale shows less MgO than the pattern of the half-calcined shale, thus indicating that some MgO had been sulfated to form the binary sulfate, $Mg_3Ca(SO_4)_4$, which is present along with $CaSO_4$ in the pattern of the sulfated shale.

The X-ray powder pattern of shale particles sulfated with 3.78% SO_2 for 3 h is predominantly that of $CaSO_4$ and $Mg_3Ca(SO_4)_4$ with no detectable MgO present (i.e. less than 5%). Otherwise, a typical shale particle sulfated under 3.78% SO_2 is

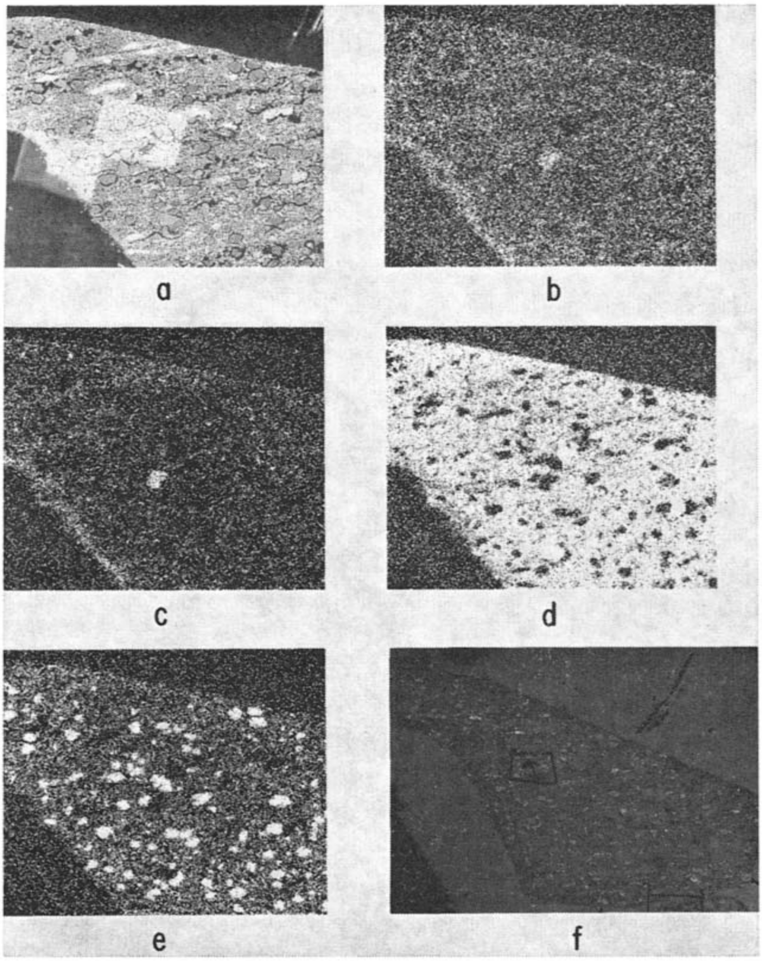
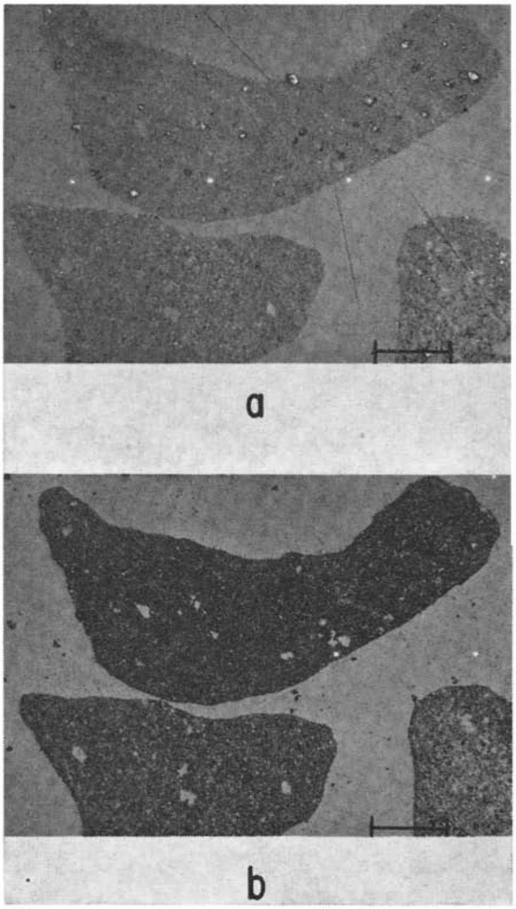


Fig. 6. Photographs of a poorly sulfated, high-silicate, low-carbonate shale particle sulfated for 3 h with 3.78% SO_2. (a) Specimen current image; (b) Ca X-ray scan; (c) S; (d) Si; (e) Al; (f) reflected light photograph (ignore box). Bright spots in (e) are amorphous alumina, which are also visible in (a), (d) and (f). Scale bar on (f) is 0.2 mm.

essentially the same as that depicted in Fig. 5. Particle-to-particle variations, due to differences in initial mineral contents, would obscure more subtle differences in the photographs of individual particles sulfated under either of the two SO_2 environments. Scanning electron microscopy photographs of one sulfated shale particle, which presumably contained little dolomite and calcite initially, is shown in Fig. 6. This particle has poor sulfation characteristics because of its high aluminum silicate content. Areas showing the highest Al concentrations are Al_2O_3, believed to have been formed by the decomposition of the mineral dawsonite. That they did not sulfate is due to the instability of aluminum sulfates under the experimental conditions used.

Qualitative differences in the sulfation properties among individual particles can be recognized on polished sections of epoxy-impregnated mounts of sulfated particles viewed in reflected light. The differences are revealed after the freshly polished surface "weathers" upon exposure for a few hours to laboratory air[7]. The



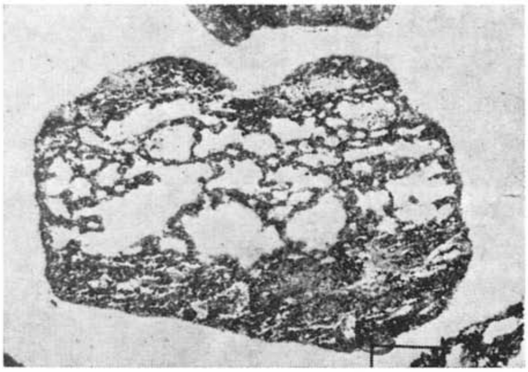


Fig. 7. Optical photographs of a polished section mount of 3 shale particles sulfated for 3 h with 3.78% SO_2. (a) Freshly polished surface; (b) weathered surface after exposure to laboratory air for 6 h. Degree of weathering (or darkening) is proportional to amount of sulfate formed, which is greatest for particle at top and least for particle at lower right. Scale bars = 0.28 mm.

Fig. 8. Optical photograph of the weathered, polished surface of a sulfated shale particle showing porous texture formed by removal of kerogen. Voids are now filled with epoxy resin following vacuum impregnation. Scale bar = 0.28 mm.

binary magnesium–calcium sulfate gradually darkens as it absorbs moisture; the relative effects are shown for three adjacent particles in Fig. 7. Similarly, this effect enhances the microstructure of the voids created by the removal of kerogen, as shown in Fig. 8.

DISCUSSION

We have demonstrated that half-calcined oil shale has short-term sulfation properties superior to those of half-calcined 1337 dolomite due to higher reaction rates. Two factors which may account for the higher rates for the shale are (1) greater porosity, which leads to increased permeability, and (2) greater tendency for MgO to form $Mg_3Ca(SO_4)_4$. In our previous studies on the sulfation of half-calcined dolomite, we observed that $CaSO_4$ formation begins on the exterior surfaces of particles and then gradually proceeds to the interiors. The marked increase in the surface area of the shale due to the removal of kerogen, then, has a pronounced effect of accelerating the sulfation process. Formation of the binary sulfate is also related to porosity. In dolomite, the minor amounts of binary sulfate present are confined to thin ribbons on exterior surfaces and cavity walls; the reaction is not only surface-controlled but stops after the surfaces become encrusted with the binary sulfate. The larger surface area of the shale then increases its capability to form more binary sulfate before the reaction is stopped by some limiting thickness of crust.

The superior sulfation characteristics of oil shale compared with 1337 dolomite are more pronounced at low SO_2 concentrations. Thus, oil shale has the potential for providing more efficient removal of SO_2, particularly at the low concentrations encountered in fluidized-bed combustors. Accordingly, a potential new use for raw and spent shale has been identified.

ACKNOWLEDGMENTS

We are grateful to Dr. John Ward Smith of the Laramie Energy Research Center, ERDA, for a generous supply of oil shale and to the following members of the Chemical Engineering Division, Argonne National Laboratory: Dr. Romesh Kumar, Group Leader, and Dr. F. A. Cafasso, Associate Division Director, for their interest and support; Dr. R. B. Snyder for the mercury porosimeter measurements; B. S. Tani for the X-ray powder patterns; and R. L. Malewicki for the SEM work.

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