

# FRACTURING OF OIL SHALE BY TREATMENT WITH LIQUID SULFUR DIOXIDE

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## Introduction

Development of oil shale deposits as sources of fuels, lubricants, and chemical feedstocks is being considered as an alternative to present reliance on conventional petroleum reserves. Procedures, advantages, and disadvantages for mining/surface processing and for *in situ* retorting have been widely discussed.<sup>1,2</sup> In the former approach, crushing of the shale is essential for efficient oil recovery. As a result of tests with a variety of mechanical crushers,<sup>3</sup> it is apparent that the effectiveness of mechanical crushing is limited by the characteristics of the shale. A slab-forming tendency allows large pieces to pass through many conventional crushers. The resilience and slippery nature of the shale limits the effectiveness of mechanical impact; furthermore, the shale often adheres to crusher surfaces. *In situ* retorting is enhanced by fracturing with explosive charges or expansion of existing fractures with fluids such as water. Fracturing by explosive charges is frequently limited to the vicinity of the charge since the explosive shock is dissipated by shale resilience. Efficient fracturing by aqueous fluids is limited by a tendency for capillary adhesion of water in the fissures and by available water supplies in arid regions where oil shale deposits often occur.

Employment of chemical comminution techniques for fracturing oil shales could circumvent many of the limitations to mechanical crushing as well as reduce or eliminate capital and maintenance costs of crushers. Our recent success in comminuting and desulfurizing coal by treatment with liquid sulfur dioxide,<sup>5</sup> suggested that similar treatments might be successful in fracturing oil shales.

Liquid  $\text{SO}_2$  is a remarkably subtle solvent with moderate Lewis acid properties, a substantial resistance to oxidation and reduction when pure, and a propensity to support a variety of ionic, free radical, and molecular reactions.<sup>6</sup> Since  $\text{SO}_2$  has a boiling point of  $-10^\circ\text{C}$ , it is easily liquified and/or removed after reaction; it can be easily manipulated without the need for exotic construction materials. Furthermore, it is an inexpensive material which is readily available in large quantities from smelting and fossil fuel combustion; if not utilized, it must be disposed of in some stabilized form at considerable expense. Thus, the direct use of sulfur dioxide could provide an alternative means of cost recovery for pollution abatement technology.

Here we wish to report the results of preliminary experiments in which oil shales are treated with liquid sulfur dioxide to effect comminution. We are, presently, unaware of any previous reports of such experiments.

### Experimental

Sulfur dioxide was dried and manipulated as described elsewhere.<sup>6</sup> Larger shale pieces (6-8 cm) were treated directly in a stainless steel autoclave reactor (Parr model 4641). Smaller shale pieces were sealed in fritted glass tubes with liquid  $\text{SO}_2$  (ca. 2:1 or less  $\text{SO}_2$ /shale by weight) to facilitate recovery of any extract. Sulfur dioxide was distilled on to the shale at  $-78^\circ\text{C}$ ; the system was then sealed and brought up to processing temperature. Temperatures of 25, 70, and  $170^\circ\text{C}$  were used; the latter temperature corresponds to supercritical conditions for  $\text{SO}_2$ . No mechanical agitation was employed. Upon cooling, the  $\text{SO}_2$ , shale, and extract were recovered. The shales were inspected immediately upon recovery and at several intervals thereafter. Sulfur analyses and infrared spectra of the shales were performed on original, processed, and processed/heated samples to determine residual  $\text{SO}_2$  content. Infrared spectra of the extracts were also obtained.

### Results and Discussion

Results for samples of Green River, Antrim, and Moroccan oil shales were obtained in these preliminary experiments. Extensive fracturing, both along and across laminations, was observed with all three shales. Initial experiments were carried out at  $170^\circ\text{C}$  for 3 to 5 hours; subsequent experiments indicated that the degree of fracturing was almost as extensive when milder conditions (e. g.  $25^\circ\text{C}$  for 1 hour) are used. Some fracturing was even observed to occur by exposure to gaseous  $\text{SO}_2$  alone. With the large lumps, laminations are frequently expanded to 1-2 cm; fractures across laminations are less pronounced but distinctly visible. Immediately upon recovery from the reactor, the samples are so brittle as to be easily broken with the fingers; after standing for a time, the samples become slightly less brittle but all fracturing is maintained. Although no quantitative tests of mechanical properties have been made, it appears that little of the resilience and slipperiness of the original shales is retained. Surfaces of the processed samples have a soft lustrous appearance.

At this stage, the mechanisms responsible for fracturing of these oil shales are not obvious. Among the mechanisms which should be considered, however, are the following: 1. partial conversion of carbonates to sulfites would disrupt microcrystalline lattices in carbonate rich shales, 2. displacement of hydroxyl groups on silica surfaces would disrupt hydrogen bonding in siliceous shales, and 3. extraction of physically and chemically bound water would break up interstitial forces in both types of shale.

The sulfur content of the shales was increased somewhat by processing in liquid  $\text{SO}_2$ ; residual sulfur increases significantly with the temperature of the treatment, however. For example, at room temperature, residual sulfur increases by 1-2% but at  $170^\circ\text{C}$ , it increases by 5-10%. Such an increase in sulfur content suggests that processing at higher temperatures is detrimental to the shale.

Upon exposure of Green River and Antrim shales to liquid  $\text{SO}_2$ , a yellow color develops in the  $\text{SO}_2$  solution which progressively deepens to a dark brown; a brown residue is isolated upon evaporation of the  $\text{SO}_2$ . Moroccan shale, on the other hand, produces an orange  $\text{SO}_2$  solution and an orange residue. It appears that the quantity of extract can be increased somewhat by use of higher temperatures. Infrared spectra of these residues reveal that water, aliphatics, and carbonyls are the predominant species although a small amount of aromatics are also obtained. Cross polarization, magic angle spinning  $^{13}\text{C}$  nmr results for the solids indicate that the carbon content in the shales themselves differs much more than do these extracts: Green River shale organic carbon is predominately aliphatic whereas Moroccan shale carbon is ca. 3:1 aliphatic/aromatic and Antrim shale carbon is ca. 1:1 aliphatic/aromatic. Thus, extraction by liquid  $\text{SO}_2$  would appear to be selective for the aliphatic components of these shales. Since the organic part of these extracts constitutes ca. 2% of the original shales, it is presumed that they represent most of the bitumen portion of the shale and that the kerogen still remains in the shale itself. These observations would, therefore, be consistent with those for extraction by more conventional solvents. Other materials are also extracted from the shales by liquid  $\text{SO}_2$ . These materials are found as colorless or light brown crystals deposited in the fissures and on the surfaces of the shale after the isolation procedures. At present, we have not identified these crystals.

The results of these experiments suggest that many of the limitations of conventional crushing and fracturing procedures are not encountered here; there are however other limitations to be dealt with. These observations are, nevertheless, sufficiently promising to warrant further detailed investigation into the utility of comminution with liquid  $\text{SO}_2$  for both surface and in situ processing of oil shales. Experiments designed to establish the generality of the observations reported here, to develop an understanding of the mechanisms involved, and to devise means of reducing the impact of present limitations to practical use are underway.

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8. See, for example, Ref. 3, Chapters 3,6,7.