

INORGANIC SULFUR SPECIES IN RETORTED OIL SHALE

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ABSTRACT

Spent shales from a series of laboratory retorting experiments carried out in a nitrogen atmosphere from 350 to 800°C were analyzed wet chemically for sulfide sulfur in addition to sulfate sulfur, pyrite sulfur and "residual" sulfur. These species accounted for about 72 to 95% of the total sulfur depending on retorting temperature. Quantitative data was also obtained for sulfur dioxide and hydrogen sulfide in the retort off-gases.

INTRODUCTION

Effective environmental impact control of oil shale retorting through process engineering depends in a fundamental way on acquiring detailed information about the physics and chemistry of the mobilization and demobilization of potential pollutants. Such processes are best understood in terms of the chemical species involved. This paper deals with the quantitative measurement of some of the sulfur species present in gas and solid products obtained from laboratory retorting of Colorado oil shale in a nitrogen atmosphere.

In a recent article Burnham and Taylor¹ reviewed in depth the literature on the occurrence of sulfur in Colorado oil shale and the work that has been reported on identifying and measuring the sulfur species that are produced during oil shale retorting. With the latter, the greatest success has been obtained in characterizing and quantifying the sulfur containing gases that are produced. With regard to

the oil and spent shale products however, the efforts at determining sulfur distribution have not extended much beyond analysis for total sulfur. In the work reported here spent shale from carefully controlled laboratory retorting experiments was analyzed for sulfate, sulfide, pyrite and "residual" sulfur by an extension of the lithium aluminum hydride method developed for raw shale by Smith, Young and Lawlor.² The gases produced during retorting were analyzed quantitatively for sulfur dioxide and hydrogen sulfide by the wet chemical procedures of EPA-Method 11.³

EXPERIMENTAL

Oil Shale

The oil shale used in this work was from the 1261.8-1263.0 footage section of the Mahogany Bed of Core Hole 15/16 Naval Oil Shale Reserve No. 1. The shale was crushed in a jaw crusher and then ground in a coffee-mill grinder to a particle size of -2.38 mm by Laramie Energy Technology Center personnel. The total available amount was about 615 g. This was sub-divided into 16 equivalent samples by spin-riffing. Eight of these subdivisions were recombined and the combined sample spin-riffled to give 16 equivalent samples. The average sample weight thus obtained was 19.16(46) g. For raw shale analysis one of these was ground in a Spex shatterbox for 5 min. to $-.149$ mm and then spin-riffled again to give 16 equivalent samples with an average weight of 1.10(5) g. Larger samples were prepared for the

retorting experiments by combining two ~19g samples after size reduction to $\sim .149$ mm and then spin-riffling to give 16 samples of 2.24(10) g.

The Fischer assay oil value for this core section was 24.9 gal ton⁻¹. An X-ray powder diffraction pattern for this material contained peaks for the tectosilicates albite (NaAlSi₃O₈), and orthoclase (KAlSi₃O₈), the zeolite analcime (NaAlSi₂O₆·H₂O), quartz (SiO₂), calcite (CaCO₃), dolomite (MgCa(CO₃)₂), pyrite (FeS₂) and dawsonite (NaAl(OH)₂CO₃).

Apparatus

The retort vessel was fabricated from 48 mm o.d. quartz glass tubing which was sealed at one end. The open end was closed with a brass cap containing an internal O-ring. The cap contained an entry port for an 8 mm quartz tube. The latter was inserted to within 2.5 cm of the closed end of the retort vessel and used as the inlet for the retort vessel gas atmosphere. A 15 mm quartz tube was sealed to the side of the vessel near the open end to provide an exit for the gases and vapors generated during retorting. A Pyrex glass system including an oil trap and a series array of five standard 30 ml impingers,³ having impinger tips with an internal diameter of 1.05 ± 0.05 mm, was attached to the exit tube for analysis of sulfur dioxide and hydrogen sulfide.

The retort vessel was heated in a nichrome-wound tube furnace having a cylindrical heating chamber 6 cm in diameter by 61 cm in length. Heating rates and soaking temperatures were controlled by an Iveron Pacific Model 2300A programmable set point controller. The temperature sensor was a Type K thermocouple located so that its tip was in the longitudinal center of the furnace hot zone between the furnace wall and the quartz retort.

Analytical Methods

The raw shale was analyzed for forms of sulfur by the method of Smith, Young and Lawlor (SYL)² which involves consecutive determinations of sulfate ion, pyrite sulfur (S₂⁻²) and organic sulfur on the same sample. The sulfate determination began with digesting the oil shale with 100 ml of boiling 10% perchloric acid to dissolve the sulfates. The filtrate was treated with 10 ml of bromine water, boiled to remove the bromine, and then the sulfate was precipitated from the filtrate with 5-10 ml of 10% barium chloride solution. The insoluble residue from the acid digestion was dried at 110°C and then treated stepwise with 50 ml of 0.6 M tetrahydrofuran solution of lithium aluminum hydride, 50 ml of water and then 50 ml of 30% perchloric acid. With the acid addition the mixture was heated and the hydrogen sulfide evolved swept by a nitrogen gas stream into a bubbler containing 250 ml of a 2.9% solution of cadmium sulfate. Titration of the hydrogen ion produced by the precipitation of the cadmium sulfide with standardized 0.1000 M sodium hydroxide led to a value for the concentration of the pyrite sulfur. The dried solid residue from the pyrite sulfur analysis was then analyzed for organic sulfur by mixing and heating with 5.5 g of Eschka mixture⁴ in a 40 ml porcelain crucible at 850°C to oxidize the sulfur. The resulting mass was washed with hot water, the filtrate treated with bromine water, boiled to remove the excess bromine and then barium sulfate precipitated by addition of 10% barium chloride solution. Total sulfur analysis on the raw shale, and later the spent shale, was also carried out by the Eschka fusion method.

For analysis of the spent shale the SYL procedure was modified and extended to include sulfide ion. The bubbler used for the cadmium

sulfide precipitation was replaced by an array of three Impingers of the type described in the Apparatus section, each containing 20 ml of a 3.3% cadmium sulfate solution adjusted to a pH of 3.0 with 0.1 M sulfuric acid solution. The solution was cooled with an ice bath. The amount of cadmium sulfide precipitated was determined iodometrically.³ Also the acid digestion for the first step of the sulfate determination was carried out in a closed system. Thus any hydrogen sulfide produced by the reaction of sulfide ion (S^{2-}) with hydrogen ion was swept into the three impinger array and its concentration subsequently determined. This will be referred to as the ESYL method.

For analyses of the sulfur dioxide and hydrogen sulfide present in the off-gases from the laboratory retort the first impinger contained 20 ml of 3% hydrogen peroxide. The second was filled with glass wool and the remaining three contained 3.3% cadmium sulfate mentioned earlier. The content of the hydrogen peroxide impinger was acidified with 100 ml of 10% perchloric acid, treated with bromine water, boiled to remove the bromine, and then 10% barium chloride solution was added to precipitate barium sulfate. The cadmium sulfide contents of the last three impingers were combined and the sulfide content determined iodometrically.

Retorting Procedure

The ~2.2 g samples used in the retorting experiments were held in shallow platinum pans. Each sample occupied a volume that was about 22 mm wide x 28 mm long x 7 mm deep. Two samples were used for each run. After flushing the retort vessel with ultra high purity grade nitrogen for 4 hr., the furnace was heated to 85°C in 5 min., held at 85°C for 10 min., heated to the desired retorting temperature at 5°C min⁻¹, held at the retorting

temperature for 90 min. and then cooled overnight to room temperature. The nitrogen flow rate during retorting was 14 ml min⁻¹. The entire content of a sample pan was used for each spent shale analysis.

Three runs were made for each temperature giving a total of six separate samples. One sample from each run was used for ESYL analysis. Two samples were used for Eschka fusion analysis and the sixth sample was stored.

RESULTS AND DISCUSSION

Analysis of the raw shale for sulfate, pyrite and organic sulfur by the SYL method produced the results given in Table 1. The predominant types were

TABLE 1. ANALYSIS OF RAW SHALE BY THE SYL METHOD

Sample	Sulfate Sulfur (wt%)	Pyrite Sulfur (wt%)	Organic Sulfur (wt%)	Total Sulfur (wt%)
1	.021	.243	.219	.483
2	.019	.249	.217	.485
3	.019	.259	.223	.501
4	.023	.255	--	--
Mean(s)	.021(2)	.252(7)	.220(3)	.490(10)

pyrite and organic sulfur with sulfate sulfur present in relatively small amounts. Three other samples were analyzed for the production of hydrogen sulfide during the perchloric acid digestion for sulfate analysis. With two of the samples no indication of hydrogen sulfide production was observed during the 60 min digestion. With the third sample a faint trace of yellow cadmium sulfide was observed in the cadmium sulfate bubbler. The amount was not sufficient for analysis. Thus this raw shale did not contain significant amounts of sulfur species

(including pyrrhotite) that could be converted to hydrogen sulfide by acid digestion.

To evaluate the effectiveness of the SYL method for measuring all the sulfur species present, two samples of raw shale were analyzed for total sulfur by Eschka fusion. The mean(s) of the two values was .5305(7)%. Thus the SYL method was successful in speciating about 92.3(1.9)% of the sulfur present in the raw shale.

Retorting experiments in a nitrogen atmosphere were carried out at 350, 500, 650 and 800°C. The weight losses observed with the raw shales on heating and the weight losses due to perchloric acid leaching of the spent shales are given in Table 2. The

TABLE 2. WEIGHT LOSS DUE TO RETORTING AND TO ACID LEACHING OF SPENT SHALE

RETORTING - RAW SHALE	
TEMPERATURE °C	% WEIGHT LOSS
350	2.90 (5)-6
500	12.35 (12)-6
650	16.85 (19)-5
800	37.01 (12)-6

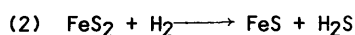
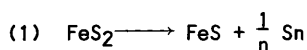
ACID LEACHING - SPENT SHALE	
TEMPERATURE °C	% WEIGHT LOSS
20	53.14 (20)-3
350	52.25 (25)-3
500	52.66 (11)-2
650	48.88 (3)-3
800	31.41 (39)-3

suffixes (e.g. -6) give the total number of samples processed. These data provided an initial measure of

the reproducibility of the retorting conditions. The standard deviations indicated consistent retorting performance.

The average values for the analyses of the spent shales for sulfate sulfur, sulfur in hydrogen sulfide obtained during digestion for the sulfate analysis (sulfide sulfur), pyrite sulfur and residual sulfur are tabulated and plotted in Figure 1. The residual sulfur was that obtained during the last step in the ESYL analysis and was designated earlier in the raw shale analysis as organic sulfur. These and all following analytical results are calculated on the basis of the raw shale samples weight. The standard deviation error bar for each point extends from 1 s below to 1 s above the point.

The sulfate sulfur values were relatively low as with the raw shale. This is consistent with the non-oxidizing nitrogen atmosphere in the retorting vessel. The pyrite sulfur decreased about 20(4)% on heating at 350°C. The average overall decrease in pyrite in the 500-650°C region was about 48(10)% while the overall decrease from 20°C to 800°C was about 83(4)%. The residual sulfur also decreased significantly at 350°C and to a much greater extent at the higher temperatures. As the pyrite sulfur and residual sulfur decreased, sulfide sulfur appeared in the spent shale. Possible mechanisms for sulfide sulfur formation include the thermal decomposition of iron pyrite and the reduction of iron pyrite with hydrogen,⁵ the latter being obtained primarily from cracking of the organic material.



The sulfide sulfur values found in the retorted shale exceeded the theoretical yields for Iron(II) sulfide in the above reactions. This was revealed by

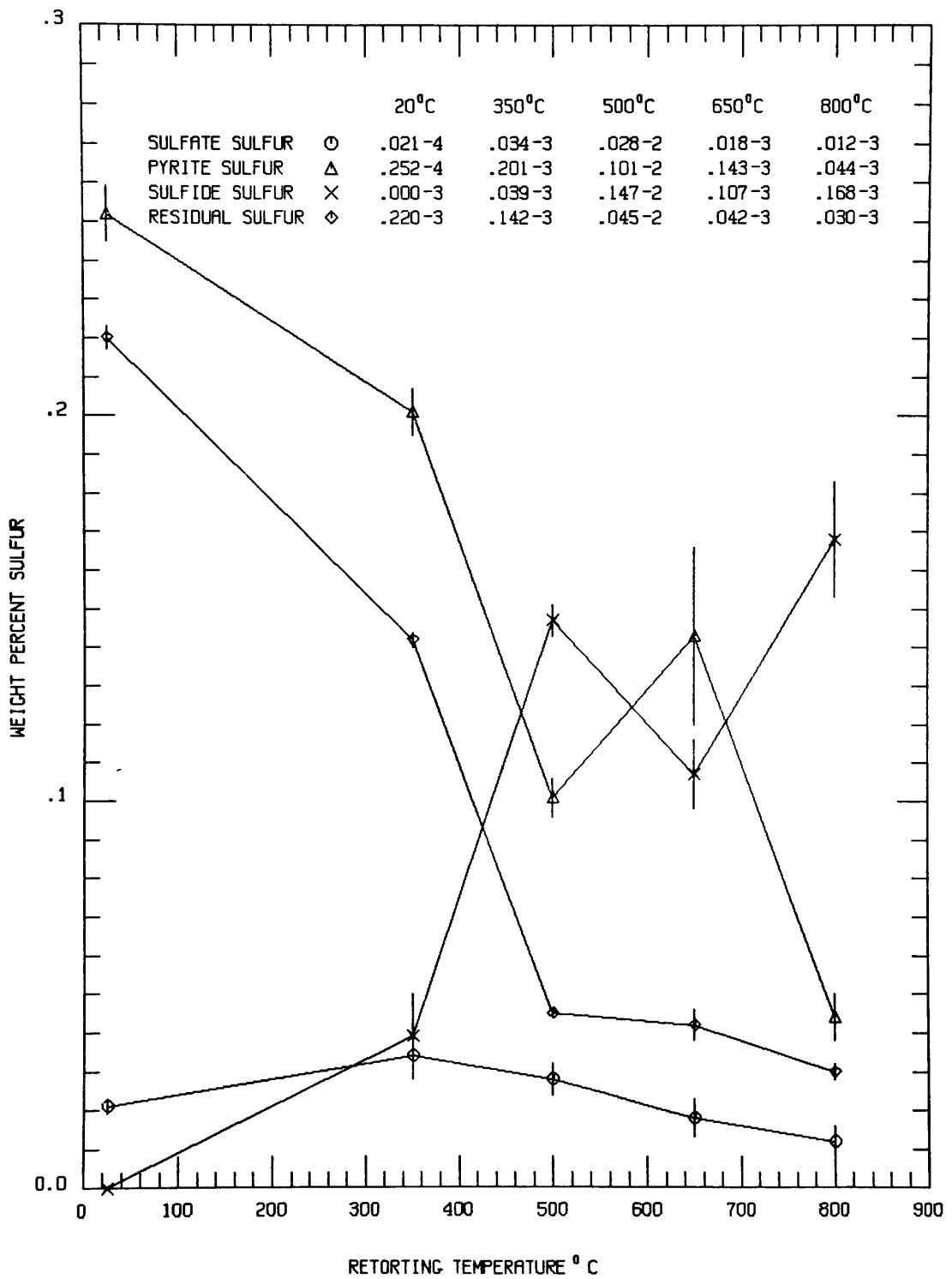
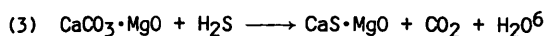


Figure 1. Weight percent values for sulfur species in spent shales retorted in a nitrogen atmosphere.

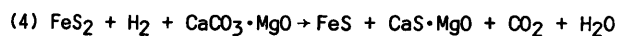
the experimental sulfide/theoretical iron(II) sulfide quotients given below. The theoretical iron(II) sulfide values were obtained by dividing the iron pyrite sulfur consumed by two.

<u>350°C</u>	<u>500°C</u>	<u>650°C</u>	<u>800°C</u>
1.51(29)	1.94(2)	2.03(50)	1.61(10)

The additional sulfide ion formed could result from the reaction of hydrogen sulfide with half-calcined dolomite on the surfaces of dolomite crystals.



Close coupling between reactions (2) and (3) is suggested by the 2:1 ratio's obtained at 500° and 650°C. Gas phase transport of one-half of the sulfur of the iron pyrite as hydrogen sulfide to the half-calcined dolomite could lead an exchange reaction involving H₂S and carbonate ion with the following net result.



Thus for this shale all of the hydrogen sulfide produced in the off-gases at 500 and 650°C may have come from the organic material.

Data were also obtained on the total sulfur content of the spent shale samples by Eschka fusion.

These data are given in Table 3 accompanied by values for total sulfur obtained by addition of speciated sulfur values for each temperature given in Figure 1. The percent sulfur speciated as calculated from these data is given in the next column of Table 3. For the lower three retorting temperatures most of the sulfur present in the raw shale was accounted for as a combination of sulfate, sulfide, pyrite and residual sulfur with the percent speciated being about the same as with raw shale. At 800°C however a significant amount of sulfur apparently was present in a form(s) other than those determinable by the ESYL method.

The decrease in Total Sulfur-Eschka Fusion from 20°C to 350°C was about one-half that found at the three higher temperatures where the total sulfur remaining in the solid residue was essentially constant. Thus it appeared that almost all of the volatile sulfur compounds were removed by 500°C. The final column contains values of percent sulfur speciated relative to the raw shale. These values are lower of course than those of the preceding column since the volatile sulfur-containing organic materials, sulfur dioxide, hydrogen sulfide and other volatile sulfur compounds lost by the raw shale during heating are not included.

TABLE 3. SULFUR IN RAW AND RETORTED SHALE

Retort Temperature	Total Sulfur Eschka Fusion (wt%)	Total Sulfur SYLE (wt%)	Sulfur Speciated in Retorted Shale (wt%)	Sulfur Speciated Relative to Raw Shale (wt%)
20°C	.531(1)-2	.490(10)-4		92.3(1.9)
350°C	.440(11)-2	.416(6)-3	94.5(2.7)	78.3(1.1)
500°C	.350(8)-2	.320(6)-2	91.4(1.7)	60.3(1.1)
650°C	.357(4)-2	.310(20)-3	86.8(5.7)	58.4(3.8)
800°C	.351(1)-2	.253(7)-3	72.1(2.0)	47.6(1.3)

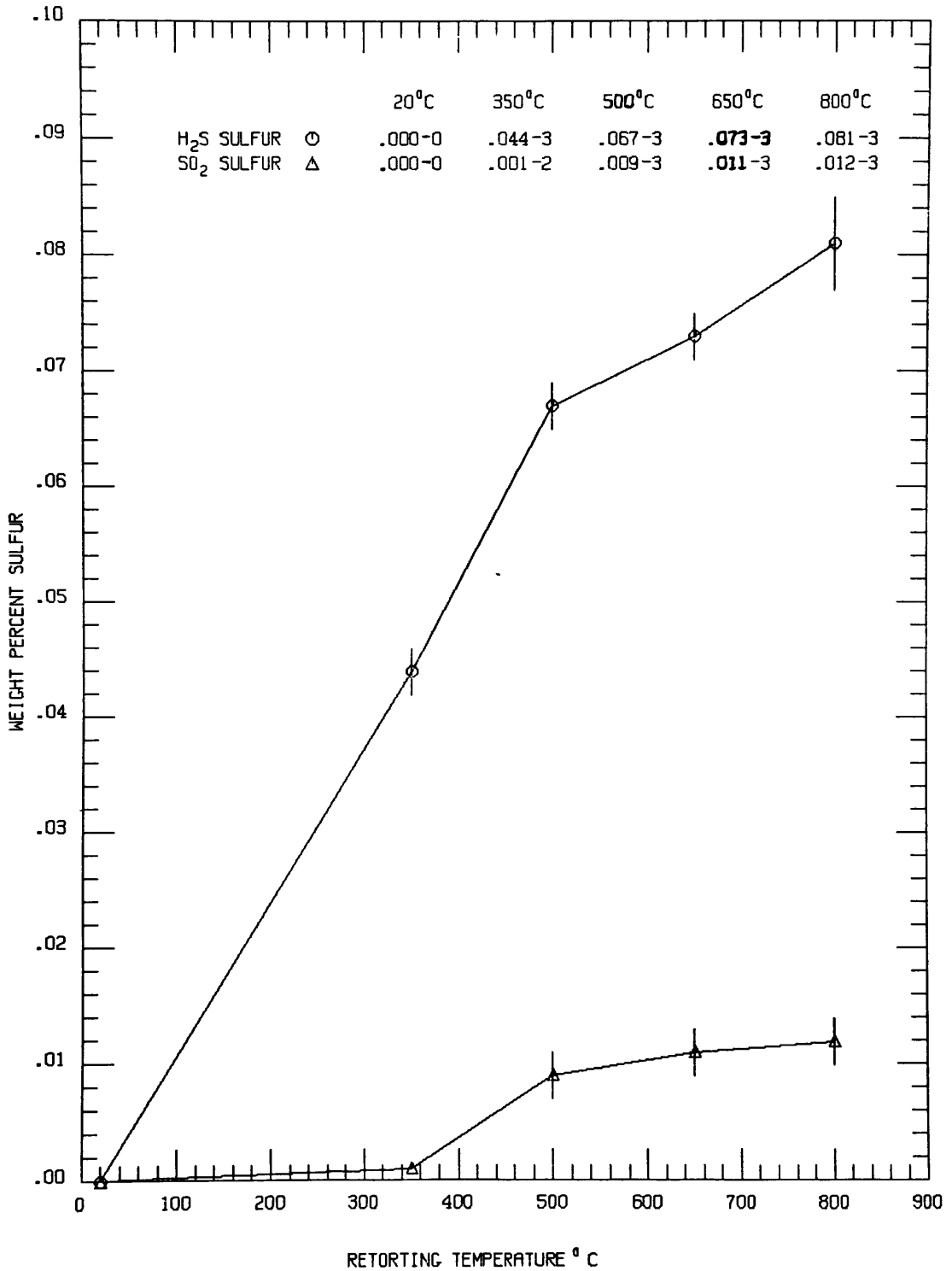


Figure 2. Weight percent sulfur in H₂S and SO₂ in retort off-gas from retorting experiments in a nitrogen atmosphere.

Average values for retort off-gas hydrogen sulfide sulfur and sulfur dioxide sulfur are tabulated and plotted with 2s error bars in Figure 2. While a significant amount of hydrogen sulfide sulfur was obtained at 350°C, the yield was substantially higher in the 500 to 800°C region. Much smaller amounts of sulfur dioxide sulfur were obtained but again the values for the 500 to 800°C region were significantly larger than the 350°C value.

When the off-gas hydrogen sulfide and sulfur dioxide weight percent values are added to those for sulfate, sulfide, pyrite and residual sulfur in the spent shale the values for percent sulfur speciated with respect to the raw shale increased to 86.8(1.2)% for 350°C, 74.6(1.3)% for 500°C, 74.2(2.0)% for 650°C and 65.2(1.6)% for 800°C.

SUMMARY

The process chemistry of sulfur was investigated in a series of laboratory scale, oil shale retorting experiments carried out in a nitrogen atmosphere at 350, 500, 650 and 800°C. The oil shale used had a Fischer assay oil yield of 24.9 gal ton⁻¹ and a total sulfur content of 0.531(1)%. The spent shale was analyzed wet-chemically for pyrite sulfur, sulfide sulfur, sulfate sulfur and "residual" sulfur. About 90% of the sulfur in the spent shale was accounted for by these species at the lower temperatures and about 70% with the 800°C product. It is believed that this is the most detailed analysis to date for the sulfur species in spent oil shale.

The retort off-gas was analyzed wet-chemically for hydrogen sulfide and sulfur dioxide. About 8% of the total sulfur in the raw shale was converted to hydrogen sulfide at 350°C and about 14% at the higher temperatures. Conversion of raw shale sulfur to sulfur dioxide ranged from about 0.2% at 350°C to about 2% at 800°C. When the values for hydrogen

sulfide and sulfur dioxide were added to those of the pyrite, sulfide, sulfate and residual sulfur from the spent shale about 87 (350°C) to 65% (800°C) of the total sulfur in the original raw shale was accounted for. The sulfur totals did not include the sulfur in the shale oils produced.

Also a possible mechanism for the net reaction between iron pyrite and half-calcined dolomite is suggested.

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