1 of 1

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Advanced Sulfur Control Concepts in Hot-Gas Desulfurization Technology

Quarterly Report
April - June 1994

Douglas P. Harrison

July 1994

Work Performed Under Contract No.: DE-AC21-94MC30012

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Louisiana State University
Department of Chemical Engineering
Baton Rouge, Louisiana

MASTER

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EXECUTIVE SUMMARY

The primary objective of this research project is the direct production of elemental sulfur during the regeneration of known high temperature desulfurization sorbents. The contract was awarded to LSU on April 12, 1994, and this quarterly report covers accomplishments during the first 2½ months of the project. The overall project is divided into five tasks containing twelve subtasks. Tasks 1 and 2 are included in the base contract which extends for six months. The remaining tasks, which include the entire experimental effort, comprise a 30-month contract option which may be exercised at the conclusion of the base contract.

Effort during the initial 2½ month period has been limited to Tasks 1 and 2, and involves a search of the literature to identify concepts for producing elemental sulfur during regeneration of known metal oxide sorbents and a thermodynamic evaluation of these concepts. While searching and evaluating the literature is a continuing process, concentrated effort on that phase is now complete and a detailed summary is included in this report. Three possible concepts for the direct production of elemental sulfur were identified in the LSU proposal, and the literature search has not uncovered any additional concepts. Thus, the three concepts being investigated involve: (1) regeneration with SO_2, (2) regeneration with mixtures of O_2 and H_2O, and (3) regeneration with H_2O. While concept (3) directly produces H_2S instead of elemental sulfur, the concept is included because the possibility exists for converting H_2S to elemental sulfur using the Claus process. Each of the concepts will ultimately be compared to the Direct Sulfur Recovery Process (DSRP) under development by RTI. DSRP involves initial sorbent regeneration to SO_2, and the inclusion of additional processing steps to reduce the SO_2 to elemental sulfur.

Thermodynamic analysis is being used to evaluate the feasibility of using specific desulfurization sorbents with each of the regeneration concepts. The thermodynamic analysis began using the simple single reaction equilibrium constant approach, and has subsequently shifted to a generalized free-energy minimization technique. The two methods produce comparable results when the reacting system is simple, but free-energy minimization is a more powerful tool in complex reacting systems such as those involved in high temperature desulfurization and regeneration. Effort on the free energy minimization analysis is continuing and results to date are summarized in this report.

Tin oxide, SnO_2, is a known desulfurization sorbent, and, according to the literature, elemental sulfur can be produced during regeneration. The free-energy minimization analysis has confirmed that elemental sulfur may be produced using either regeneration with SO_2 or with O_2-H_2O mixtures, and has defined the temperature, pressure, and regeneration gas composition ranges needed to maximize sulfur formation.

Zinc oxide, ZnO, is well-known for its ability to reduce H_2S concentrations to quite low levels during the desulfurization phase. Much of the previous high temperature desulfurization research has utilized ZnO, either alone or in various mixed oxide forms ($ZnFe_2O_4$ and $ZnO•xTiO_2$) because of its high affinity for sulfur. This same high affinity, however, renders

the direct production of elemental sulfur during regeneration quite difficult. We have found no literature references in which elemental sulfur production is claimed, and the thermodynamic analysis has failed to identify any conditions under which significant concentrations of elemental sulfur can be formed during ZnS regeneration.

LITERATURE SEARCH

Computer aided literature searches of the Chemical Abstracts and NTIS data bases have been carried out to identify possible concepts for elemental sulfur production during sorbent regeneration and to collect applicable data from the literature. In addition, the computer-aided searches have been supplemented by manual searching of recent (1987 - 1994) Chemical Abstracts volumes.

As might be expected, the literature contains many papers which address the desulfurization phase of the cyclic process. There are relatively few papers, however, which address the regeneration phase and still fewer which examine the formation of elemental sulfur during regeneration. The literature search failed to identify any regeneration concepts to produce elemental sulfur other than those identified in the original LSU proposal. These concepts, and the generic reactions involved in each, are classified as follows:

(1) Regeneration With SO_2

$$2MeS(s) + SO_2(g) \leftrightarrow 2MeO(s) + \frac{3}{2}S_2(g)$$

(2) Regeneration With H_2O-O_2 Mixtures

$$MeS(s) + \frac{1}{2}O_2(g) \leftrightarrow MeO(s) + \frac{1}{2}S_2(g)$$

$$MeS(s) + \frac{3}{2}O_2(g) \leftrightarrow MeO(s) + SO_2(g)$$

$$MeS(s) + H_2O(g) \leftrightarrow MeO(s) + H_2S(g)$$

$$SO_2(g) + 2H_2S(g) \leftrightarrow 2H_2O(g) + \frac{3}{2}S_2(g)$$

(3) Regeneration With H_2O

$$MeS(s) + H_2O(g) \leftrightarrow MeO(s) + H_2S(g)$$

The sulfur product using concept (3) is $H_2S(g)$ instead of elemental sulfur. The concept is included, however, because Claus technology for converting H_2S to elemental sulfur is well established commercially.

The following presentation is divided among the three regeneration concepts with an additional section summarizing the DSRP concept. Each significant paper identified in the literature search is briefly summarized.

Regeneration With SO_2

A. Schrodt, J.T., and Best, J.E., "Sulfur Recovery from Fuel Gas Desulfurization Sorbent," AIChE Symposium Series, 74 (No. 175), 189 (1978).

This article describes a fly ash (Fe_2O_3 active species) sorbent, which was regenerated with SO_2. Schrodt dismisses the concept because the equilibrium conversion of SO_2 is small at the regeneration temperature. Hence, the regeneration gas would have to be cooled, sulfur removed, then reheated and recycled.

B. Tseng, S.C., Tamhankar, S.S., and Wen, C.Y., "Kinetic Studies on the Reactions Involved in the Hot Gas Desulfurization Using a Regenerable Iron Oxide Sorbent II. Reactions of Iron Sulfide With Oxygen and Sulfur Dioxide," Chem. Eng. Sci., 36, 1287 (1981).

The sorbent was 45% Fe_2O_3/55% SiO_2, and the experimental study utilized a TGA reactor. Regeneration with SO_2 was studied over the temperature range of 760 - 860°C at 1 atm using 62.5% SO_2/balance N_2. Regeneration proceeded in two stages beginning with the formation of Fe_3O_4 and then Fe_2O_3. The reaction was first order in SO_2 and the global rate depended on particle size, indicating that diffusion was important. Data obtained from powdered sorbent were used to estimate the temperature dependence of the rate constant while pellet data were used to estimate effective diffusivity. The global reaction rate using SO_2 was much smaller than the global rate using O_2.

C. Anderson, G.L., Garrigan, P.C., and Berry, F.O., "Elemental Sulfur Producing High Temperature Fuel Gas Desulfurization Sorbent," Proc. of the 17th Intersociety Energy Conversion Engineering Conf., pp. 869-873, 1982.

Regeneration of sulfided zinc aluminate and zinc chromite spinels was studied at 982°C using 13% SO_2. The sorbent was capable after 40+ cycles of removing about 10% of the stoichiometric maximum H_2S from the feed gas. The per cent elemental sulfur appearing in the regeneration product gas increased with increasing temperature and decreasing SO_2 partial pressure. At 980°C and moderate SO_2 pressure, 50% of the total sulfur appeared as elemental sulfur. At temperatures below 760°C, negligible elemental sulfur was obtained.

D. Anderson, G.L., and Berry, F.O., "Development of a Hot Gas Cleanup System," Proc. of the 7th Annual Gasification and Gas Stream Cleanup Systems Review Meeting, DOE/METC-87/6079, Vol. 2 (DE87006496), August 1987.

Two sorbents, cobalt titanate on titania and zinc oxide on zinc aluminate were studied. In the desulfurization cycle, fuel gas passes first through the cobalt titanate bed where 67% of the H_2S is removed and then through the ZnO bed where H_2S concentration is reduced to less than 20 ppm.

The ZnO bed is regenerated to SO_2 with O_2. The resulting SO_2 is combined with recirculating SO_2 to regenerate the cobalt titanate bed to elemental sulfur. Sulfur is removed by condensation, and unreacted SO_2 is recycled.

Cobalt titanate regeneration was carried out at 870°C with a variety of N_2/SO_2 mixtures, and the composition of the product gas approached equilibrium. Elemental sulfur production decreased with increasing SO_2 pressure. At $P_{SO_2} = 0.2$ atm, the production rate was $\sim$ 0.9 mol S/mol SO_2 while at $P_{SO_2} = 1$ atm, the production rate was $\sim$ 0.3 mol S/mol SO_2.

Economic estimates for a 100 MW coal gasification - MCFC plant estimated the sulfur recovery cost to be $277/ton S and that the process added 20.3 mills/kwh to the cost of electricity.

E. Ayala, R.E., and Gal, E., "Process and Apparatus for the Recovery of Sulfur and Reusable Metal Oxide from Spent Sulfide Sorbents," Can. Pat. Appl. 2,055,930, Jan. 1993.

The process comprises introducing a first gas containing SO_2 and O_2 in a concentration less than the stoichiometric amount required for complete oxidation of the spent sulfide into the first regeneration stage to generate elemental S, and introducing a second gas containing SO_2 and excess O_2 for complete oxidation of the sulfide into the second regeneration stage. S(g) formed in the first stage is removed prior to introducing the second gas. An O-containing gas is then introduced into the third stage for cooling and purging the reusable oxide. Gases rich in SO_2 and lean in O, derived from the regeneration stages, are removed from the regenerator as off-gas, and recycled as first and second gas into the regenerator.

F. Fitting, A., and Hirsch, M., "Sulfur Recovery from Sulfidic Materials in a Recirculating Fluidized Bed," Ger. Offen. DE 3,926,723, Feb. 1991.

The sulfidic raw materials are added to the upper part, and the recirculating gas containing O and SO_2 are added to the lower part of the reactor. The amount of O is controlled to be sufficient for both the oxidation of the Fe in the sulfidic materials and for supplying the required process heat by partial oxidation of S to SO_2. The S(g) and SO_2-containing suspension from the top of the reactor are separated in a cyclone. The separated solids are returned to the central section of the reactor, the gas is cooled to condense the S, and most of the residual SO_2-containing gas is recirculated to the reactor as fluidizing gas. The desulfurized solids are drawn off from the bottom of the reactor.

G. Patrick, V., and Gavalas, G.R., "Reduction, Sulfidation, and Regeneration of Mixed Iron-Aluminum Oxide Sorbent," Ind. Eng. Chem. Res., 32, 519-532, 1993.

The addition of Al_2O_3 is said to stabilize the oxidation state of Fe, which is desirable because the oxide with the higher oxidation state will produce a lower level of H_2S in the effluent gas during sulfidation. Fe_2O_3 is also interesting because of the possibility of regenerating with SO_2.

The reactor was a 1 cm ID quartz tube containing 4 to 6 cm of a mixture of sorbent granules and inert alumina particles. Sulfidation was studied at 600 - 650°C using a feed gas containing H_2, H_2O, H_2S and N_2 at a rate of $\sim$ 200 cm^3/min (STP). The outlet H_2S level prior to breakthrough was $<$ 80 ppm at 600°C and was maintained for several cycles. Sorbent conversion at breakthrough was 40-60%. At 650°C, the H_2S level was $<$ 100 ppm up to sorbent conversions of 40%. The performance was much better than for sorbents made with pure Fe_2O_3.

Regeneration was carried out using air-N_2, air-H_2O, SO_2-air and pure SO_2. Regeneration with 20 cm^3/min of pure SO_2 was carried out at 700°C, and the elemental sulfur recovery was within $\pm$ 5% of the theoretical amount. With a regeneration gas consisting of 94% SO_2, 1% O_2 at 700°C, the elemental sulfur recovery was 80% of that obtained with pure SO_2. Reaction of FeS with SO_2 is much slower than reaction with O_2.

H and I. Copeland, R.J., "High Temperature Regenerable H_2S Removal Agents," U.S. Pat. 5,271,907, Dec. 1993.

Copeland, R.J., "High Temperature H_2S Removal," Proceedings of the Symposium on Coal Fired Power Systems' 93 - Advances in IGCC and PFBC, Morgantown WV, June 1993.

The process uses two sorbent beds, one containing zinc ferrite and the other stannic oxide. The sulfided zinc ferrite is regenerated to SO_2, which is then used to regenerate the SnS to elemental sulfur. Desulfurization occurs first over SnO_2 where the H_2S concentration is reduced from 10,000 - 30,000 ppm to about 200 - 1000 ppm (90 - 99% removal). Partially desulfurized gas is then contacted with zinc ferrite where the H_2S content is lowered to less than 20 ppm (99.8% removal).

Sulfided zinc ferrite is regenerated with air to produce SO_2 with the SO_2 used to regenerate SnS to produce elemental sulfur. The patent describes a process for the recovery of tin and refabrication of the sorbent pellet, which is necessary because of sintering after about 20 cycles. Using pure SO_2 the SnS regeneration reaction at 850K was 35% complete after 1 hr, 68% complete after 5 hrs, and 94% complete after 10 hrs. At 973K, regeneration was 97% complete in 1 hr, and 98% complete in 2 hrs.

Refabrication is expected to be required after about 20 cycles. Refabrication is accomplished by converting the SnS to $SnSO_4$ using H_2SO_4, and then decomposing the $SnSO_4$ to SnO_2 at 360°C. The process can be carried out in fixed bed, moving bed, or fluidized bed reactors.

Regeneration With O_2 and Steam

A. Joshi, D.K., et al., "Hot Low-Btu Producer Gas Desulfurization in Fixed-Bed of Iron Oxide-Fly Ash," DOE/FE-2257-3, 1979.

The sorbent was 40% Fe_2O_3 on silica gel which had previously been sulfided. At 538°C using 95% H_2O and 5% air at a gas hourly space velocity (STP) of 600, 75% of the sulfur in the regeneration gas was in elemental form.

B. Schrodt, J.T., "Hot Gas Desulfurization (I) Use of Gasifier Ash in a Fixed Bed Process," DOE/ET/10463-Ti (1980).

Using previously sulfided fly ash sorbent, elemental sulfur yields up to 30% during regeneration are reported.

C. Grindley, T., and Steinfeld, G., "Development and Testing of Regenerable Gas Desulfurization Sorbents," DOE/MC/16545-1125, 1981.

The sorbent, 45% Fe_2O_3 on SiO_2, was studied in the METC 2-inch fixed-bed reactor. They report the following regeneration results:

a) 95% steam/5% air at inlet temperature of 538°C. Virtually all of the sulfur was liberated in 39 hours, approximately 75% as elemental sulfur and the bulk of the remainder as H_2S.

b) 90% steam/10% air gave complete regeneration in 20.5 hours yielding ~ 15% elemental sulfur and the rest divided equally between H_2S and SO_2.

c) 50% steam/50% air gave complete regeneration in 7.5 hours with only ~ 1.5% of the sulfur in elemental form and the bulk of the remainder as SO_2.

D. Geus, J.W., and Van der Waal, W.J.J., "Desulfurization of Synthesis Gas by Iron Oxide Absorbent," Proc. of the 8th International Conference on Catalysis, 2, II245 - II256 (1985).

The sorbent was hydrated Fe_2O_3 on silica gel containing 10 to 50% Fe_2O_3 prepared by injection of $Fe(NO_3)_3$ into a suspension of silica at pH of 5.8 - 6.2. The product was calcined at 500°C and small particles of Fe_2O_3 were well dispersed over the support.

Desulfurization was studied at 400°C using a gas containing 1% H_2S. Fe(III) was reduced to Fe (II). The water gas shift reaction occurred to some extent. Some COS was formed but it tended to hydrolyze to CO_2 and H_2S. The sulfur capacity ranged from 0.3 to 0.5 (S/Fe) depending on iron loading, and was lower at high iron loading.

Regeneration was studied at 250°C using 1% O_2 in N_2, and the product sulfur was exclusively in elemental form. Gas phase oxidation of sulfur vapor began at 250 - 300°C. Careful control of O_2 content was necessary at the end of the regeneration to avoid formation of SO_2. Some of the SO_2 formed tended to react with FeS to give elemental sulfur.

The sorbent was stable after many sorption/regeneration cycles. Pseudo first order rate constants are reported. The vapor pressure of sulfur at 250°C is only ~ 15 mm Hg so that the sulfur content of the regeneration gas was quite low.

E. Van der Waal, W.J.J., "Desulfurization of Process Gas by Means of Iron Oxide on Silica Sorbents," Ph.D. Dissertation, University of Utrecht, 1987.

The reactions were studied in a micro-fixed bed reactor, a 1 cm diameter quartz tube, holding 2 cm^3 of sorbent. Effects of temperature (200 - 500°C), O_2 content of the regenerating gas, space velocity, and sorbent structure were studied, and key observations follow:

a) For unsupported Fe_2O_3 the S/SO_2 ratio was unity for the first regeneration run, falling to 0.3 after five sulfidation/regeneration cycles.

b) For supported Fe_2O_3 the S/SO_2 ratio was much larger, depending on O_2 content of the regeneration gas.

c) Low temperature, low O_2 content, and high space velocity increased the yield of elemental sulfur. At 250°C, no SO_2 formed, but the sorbent was soon coated with liquid sulfur so that regeneration was incomplete.

F. Kay, D.A.R., and Wilson, W.G., "Method for the Regeneration of Sulfided Cerium Oxide Back to a Form That is Again Capable of Removing Sulfur from Fluid Materials," U.S. Patent 4,857,280, Aug. 1989.

The CeO_2 sorbent is first reduced to a composition between ceric (CeO_2) and cerous (Ce_2O_3) forms. This material reacts with H_2S to form an oxysulfide (Ce_2O_2S). Sulfidation was studied at 800°C with a feed gas containing 1% H_2S. Two levels of desulfurization were achieved. For ~ 15 minutes, the effluent gas contained < 50 ppm H_2S. The H_2S content then rose to 1500 ppm at 20 minutes and to 3000 ppm at 60 minutes.

Regeneration was carried out at > 900°C to avoid $Ce_2(SO_4)_3$ formation and below 1250°C to avoid sintering. At 920°C using a regeneration gas containing 20% O_2 and 80% N_2, sulfur was observed at the top of the reactor early in the reaction. After about 35 minutes no more elemental sulfur was observed.

Formation of elemental sulfur is by the reaction $Ce_2O_2S + O_2 \rightarrow 2CeO_2 + \frac{1}{2}S_2$ and the competing reaction is $Ce_2O_2S + \frac{1}{2}\frac{3}{2}O_2 \rightarrow 2CeO_2 + \frac{1}{2}SO_2$. No quantitative information on the amount of elemental sulfur is given.

G. Kay, D.A.R., Wilson, W.G., and Jalan, V., "High Temperature Thermodynamics and Applications of Rare Earth Compounds Containing Oxygen and Sulfur in Fuel Gas Desulfurization and SO_x and NO_x Removal," J. of Alloys and Compounds, 192, 11 (1993).

The paper summarizes thermodynamic data for the Ce-O-S and La-O-S systems. Various oxides, sulfides, and Ce_2O_2S are included. Standard free energies of formation based directly on experimental data in the 1071 - 2000K range are given for cerium. Calculated value of $\Delta H_f°$, S°, and C_p are also presented. The authors conclude that CeO_2 should be a good sorbent for fuel gas, forming Ce_2O_2S when sulfided.

Experiments on fuel gas desulfurization using a microreactor reduced the H_2S concentration from 10,000 to 900 ppm using CeO_2 at 900°C, from 10,000 to 650 ppm using CeO_2/10% La_2O_3 at 800°C, and from 10,000 to 400 ppm using CeO_2/10% La_2O_3 at 1000°C. When the Ce_2O_2S was regenerated under "O_2-starved" conditions, elemental sulfur was obtained.

Literature sources of the thermodynamic data are given.

H. Wilson, W.G., Recent Calculations of Concentrations of H_2S in Equilibrium With CeO_2," Personal Communication, July 1994.

Thermodynamic calculations based on new data are included [Kay and Davivedi; Knacke Kubaschewski and Hasselmann]. Equilibrium H_2S concentration is reported as a function of fuel gas quality factor [QF = % (CO + H_2)/% (CO_2 + H_2O)].

At 800°C, old data gave H_2S concentrations from 1000 ppm at QF = 2 to 8.5 ppm at QF = 25. At the same temperature the new data give ~ 32 ppm at QF = 2 and 5 ppm at QF = 25. Microreactor experiments confirm a low H_2S concentration for 30 - 50 minutes at the start of desulfurization runs. Particularly encouraging were experiments using CeO_2/10%•SrO.

First run: ~ 10 ppm H_2S for 210 minutes
Second run: ~ 20 ppm H_2S for 50 minutes rising to ~ 250 ppm until 200 minutes
Third run: similar to second.

The rise to 250 ppm is attributed to formation of a Ce_2O_2S shell on the surface of sorbent particles, which suggests the need for a high surface area form of sorbent.

I. Wilson, W.G., "Recent Developments in Desulfurization of Fuel Gases With Cerium Oxide," Personal Communication, July 1994.

This is a follow-up of the previous presentation (item F). Microreactor runs show low H_2S (~ 10 ppm) for ~ 50 minutes, in agreement with thermodynamic calculations. This is followed by a rise to ~ 250 ppm until 200 min. The rise is attributed to low surface area and SrO dopant coming out of CeO_2 solution. Methods are described for making a high surface area CeO_2 in the form of nanometer crystals on Al_2O_3. However, high temperature regeneration (> 800°C) causes loss of surface area, and a reaction between Al_2O_3 and CeO_2, which destroys the ability of CeO_2 to desulfurize fuel gases.

Thermodynamic calculations indicate that low temperature regeneration can lead to formation of elemental sulfur without damaging the ability of CeO_2 to remove H_2S.

Regeneration With H_2O/Conversion of H_2S to Elemental Sulfur

A. Ganguly, N.D., and Bannerjee, A.C., "Recovery of Sulfur from Iron Pyrite," Ind. Eng. Chem. Process Des. Devel., 12, 56 (1973).

This paper reports on the reaction of FeS_2 with H_2O at 900 - 1100°C. At 1000°C, 1 atm, 33.2 x 10^4 v/v/hr space velocity, and 15 minute reaction time, 84.5% of the total sulfur was recovered as elemental sulfur and 13.7% as H_2S/SO_2. The effluent gas also contained an appreciable amount of H_2.

B. Tamhankar, S.S., Garimella, S., and Wen, C.Y., "Kinetic Study on the Reactions Involved in Hot Gas Desulfurization Using a Regenerable Iron Oxide Sorbent III. Reactions of the Sulfided Sorbent With Steam and Steam-Air Mixtures," Chem. Eng. Sci., 40, 1019 (1985).

The regeneration was studied in a TGA and the reaction was believed to be $3FeS + 4H_2O \rightleftharpoons Fe_3O_4 + H_2 + 3H_2S$. The formation of Fe_3O_4 (only) was confirmed by Mossbauer spectroscopy.

The sorbent was 45 wt % Fe_2O_3 on SiO_2 and particle sizes ranging from powder to pellets were used. At 550 - 700°C, the reaction was first order in steam. Intrinsic rate constant was determined using the smallest particle size and effective diffusivity was obtained from the pellet data. The reaction was slow compared to air oxidation, requiring a reaction time of hours compared to minutes for air.

C. Sohn, H.Y., and Kim, D., "Intrinsic Kinetics of the Reaction Between Zinc Sulfide and Water Vapor," Metall. Trans. B, 18B, 451 (1987).

The reaction $ZnS + H_2O \leftrightarrow ZnO + H_2S$ was studied in a TGA using $< 1 \mu m$ particles of ZnS. 0.5 to 2.5 L/min of steam - N_2 mixtures were used over the range of 640 - 1200K at 38.5 Pa gage. The reaction was complete in 20 - 80 minutes at temperatures between 1023 and 1160K, and was first order in steam concentration. A rate equation was determined which included a C_{H_2S} term. They did not study the effect of C_{H_2S} so the equation was tested only for $C_{H_2S} = 0$.

D. Wakker, J.P., Gerritsen, A.W., and Moulijn, J.A., "High Temperature H_2S and COS Removal With MnO and FeO on γ - Al_2O_3 Acceptors," Ind. Eng. Chem. Res., <u>32</u>, 139 (1993).

The sorbent is said to be $FeAl_2O_4$ or $MnAl_2O_4$ prepared by impregnating 0.25 to 0.42 mm γ - Al_2O_3 particles with manganese acetate or iron ammonium oxalate followed by calcination in air at 575°C.

The desulfurization reaction is said to be $MeO/Al_2O_3 + H_2S \rightleftharpoons MeS/Al_2O_3 + H_2O$. The reaction was studied at 675 - 1075K with optimum capacity and stability at 875K. Because the reaction is reversible, the presence of H_2O decreases the ability of the sorbent to remove H_2S during desulfurization and creates the possibility for regeneration with steam to give a high concentration of H_2S. No data are given on the regeneration. 400 or more sulfidation/regeneration cycles are claimed.

E. Nielsen, P.E.H., Rudbeck, P., and Christiansen, H. "Steam Regenerable Sulfur Absorption Masses and Their Application in IGCC Plants," paper presented at EPRI Coal Gasification Conference, San Francisco, October, 1991.

H_2S is removed by sorption on SnO_2 by the following reaction:

$$SnO_2 + H_2 + H_2S \rightleftharpoons SnS + 2H_2O$$

Experiments on desulfurization of a simulated coal gas (60% H_2, 16% H_2O, 13% CO, 11% CO_2) at 350 psi and 777°F are reported. H_2S was reduced from 4500 ppm in the feed to ~ 250 ppm in the effluent gas at a space velocity of 2650 hr^{-1}.

Regeneration was carried out by reversing the above reaction at 930°F, 350 psi, and space velocity of 1100 hr^{-1}. 30 moles steam per mole sulfur were required. Mole fraction of H_2S in the regenerator effluent was 0.02 to 0.25.

In a commercial plant, additional processing would be required to seperate the H_2S from the steam and H_2 in the effluent gas. The H_2S wouuld then be sent to a sulfur recovery unit.

DIRECT SULFUR RECOVERY PROCESS

A. Gangwal, S.K., McMichael, W.J., and Dorchak, T.P., "The Direct Sulfur Recovery Process," Envir. Prog., 10, 186 (1991).

RTI, with support from METC, is developing a process in which SO_2 in the regenerator off-gas reacts with sodium aluminate sorbent in an additional fixed bed. This bed can then be regenerated to elemental sulfur. In experiments described, as much as 95% of the sulfur was recovered in elemental form.

B. Lin, C.M.H., Chen, D.H., Hopper, J.R., Agarwal, S.K., Jang, J.L., Ganwal, S.K., and Dorchak, T.P., "Equilibrium Modified Kinetic Analysis for the Direct Sulfur Recovery Process," paper to be submitted to J. of Cat., Dec. 1993.

The DSRP involves reaction of SO_2 with coal gas to form elemental sulfur. This paper describes experimental kinetic studies on the reactions involved. Kinetic data from a mincrocatalytic reactor were analyzed to obtain rate equations. Rate equations for the H_2 - SO_2 and CO-SO_2 reactions represent experimental data within 5% for SO_2 conversion and H_2S selectivity. A mechanistic model was derived to calculate catalyst effectiveness factors. The rate equations and effectiveness factors were used successfully to simulate bench-scale DSRP data using the equilibrium-modified kinetics method.

C. Gangwal, S.K., and McMichael, W.J., "Bench-Scale Testing and Evaluation of the Direct Sulfur Recovery Process," Quarterly Report, Contract DE-AC-21-90MC27224, DOE/METC, June 1993.

The DSRP produces elemental sulfur by reacting regenerator off-gas containing SO_2 with coal gas over an appropriate catalyst. This report describes tests in a bench-scale fixed-bed reactor using 1 liter of catalyst in a 4" schedule 160 pipe. The feed to the reactor was simulated regenerator off gas (2.06% SO_2, 13.11% H_2O, balance N_2) mixed with dry KRW type coal gas (5.9% CO_2, 17.7% CO, 11.8% H_2, 0.6% H_2S).

Temperature (524 - 662°F) and space velocity (1250 - 7500 scc/cc/hr) had little effect on conversion of SO_2 to elemental sulfur. Pressure had a strong effect with conversion to sulfur rising from 18.1% to 96% as pressure rose from 1.7 to 21.4 atm. The optimum reducing gas/SO_2 ratio was 2.0. Maximum conversion of 95.8% was obtained at 627°C, 21.4 atm, 3750 scc/cc/hr, and reducing gas/SO_2 ratio of 2.0. All of these results confirmed earlier laboratory-scale studies in a 1 inch reactor.

Additional experiments were done at high SO_2 concentration (7.5 to 12.4%, balance N_2) mixed with a dry GE/air blown Lurgi gas (16% CO_2, 11.1% CO, 0.6% H_2S, 4.6% CH_4, 22.8% H_2, balance N_2). Temperature and SO_2 concentration had little effect on conversion to elemental sulfur. Increasing pressure, space velocity, and reducing gas/SO_2 ratio all increased the conversion to sulfur. Best results were obtained at 14.6 atm, 2500 scc/cc/hr, 1.84 reducing gas/SO_2 where SO_2 conversion was 88%.

This report refers to an earlier preliminary economic analysis where DSRP was compared with other processes for converting a dilute SO_2 stream to elemental sulfur. The other processes were Wellman Lord/augmented Claus and Wellman Lord/Beavon-Stretford processes. The DSRP can produce a ton of sulfur for considerably less and at lower capital investment than these competing processes.

THERMODYNAMIC ANALYSIS

The purpose of the thermodynamic analysis is to identify candidate sorbents which possess the dual ability of being able to remove H_2S from coal gas with high efficiency, and of producing elemental sulfur directly during the regeneration phase. Extensive thermodynamic analyses of H_2S removal capability have been published, e.g., by Westmoreland and Harrison [Env. Sci. and Tech., 10 659 (1976)], but no comprehensive prior analysis of the regeneration phase has been performed.

Single Reaction Equilibrium Analysis

We began the analysis by using the single reaction, equilibrium constant approach which is illustrated by the following desulfurization and regeneration reactions involving tin oxide sorbent:

$$SnO_2(s) + H_2S(g) + H_2(g) \rightarrow SnS(s) + 2H_2O(g)$$

$$SnS(s) + SO_2(g) \rightarrow SnO_2(s) + S_2(g)$$

Selected results using this approach were reported in the May monthly report for the zinc, iron, manganese, and tin systems.

The well known ability of ZnO to reduce H_2S to quite low concentrations was confirmed. The problem with zinc during the reduction-desulfurization cycle is the tendency for ZnO to be reduced to volatile elemental zinc at high temperature, a problem which has also been confirmed in experimental tests. The single reaction analysis confirmed another known problem encountered during the regeneration of ZnS, namely the strong tendency for $ZnSO_4$ formation. There appears to be little chance of producing high concentrations of S_2 from ZnS using any of the regeneration concepts. Steam regeneration to H_2S is not feasible since it is simply the reverse of the desulfurization reaction which, as previously mentioned, is strongly favored.

Iron has also been studied extensively as a desulfurization sorbent, and iron holds promise for the production of elemental sulfur during regeneration. Single reaction analysis of iron is complicated by the multiple possible oxidation states ranging from Fe_2O_3 to metallic iron. The intermediate oxidation states of Fe_3O_4 and FeO are likely to be stable under most conditions of interest; Fe_3O_4 is more effective for removing H_2S than is FeO, but less effective than ZnO. The iron system does not suffer from the metal volatility problem associated with zinc and the fact that iron sulfate is less stable than $ZnSO_4$ simplifies, at least in principle, the regeneration step. Several literature references indicate that elemental sulfur formation from FeS is possible. This possibility was confirmed by the single reaction thermodynamic analysis so iron is a definite candidate for further consideration.

Analysis of the manganese system showed that MnO is the probable stable oxide throughout the range of conditions of interest. The vapor pressure of elemental manganese is several orders of magnitude less than that of zinc, and the sulfur removal potential of MnO is intermediate to that of ZnO and Fe_2O_3. Sulfate formation will be a problem during regeneration as $MnSO_4$ is somewhat more stable than $ZnSO_4$. While the possibility of producing some elemental sulfur exists, at this time we do not consider manganese as a strong candidate.

On the other hand, tin does appear to be a strong candidate. Although less effective than ZnO for removing H_2S, SnO_2 can achieve reasonably high desulfurization efficiency. Tin sulfate is less stable than the other sulfates and the direct reaction with SO_2 to free elemental sulfur is favored. The temperature response of SnO_2 for desulfurization is opposite that of the other oxides. Instead of the desulfurization capability decreasing monotonically with increasing temperature, the SnO_2 system shows a maximum desulfurization capability at an intermediate temperature. Quantitative results for the desulfurization and regeneration capabilities of tin are presented in the following section.

Free Energy Minimization

Unlike the single reaction, equilibrium constant method of analysis, free energy minimization involves a global approach to determining the overall system equilibrium. For example, free energy minimization of systems characteristic of the reduction-desulfurization cycle will yield the form of the stable oxide and sulfide, and the maximum desulfurization potential. In addition, at a specified temperature and pressure, the overall coal gas equilibrium composition is determined. Equilibration within the gas phase also may have an effect on H_2S removal. For example, if the H_2O content is increased by gas phase reactions within the desulfurization reactor, the H_2S removal capability will be decreased. This method of analysis also identifies conditions at which carbon deposition is likely.

We are currently in the process of utilizing the free energy minimization program, CHEMQ, for the computation of compositions of specified initial mixtures at given temperatures and pressures. The computational method was originally implemented at LSU for NASA and used to study equilibrium compositions produced from ablation heat shields during space vehicle re-entry. An earlier version of this program was used in 1976 by Westmoreland and Harrison (Evaluation of Candidate Solids for High-Temperature Desulfurization of Low-Btu Gases, Environmental Science and Technology, 10, 659, 1976) to examine the desulfurization potential of a number of metal oxides. The current version of CHEMQ is more user friendly and is PC-based.

Implementation of CHEMQ requires the user to specify the composition of the initial mixture, which may include gaseous, liquid, and solid species, and the temperature and pressure combinations of interest. The CHEMQ data base, which currently consists of 1322 species, is searched and all species whose elements are present in the initial mixture are considered. The data for each specie consist of the constants, A_1 through A_7, required to calculate the Gibbs free energy from the equation

$$\frac{F_T^{\circ}}{RT} = A_1(1-\ln T) - \frac{A_2T}{2} - \frac{A_3T^2}{6} - \frac{A_4T^3}{12} - \frac{A_5T^4}{20} + \frac{A_6}{T} - A_7$$

The number of mols of each component are then calculated which minimize the free energy of the system subject to the elemental material balance constraint established by the initial mixture. In the calculation procedure, the gas phase is assumed to be ideal and condensed species are assumed to form pure phases having an activity of 1.0.

The existing data base contains many of the compounds of interest to this study. However, data for some species are missing and we are in the process of enlarging the CHEMQ data base to include the components. Probably the most important missing components are the gaseous sulfur species S_3, S_4, S_5, S_6, and S_7. The existing data base considers gaseous elemental sulfur only as S, S_2, and S_8. In addition, certain condensed phase species involving candidate metals will be added to the data base.

The following discusses results obtained when CHEMQ was used to analyze the thermodynamic feasibility of SnO_2 as a sorbent. Both the reduction-desulfurization and regeneration phases are considered.

In the reduction-desulfurization analysis one mol of tin oxide in the highest oxidation state, SnO_2, was "mixed" and allowed to reach equilibrium with one mol of a Texaco coal gas of the following composition:

H_2S	1.04%	H_2	31.05%
H_2O	16.80%	CO	39.87%
CO_2	10.62%	COS	0.10%
NH_3	0.21%	CH_4	0.31%

For free energy minimization purposes, this is equivalent to an arbitrary mixture having the following elemental proportions:

$Sn = 1$
$O = 2.7801$
$H = 0.9965$
$S = 0.0104$
$C = 0.5090$
$N = 0.0021$

Equilibrium composition was calculated over a temperature range of 750 to 1050K at 1, 5, and 25 atm total pressure. 84 of the 1322 species in the CHEMQ data base met the elemental composition criteria, and 16 of the species were present at equilibrium in significant quantities (mol fraction $\geq 5 \times 10^{-6}$) at at least one of the temperature-pressure combinations considered. Table I lists the 84 species divided into gaseous and condensed phases. The 16 significant species are listed separately at the top of the table.

The five major gaseous species are CO_2, H_2O, H_2, CO, and CH_4, and the mol fraction of each at equilibrium is plotted as a function of temperature at $P = 1$ atm in Figure 1. The temperature interval between successive calculation points varies, with smaller increments near 850K and larger increments at lower and higher temperatures. The smaller increments near 850K and the changes in the component mol fractions near this temperature are due to changes in the species present in the condensed phases. The equilibrium mol fractions of CO_2 and H_2O decrease over the temperature range of 750 to 850K, but increase at higher temperature. CO and H_2 mol fractions show opposite behavior, increasing at low temperature and decreasing thereafter. CH_4 decreases throughout the temperature range and becomes negligible at about 1000K. There is a significant change in the slope of the CH_4 curve near 850K.

Figure 2 indicates in bar chart form the changes which occur in the condensed species over the temperature range of interest. Carbon deposition is thermodynamically favored between 750 and 850K, but no carbon should be deposited at higher temperature. Thus, the end of carbon deposition correlates with the change in the gaseous component mol fractions.

Excess tin oxide should be present as $SnO_2(2)$ at low temperature, but by 820K, $SnO_2(3)$ is the stable oxide form. The tin sulfide product of the desulfurization reaction should be present as SnS(A) to 875K, but as SnS(B) at higher temperature. Reduction of excess oxide to elemental tin liquid, Sn(L), is predicted at 900K and above. The oxide, SnO(s), is by-passed completely, and, by the time elemental tin is formed, the temperature is above the solid melting point. SnS is somewhat volatile and its presence in the gas phase is predicted at temperatures of 850K and higher.

Equilibrium H_2S and total gas phase sulfur concentrations are shown in Figure 3 as a function of temperature and pressure. COS and SnS are the additional gas phase sulfur compounds. At each pressure, the equilibrium concentrations initially decrease with increasing temperature, reach a minimum, and increase thereafter. The minimum sulfur concentration of about 40 ppm at 1 atm occurs near 850K. However, both the minimum sulfur concentration and

Table I
Eighty-Four Species Present in the CHEMQ Data Bank Composed of the Elements Sn, O, H, S, C, and N

Significant Species	($y_i \geq 5 \times 10^{-6}$)		
Gas Phase	CH_4	CO	COS
	CO_2	H_2	H_2O
	H_2S	NH_3	N_2
	SnS		
Condensed Phase	C(gr)	Sn(L)	SnO_2(2)
	SnO_2(3)	SnS(A)	SnS(B)
Other Species	($y_i < 5 \times 10^{-6}$)		
Gas Phase	C	CH	CH_2
	Formaldehyde	Formic Acid	CH_3
	Hydroxymethylene	Methyloxide	Methanol
	CN	NCN Rad	CNN Rad
	CS	CS_2	C_2
	C_2H Rad	Acetylene	Ketene
	C_2H_3 Rad	Methyl Cyanide	CH_3CO Rad
	Cyanogen	CCO Rad	C_3
	C_3H_3 Rad	Cyclopropene	Propyne
	Allene	C_3H_5 Rad	Cyclopropane
	Propylene	Propylene Oxide	1-Propyl Rad
	N- propyl Rad	Propane	1-Propanol
	Carbon Suboxide	C_4	Butadiyne
	Butan - 1 en - 3 yn	Cyclobutadiene	2-Butyne
	1,3-Butudiene	2-Butene Trans	2-Butene Cis
	Isobutene	1-Butene	(Acetic Acid)$_2$
	s-Butyl Rad	N-Butyl Rad	T-Butyl Rad
	Isobutane	N-Butane	Carbon Subnitride
	C_5	Cyclopentadiene	Cyclopentane
	1-Pentene	N-Pentyl Rad	T-Pentyl Rad
	$CH_3C(3H_3)_2$ CH_3	Pentane	Isopentane
	Hexatriyne	Phenyl Rad	Phenoxy Rad
	Benzene	Phenol	Cyclohexane
	N-Hexyl Rad	Benzaldehyde	Toluene
	Cresol	1-Heptene	N-Heptyl Rad
	N-Heptane	1-Octene	N-Octyl Rad
	Octane	Iso-Octane	N-Nonyl Rad
	Napthlene	Azulene	N-Decyl Rad
	O-Biphenyl Rad	Biphenyl	Jet - A(G)
	Bibenzyl	H	HCN
	HCO Rad	HNCO	HNO
	HNO_2	HNO_3	HO_2
	H_2N_2	H_2O_2	H_2SO_4
	N	NO	NO_2
	NO_3	N_2H_2	NH_2NO_2
	N_2O_5	N_3	N_3H
	O	OH	O_2
	O_3	S	SH
	SN	SO	SO_2
	SO_3	S_2	S_2O
	S_8	SN	SNH_4
	SNO		
Condensed Phase	Benzene(L)	Toluene(L)	Octane(L)
	Jet-A(L)	H_2O(s)	H_2O(L)
	H_2SO_4(L)	$N_2H_8SO_4$	S(s)
	S(L)	Sn(s)	Sn(L)
	SnO(s)	SnO_2(1)	SnS(L)
	$SnSO_4$(s)	SnS_2(s)	SnS_2O_8(s)
	Sn_2S_3(s)	Sn_3S_4(s)	

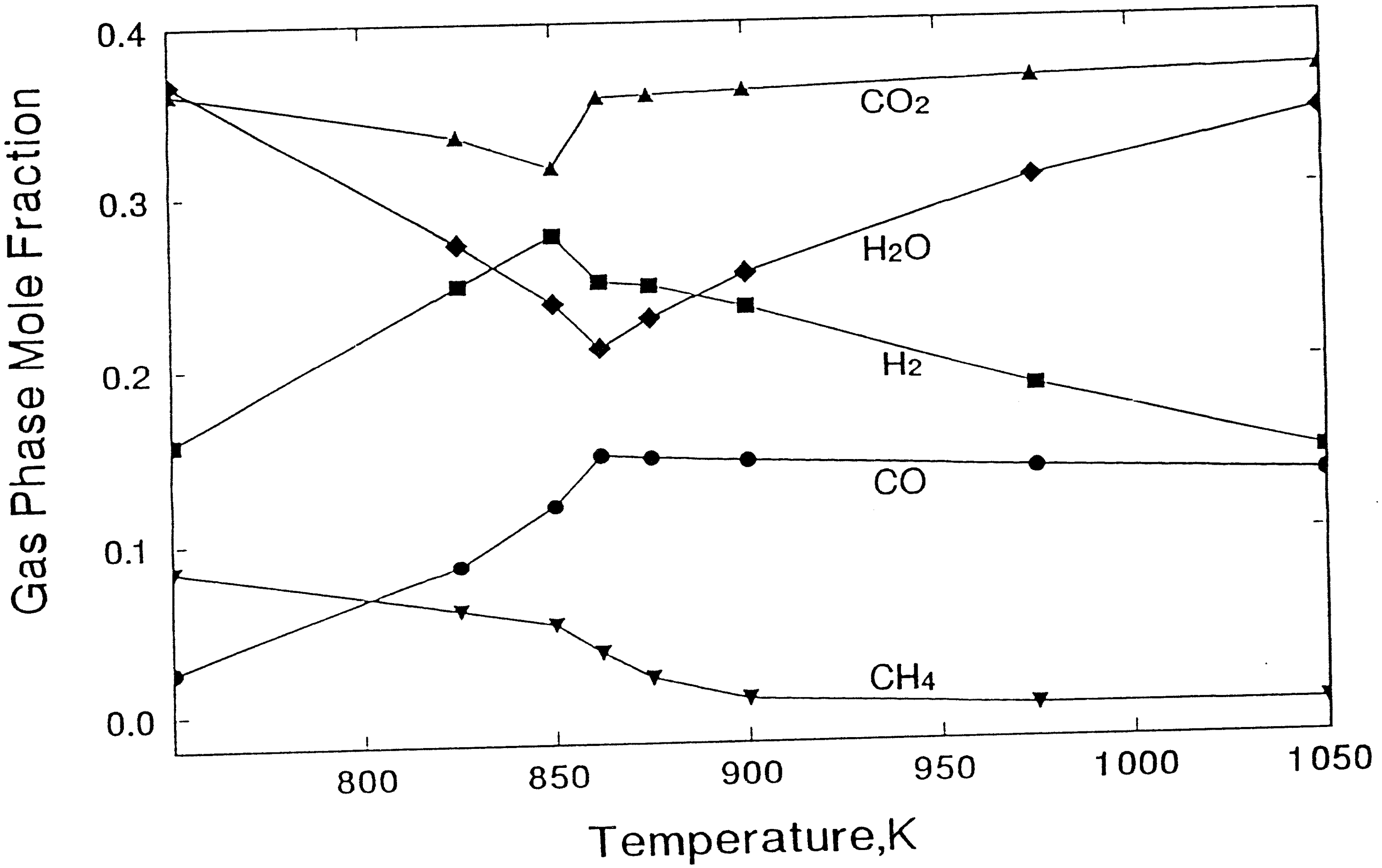


Figure 1. Equilibrium Mol Fractions of the Five Major Gaseous Species at 1 atm: 1 mol of Texaco Gas and 1 mol of SnO_2

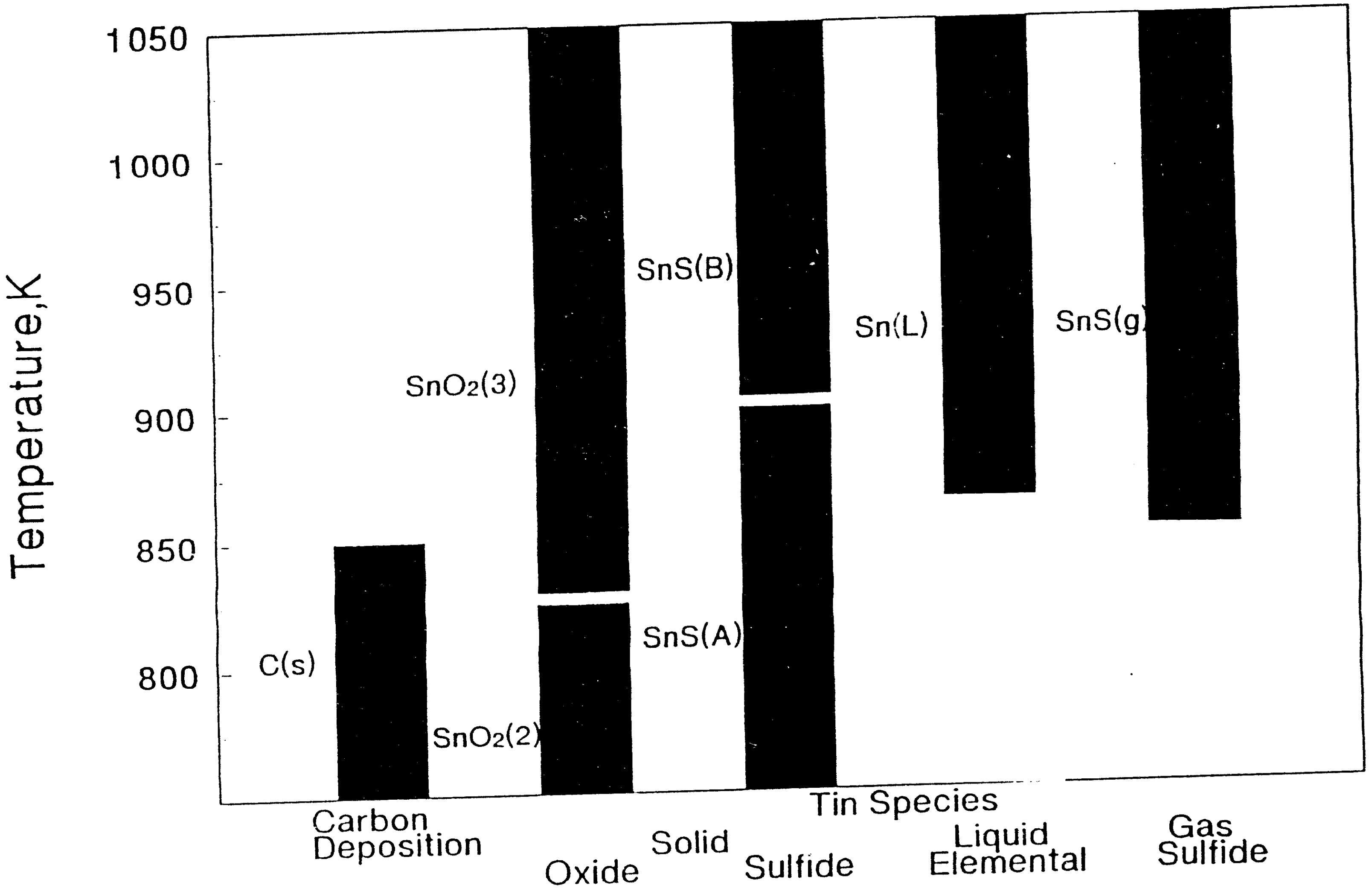


Figure 2. Equilibrium Carbon Deposition Tendency and Distribution of Tin Species at 1 atm: 1 mol of Texaco Gas and 1 mol of SnO_2

the temperature corresponding to that minimum are functions of pressure. At low temperature, the concentrations of COS and SnS are small compared to H_2S. SnS becomes the dominant "other" sulfur species at high temperature, particularly at low pressure. For example, at 1050K and 1 atm, the equilibrium SnS concentration of 3300 ppm is greater than the H_2S concentration of 1910 ppm. However, at 1050K and 25 atm, the H_2S concentration of 1870 ppm is more than 10 times greater than the SnS concentration. COS equilibrium concentration is relatively small at all conditions, with the maximum value of 60 ppm occurring at 1050K and 25 atm.

The importance of the generalized free-energy minimization approach is illustrated by the Figure 3 results. Single reaction analysis of the primary desulfurization reaction

$$SnO_2 + H_2S + H_2 \leftrightarrow SnS + 2H_2O$$

would not show any effect of pressure since there is no change in the number of gas phase mols. However, pressure alters the equilibrium concentrations of H_2 and H_2O, which obviously has an effect on H_2S removal. In addition, the single reaction approach would give no indication of the volatility of SnS at high temperature, or the carbon deposition tendency at low temperature.

Total fractional removal of sulfur from the gas phase as a function of temperature and pressure is shown in Figure 4. The curves are effectively mirror images of the concentration curves of Figure 3. At 1 atm the potential sulfur removal can exceed 90% over the temperature range of 775 to 925K, and can exceed 95% between approximately 825 and 875K. At 5 atm, 90% sulfur removal is possible from 850 to 960K, and at 25 atm the 90% sulfur removal temperature window is a narrow 960 to 990K.

None of the temperature and pressure combinations, however, are totally by satisfactory for efficient desulfurization of the Texaco gas. Carbon deposition is a potential problem at lower temperatures while SnS vaporization is significant at high temperatures. The formation of liquid elemental tin is an additional problem which was not encountered at 1 atm, but would occur at higher pressure. The problems with carbon deposition and formation of elemental tin are dependent on the gas composition. Texaco gas is both highly reducing and has a high carbon content. The ratio of $[C/(O + H)]$ provides a measure of the carbon deposition tendency while the ratio of $[(CO + H_2)/(CO_2 + H_2O)]$ is a measure of the reducing power of the gas. Both of these ratios are considerably higher in the Texaco gas than, for example, a KRW gas. With a lower carbon, less reducing coal gas, it may be possible to identify operating conditions where high desulfurization is possible and where carbon deposition and reduction to elemental tin are not favored. The formation of SnS vapor, in contrast, is effectively independent of gas composition, and the conditions required to avoid SnS vapor will be the same for any coal gas composition.

This is an appropriate time to stress several points which should be kept in mind when analyzing the results of all thermodynamic calculations. The results cannot be more accurate

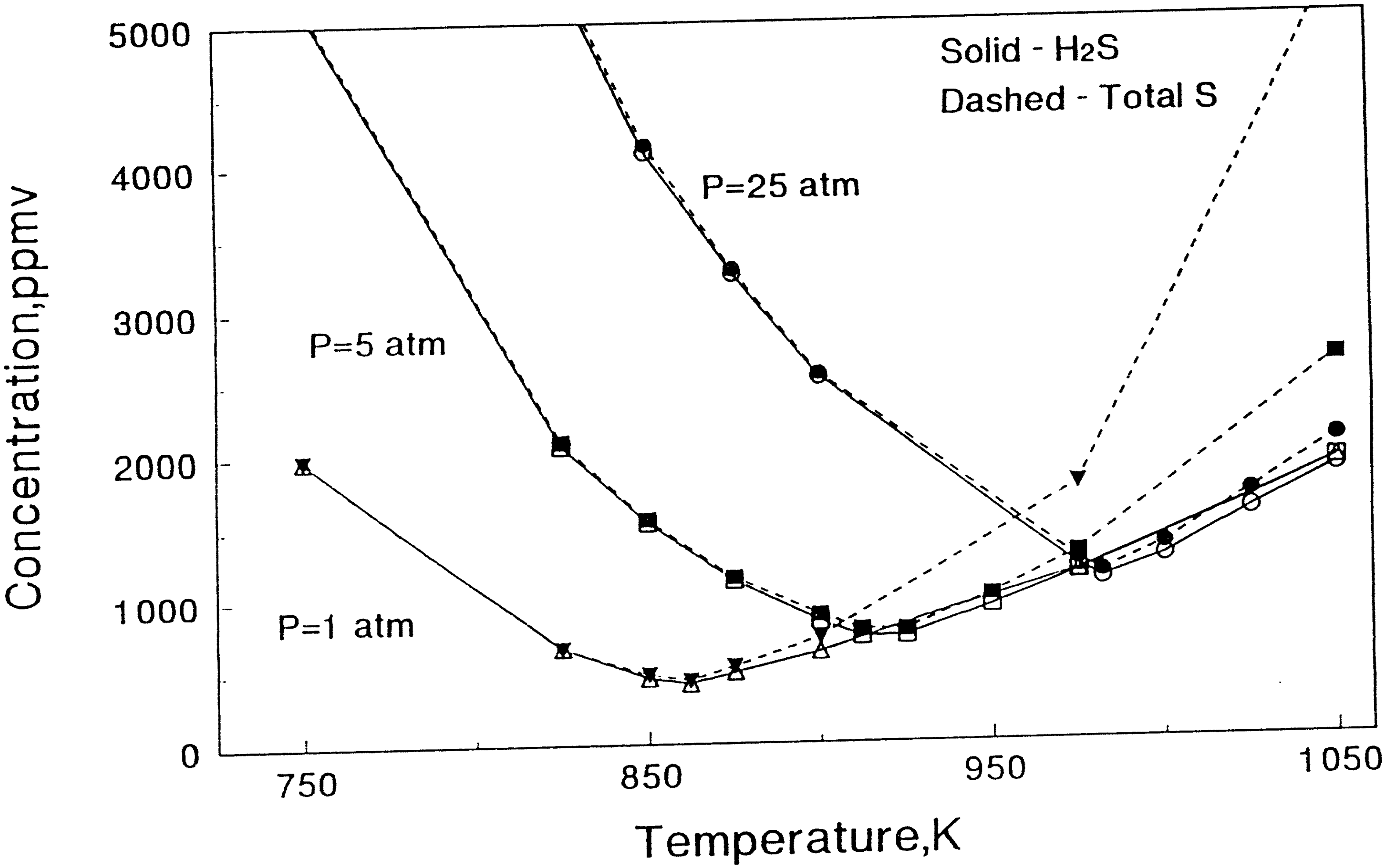


Figure 3. Equilibrium Concentrations of H_2S and Total Sulfur in the Gas Phase: 1 mol of Texaco Gas and 1 mol of SnO_2

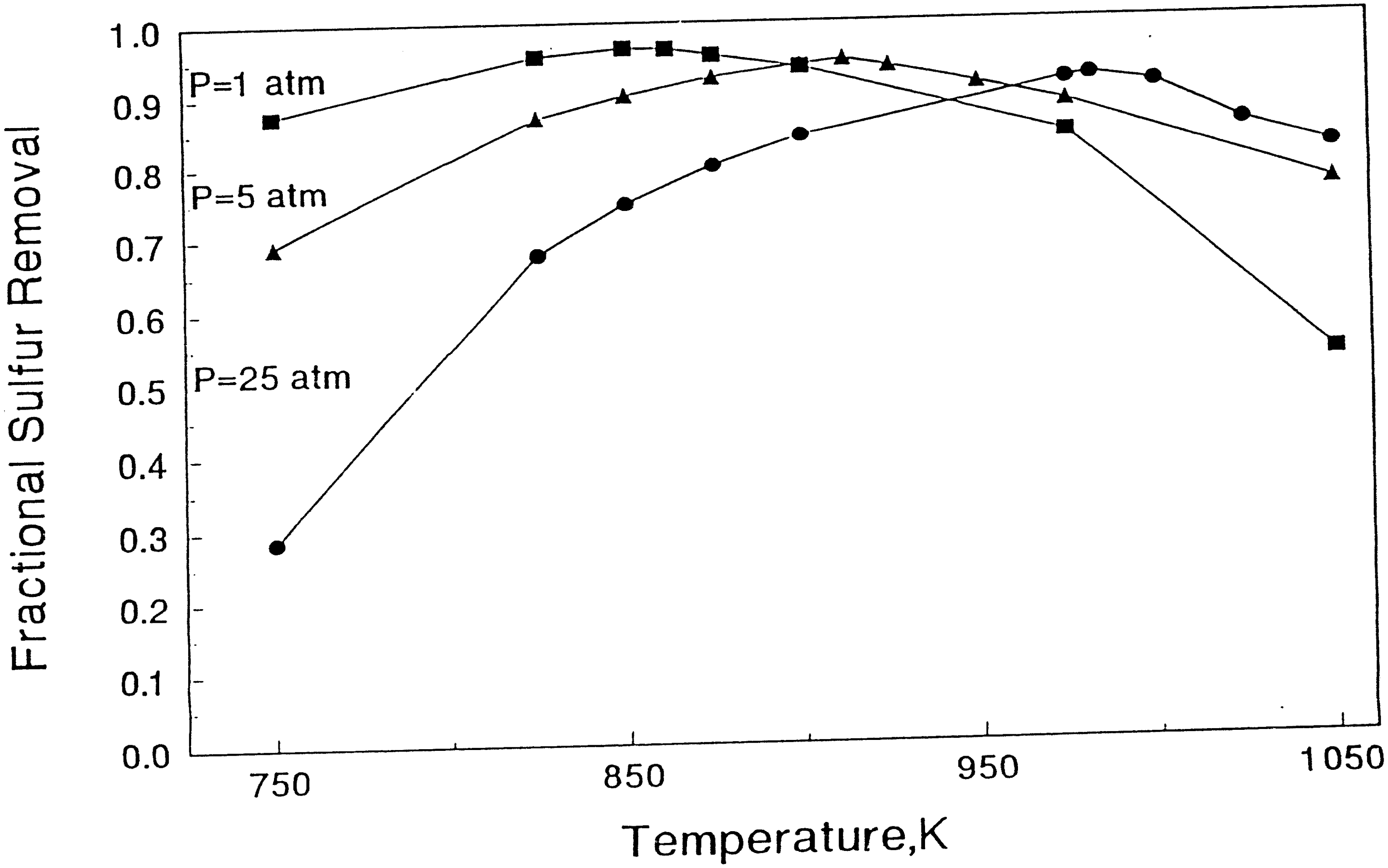


Figure 4. Equilibrium Fractional Sulfur Removal: Texaco Gas and SnO_2

than the data from which they were obtained. The accuracy of the free energy data for some species is questionable. One should always remember that equilibrium conditions are not always achieved or even closely approached in actual systems. In particular, at low temperature, an actual system is likely to be controlled by kinetics instead of thermodynamics.

Free energy equilibrium analysis during the regeneration phase has analyzed the two direct sulfur recovery concepts which have been identified in the literature survey -- regeneration using SO_2 and using a mixture of O_2, H_2O, and inert. Results using both concepts are summarized in the following.

Several cases involving the equilibrium between 1 mol of SnS(s) and varying mols of SO_2 have been evaluated over the temperature range of 750 to 1125K and at pressures of 1, 5, and 25 atm. Thirty possible equilibrium species for this Sn-O-S system which are included in the CHEMQ data base are identified in Table II. Six gas phase and two condensed phase species were present in the equilibrium product with mol fractions equal to or greater than 5×10^{-6} at at least one of the conditions. Important omissions from the data base for this analysis are the gaseous sulfur species S_3, S_4, S_5, S_6, and S_7. We are currently in the process of enlarging the data base to include these and other compounds.

Selected equilibrium results for an initial mixture consisting of 3 mols of SO_2(g) and 1 mol of SnS(s) are summarized in Table III. The desired reaction in this case is

$$\mathrm{SnS(s)} + \mathrm{SO_2(g)} \rightarrow \mathrm{SnO_2(s)} + \mathrm{S_2(g)}.$$

If this reaction went to completion and no other reactions occurred, the gas phase would contain 50% SO_2 and 50% elemental sulfur and the only condensed specie would be SnO_2(s).

Temperature and pressure conditions illustrated in Table III are just above and just below the $SnSO_4$(s) decomposition temperature. At lower temperatures, SnS(s) reacts with SO_2(g) to form $SnSO_4$(s). Significant amounts of elemental sulfur are produced in the gas phase at these conditions because of the transfer of oxygen to the solid phase. However, no sulfur is transferred to the gas phase. It is not until the sulfate decomposition temperature is exceeded that sorbent regeneration, as measured by the net transfer of sulfur from the solid to the gas phase, occurs.

At 1 atm and 960K, the sulfur is distributed with 25% in the condensed phases (all as $SnSO_4$) and 75% in the gas phase (as a mixture of SO_2, S_2, and S_2O). Since this distribution between phases is the same as in the original mixture, no net regeneration has occurred. At 990K and 1 atm, partial regeneration has been accomplished, and, by 1050K, regeneration is complete. SnO_2(s), the original sorbent, is the only component present in the condensed phase, and 48% of the gas phase sulfur is present as S_2 with the remaining 53% present as oxidized species (primarily SO_2). This gas phase distribution is quite close to the ideal 50% elemental sulfur represented by the single primary regeneration reaction. A problem associated with low pressure regeneration and which is illustrated in Table III is the appearance of SnS(g) at 1125K.

Table II
Thirty Species Present in the CHEMQ Data Bank
Composed of the Elements Sn, S, and O

Significant Species	($y_i \geq 5 \times 10^{-6}$)		
Gas Phase	SO	SO_2	S_2
	S_2O	S_8	SnS
Condensed Phase	$SnO_2(3)$	$SnSO_4(s)$	
Other Species	($y_i < 5 \times 10^{-6}$)		
Gas Phase	O	O_2	O_3
	S	SO_3	Sn
	SnO		
Condensed Phase	S(s)	S(L)	Sn(s)
	Sn(L)	SnO(s)	$SnO_2(1)$
	$SnO_2(2)$	SnS(A)	SnS(B)
	SnS(L)	$SnS_2(s)$	$SnS_2O_8(s)$
	$Sn_2S_3(s)$	$Sn_3S_4(s)$	

Table III
Equilibrium Analysis for the Regeneration of SnS(s)
With Three Mols of SO_2(g) at Selected Conditions
Near the $SnSO_4$(s) Decomposition Temperature

Temp., K	960	990	1050	1125	990	1050	1125	990	1050
Press., atm	1	1	1	1	5	5	5	25	25
Condensed Phase Composition, mol fraction									
SnO_2(s)	0.00	0.35	1.00	1.00	0.00	1.00	1.00	0.00	1.00
$SnSO_4$(s)	1.00	0.65	0.00	0.00	1.00	0.00	0.00	0.61	0.00
S(L)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.39	0.00
Gas Composition, mol fraction*									
SO_2	0.49	0.57	0.66	0.66	0.50	0.66	0.66	0.70	0.68
S_2	0.48	0.41	0.32	0.31	0.45	0.31	0.31	0.21	0.27
S_2O	0.02	0.02	0.02	0.02	0.03	0.03	0.03	0.03	0.04
S_8	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.06	0.01
SnS	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Sulfur Distribution (as S), fraction									
Condensed Phase	0.25	0.16	0.00	0.00	0.25	0.00	0.00	0.41	0.00
Gas Phase	0.75	0.84	1.00	1.00	0.75	1.00	1.00	0.59	1.00
Sulfur Distribution Within Gas Phase, fraction									
Elemental	0.64	0.57	0.48	0.47	0.63	0.47	0.47	0.55	0.46
Oxide	0.36	0.43	0.53	0.53	0.37	0.53	0.53	0.45	0.54
Metal Sulfide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

*only species having mol fractions ≥ 0.01 are included

Regeneration at higher pressure retards the formation of SnS(g), but also shifts sulfate decomposition to a higher temperature. At both 5 and 25 atm, $SnSO_4$(s) decomposition is predicted to be complete by 1050K. Equilibrium gas composition above the sulfate decomposition temperature is only a weak function of pressure. For example, at 1050K, the fraction of gas phase sulfur in elemental form is 0.48 at 1 atm, 0.47 at 5 atm, and 0.46 at 25 atm. However, an additional problem which may be encountered when regenerating at high pressure is the possible formation of liquid elemental sulfur. Sn(L) is predicted at 990K and 25 atm.

The sulfate decomposition temperature can be lowered by reducing the partial pressure of SO_2 in the gas phase, which may be accomplished by reducing to ratio of SO_2 to SnS in the original mixture and/or by adding an inert such as N_2 to the initial mixture. The effect of reducing the ratio of SO_2 to SnS is relatively small, however. At 1 atm with a ratio of 2.3 mols SO_2 per mol SnS, $SnSO_4$(s) decomposition should be complete by 990K, thus providing the possibility of 50K lower regeneration temperature. With an initial mixture consisting of 1 mol SnS, 3 mol SO_2, and 3 mol N_2, $SnSO_4$(s) should be completely decomposed by 950K, permitting regeneration to occur at about 100K lower temperature. This approach, however, has the disadvantage of involving larger flow rates of permanent gases which would increase the load on the sulfur condenser and on the recycle compressor. The distribution of gas phase sulfur species when N_2 is included does not change significantly at temperatures above the sulfate decomposition temperature. The fraction of sulfur present in elemental form remains slightly less than 0.5.

The other concept for producing elemental sulfur during sorbent regeneration involves feeding a mixture of O_2, H_2O, and inerts with careful control of reaction conditions to maximize the amount of elemental sulfur formed. Selected results of a free energy equilibrium analysis when the feed consists of 1 mol of SnS(s), 1 mol of O_2(g), and 1 mole of H_2O(g) are summarized in Table IV. Sulfate formation and decomposition is also important with this concept, and the chosen temperature and pressure combinations are just below and just above the sulfate decomposition temperature. The condensed phases are also more complex, and complete sorbent regeneration (complete transfer of solid to the gas phase) is not possible at these conditions.

At 1 atm, sulfate decomposition is complete by 900K, but a small amount of sulfur remains in the solid phases, as SnS_2(s) to 975K and as SnS(s) at 1050K. At 1050K the fractional regeneration corresponding to 6% of the sulfur remaining in the solid is 0.76. The fraction of the gas phase sulfur which is in elemental form increases with temperature and reaches 0.56 at 1050K. The remaining sulfur in the gas phase is divided between oxidized (primarily SO_2) and reduced (primarily H_2S) forms.

Increasing the pressure delays sulfate decomposition to between 975 and 1050 at 5 atm, and to between 1050 and 1125K at 25 atm. The maximum fraction of total sulfur transferred to the gas phase is

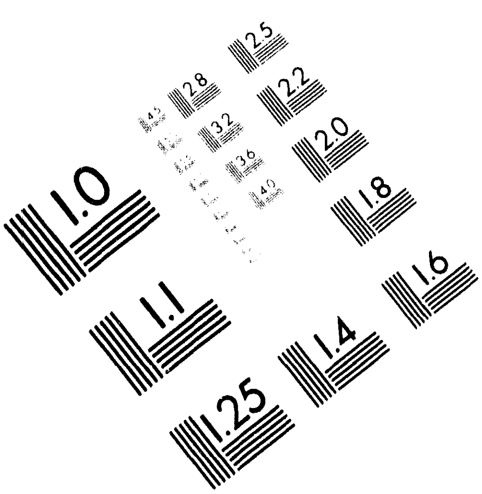
Table IV
Equilibrium Analysis for the Regeneration of One Mol SnS(s) With One Mol of O_2(g) and One Mol of H_2O(g) at Selected Conditions Near the Sulfate Decomposition Temperature

Temp., K	875	900	975	1050	900	975	1050	975	1050	1125
Press., atm	1	1	1	1	5	5	5	25	25	25
Condensed Phase Composition, mol fraction										
SnO_2(3)	0.76	0.91	0.96	0.94	0.53	0.74	0.97	0.51	0.58	0.96
SnS(B)	0.00	0.00	0.00	0.06	0.00	0.00	0.00	0.00	0.00	0.00
$SnSO_4$(s)	0.10	0.00	0.00	0.00	0.28	0.14	0.00	0.30	0.31	0.00
SnS_2(s)	0.13	0.09	0.04	0.00	0.19	0.13	0.00	0.19	0.00	0.00
Sn_2S_3(s)	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.11	0.04
Gas Composition, mol fraction										
H_2O	0.60	0.54	0.52	0.53	0.71	0.60	0.51	0.71	0.65	0.51
H_2S	0.18	0.17	0.18	0.15	0.22	0.21	0.19	0.25	0.25	0.20
SO_2	0.12	0.15	0.11	0.12	0.03	0.09	0.13	0.02	0.04	0.15
S_2	0.09	0.13	0.17	0.18	0.03	0.09	0.15	0.02	0.05	0.13
S_2O	0.00	0.01	0.01	0.01	0.00	0.00	0.01	0.00	0.00	0.01
SnS	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sulfur Distribution (as S), fraction										
Condensed Phase	0.37	0.18	0.07	0.06	0.66	0.39	0.08	0.68	0.57	0.11
Gas Phase	0.63	0.82	0.93	0.94	0.34	0.61	0.92	0.32	0.43	0.89
Sulfur Distribution Within Gas Phase, fraction										
Elemental	0.38	0.44	0.53	0.56	0.18	0.36	0.48	0.12	0.23	0.42
Oxidized	0.25	0.27	0.19	0.20	0.12	0.21	0.23	0.07	0.12	0.27
Reduced	0.37	0.29	0.28	0.24	0.70	0.42	0.21	0.80	0.63	0.23
Metal Sulfide	0.00	0.00	0.00	0.00	0.00	0.01	0.08	0.01	0.02	0.08

about 0.9 at both pressures, with SnS_2 or Sn_2S_3 remaining in the solid phase. H_2S is favored by high pressure, and the fraction of elemental sulfur in the gas phase is reduced. The formation of SnS(g) is again of concern, particularly at the high temperature needed to achieve sulfate decomposition at high pressure. No problem with the formation of S(L) is indicated in Table IV.

In spite of the fact that the gas phase elemental sulfur yields are somewhat lower using the O_2/H_2O concept than using SO_2, we feel than SnS(s) regeneration with O_2/H_2O is a concept worthy of experimental study. Added operating flexibility exists since the regeneration gas flow rate and the proportions of O_2 and H_2O can be independently varied. The ability to produce high concentrations of both H_2S and SO_2 creates the possibility of feeding the regeneration gas, after condensation of elemental sulfur and steam, directly to a Claus plant for additional sulfur recovery.

ZnO is well known to have superior desulfurization potential to SnO_2. However, ZnS will not react to any appreciable extent with SO_2, so this concept cannot be used either to regenerate the ZnO(s) or to produce elemental sulfur. Similarly, free energy analysis of the regeneration of ZnS using the O_2/H_2O concept indicates that the amount of elemental sulfur which can be formed is quite small. These results confirm our feeling expressed in the LSU proposal that the use of zinc-based sorbents may be limited to a polishing mode if elemental sulfur recovery is to be achieved during regeneration.



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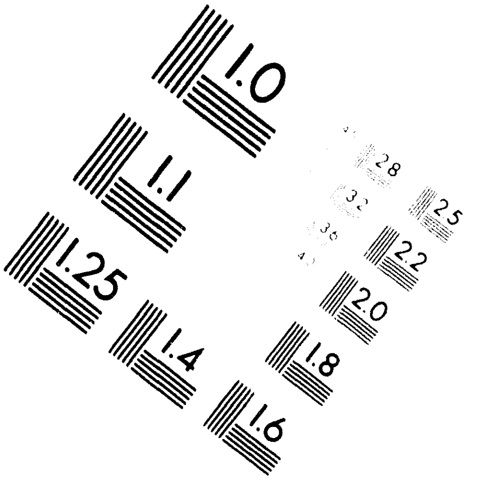

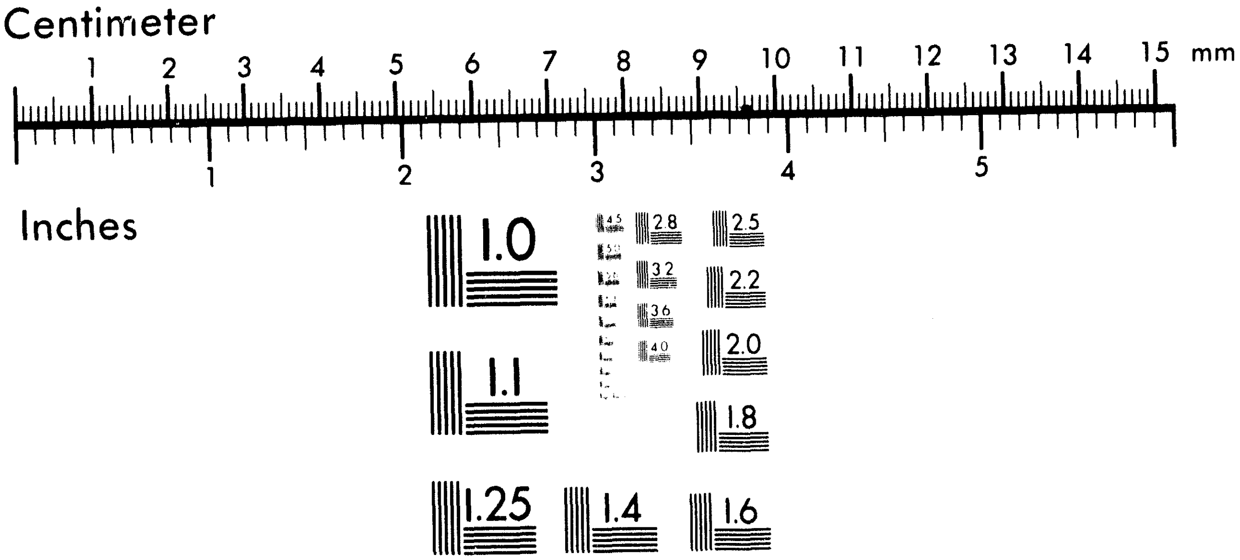

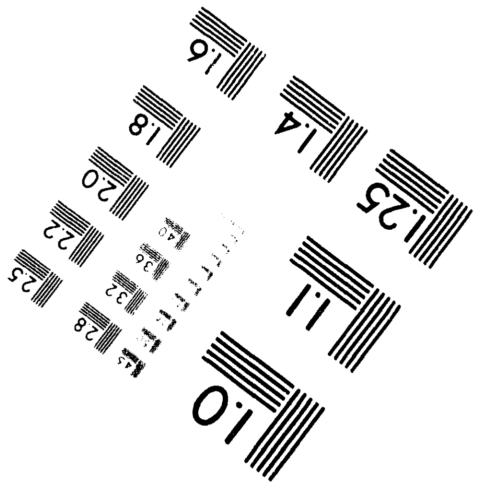

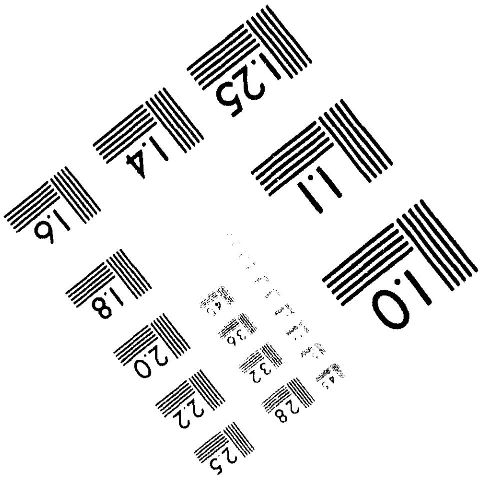

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