

ADVANCED SULFUR CONTROL CONCEPTS IN HOT-GAS DESULFURIZATION TECHNOLOGY: PHASE 1. FEASIBILITY OF THE DIRECT PRODUCTION OF ELEMENTAL SULFUR DURING THE REGENERATION OF HIGH TEMPERATURE DESULFURIZATION SORBENTS

Topical Report

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EXECUTIVE SUMMARY

This topical report describes the results of Phase I research performed during the first six months of a three-year contract to study the feasibility of the direct production of elemental sulfur during the regeneration of high temperature desulfurization sorbents.

The Morgantown Energy Technology Center of the U.S. Department of Energy has primary responsibility for development of advanced power systems to enable the nation's vast coal reserves to be used in an economical and environmentally acceptable manner. Integrated gasification-combined cycle (IGCC) power generation has emerged as a major thrust in meeting this responsibility. IGCC power plants are attractive because of their low emissions and increased electrical generation efficiency.

Many of the contaminants present in coal emerge from the gasification process in the coal gas. These contaminants, in the form of H_2S , NH_3 , halogens, etc., must be removed prior to power generation. Using current technology, these contaminants can only be removed at low temperatures which requires that the coal gas be cooled, treated, and reheated prior to power generation. The process would be simplified and the overall efficiency increased if the contaminants could be removed at high temperature.

Much effort has gone into the development of a high-temperature metal oxide sorbent process for removal of H_2S from the coal gas. A number of sorbents based upon metals such as zinc, iron, manganese and others have been studied. In order for high temperature desulfurization to be economical it is necessary that the sorbents be regenerated to permit multicycle operation. Current methods of sorbent regeneration involve oxidation of the metal sulfide to reform the metal oxide and free the sulfur as SO_2 .

An alternate regeneration process in which the sulfur is liberated in elemental form is preferable. Elemental sulfur may be easily stored and transported, and it is the typical feed to sulfuric acid plants. Although research to convert SO_2 produced during sorbent regeneration to elemental sulfur is on-going, the direct production of elemental sulfur would be preferred.

The overall objective of the current research is to study simpler and economically superior processing of known sorbents capable of producing elemental sulfur during regeneration. This topical report summarizes the first steps of this effort. A literature search has been completed to identify possible regeneration concepts and to collect relevant thermodynamic, kinetic, and process data. Three concepts involving reaction with SO_2 , partial oxidation using an $O_2 - H_2O$ mixture, and steam regeneration have been identified. The first two concepts result in the direct production of elemental sulfur while H_2S is the product of steam regeneration. This concept is of potential interest, however, since existing Claus technology can be used to convert H_2S to elemental sulfur.

Following the literature search, a thermodynamic analysis, based upon free-energy minimization was carried out to evaluate candidate sorbents for possible use with the three regeneration concepts. As a result of the thermodynamic analysis, we conclude that sorbents

having the strongest affinity for H_2S removal will be the most difficult to regenerate with elemental sulfur as the byproduct. Consequently, zinc-based sorbents, which have been extensively studied because of their ability to reduce H_2S to 10 to 20 ppm levels, are not suitable for regeneration to elemental sulfur. Sorbents such as iron, tin, and cerium oxides, which are less effective at removing H_2S during the desulfurization cycle, are more amenable to elemental sulfur formation. In particular, sorbents based upon tin and cerium possess thermodynamic properties which make them uniquely attractive for the production of elemental sulfur during regeneration.

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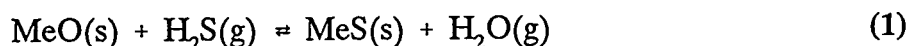
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INTRODUCTION

The integrated gasification combined cycle (IGCC) process combines coal gasification with electric power generation. This process creates the possibility of utilizing the nation's large coal reserves with greater efficiency and with less environmental impact than the current pulverized coal-steam cycle. In order to optimize the IGCC process it is necessary to remove a number of contaminants from the coal gas prior to power generation. Control of particulate matter and a number of gaseous and vapor-phase compounds including tars, ammonia, halogens, alkali species, and sulfur compounds (primarily H₂S) may be required. The sulfur compounds, which constitute the primary emphasis of this study, must be removed both to meet environmental standards and to prevent corrosion of the turbine blades.

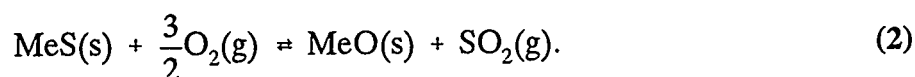
Various liquid scrubbing processes are available for H₂S removal, but such processes do not integrate well with the gasification and power generation sections of the IGCC process. Hot coal gases must be cooled to near ambient temperature, scrubbed, and then reheated prior to entering the power generation section. Energy losses, which decrease the efficiency of electricity production, and gas-to-gas heat exchangers, which are necessarily large and expensive, are the inevitable result of liquid scrubbing processes for sulfur removal.

High temperature desulfurization based on the noncatalytic reaction of H₂S with an appropriate solid metal oxide sorbent can eliminate many of the problems associated with low temperature sulfur removal and allow the overall IGCC process to operate at higher efficiency. The general high temperature desulfurization reaction may be represented by



Metal oxides sorbents having high sulfur capacity and the capability of reducing the H₂S content of the coal gas to less than 100 ppmv are available. However, economic considerations require that the sorbent be regenerable and able to withstand many desulfurization-regeneration cycles. For these reasons the sorbents must possess good mechanical strength and be resistant to attrition and sintering at the temperatures of interest.

The regeneration reaction which has received the most attention in the past involves direct oxidation of both the metal and sulfur species. This reaction is represented generically by



Metal sulfate formation is often favored at lower reaction temperatures, requiring the regeneration reaction to be carried out above the sulfate decomposition temperature. Reaction (2) is also highly exothermic, leading to complicated reactor temperature control problems. Sulfate formation on the one hand and high regeneration temperatures on the other contribute to degrading the mechanical strength of the sorbent and to accelerating sintering. In order to control

the regenerator temperature, it is necessary to use large quantities of inerts in the regeneration feed gas. Therefore, the SO₂ concentration in the regeneration product gas is low, which introduces the final, and perhaps most important, problem. How can the SO₂ be converted to a usable form or disposed of in an environmentally acceptable fashion?

For fluidized-bed gasifiers employing in-bed primary desulfurization using a calcium-based sorbent, it may be possible to recycle the regenerator product gas to the gasifier where SO₂ can be removed, ultimately as CaSO₄(s). This approach, however, cannot be used with all gasifier types. Even when applicable, this solution of the atmospheric SO₂ problem creates a troublesome solid waste disposal problem. In some instances, it may be possible to convert the SO₂ to sulfuric acid. However, as previously stated, regeneration reactor temperature control problems require that the product gas SO₂ concentration be low. Thus, the regenerator product gas does not integrate well with the conventional sulfuric acid process. In addition, transportation of sulfuric acid to markets is both expensive and potentially dangerous. It is most desirable to obtain elemental sulfur as the product of sorbent regeneration. Solid or liquid sulfur is easily and safely transportable, and is the usual feedstock to sulfuric acid plants.

The overall objective of the current research project is to investigate alternative regeneration concepts which lead to elemental sulfur. The complete project is scheduled to last for three years and consists of several phases: literature review, thermodynamic analysis, experimental studies, process analysis, and economic evaluation. This report summarizes results from the first two phases consisting of the literature review and thermodynamic analysis.

LITERATURE REVIEW

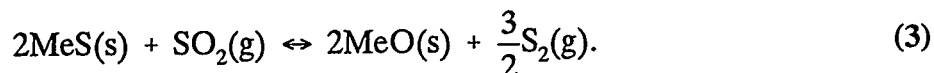
Preliminary research carried out in conjunction with the preparation of the LSU proposal identified three possible regeneration concepts which could lead to elemental sulfur. Since the contract was awarded, more extensive literature searches, both computer-based and hand-searches, have been carried out to identify possible additional concepts and to collect thermodynamic, kinetic, and process data.

The literature contains many references to high-temperature desulfurization of coal-derived gases using metal oxide sorbents. However, there are fewer references to regeneration studies, and still fewer to elemental sulfur formation during regeneration. While a great deal of useful information has resulted from the literature search, we have not identified concepts which may lead to elemental sulfur other than those identified in the proposal preparation stage.

Basic chemistry of each of the three concepts plus a summary of the literature pertaining to each concept is presented below. We view each concept as ultimately being a problem in chemical reactor optimization in which we seek to identify temperature, pressure, gas composition, space velocity, and sorbent properties which will maximize the yield of elemental sulfur during sorbent regeneration.

Regeneration With SO₂

The reaction between metal sulfide and SO₂ to yield elemental sulfur directly is well known. The generic reaction may be written as



The problem is to identify metal oxide systems which possess the necessary desulfurization capability, and, when sulfided, are sufficiently reactive with SO₂. In some systems, metal sulfate formation may be favored, in which case it will be necessary to operate above the sulfate decomposition temperature. At low temperatures and high pressures liquid elemental sulfur may be formed. One must always be concerned with the possible formation of liquid or gaseous metal compounds. Operating conditions must be defined which avoid these problems. The literature provides guidance to the selection of appropriate metal oxide systems, and thermodynamic analysis (to be discussed in the next section of this report) can be used to help identify appropriate reaction conditions.

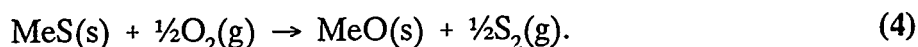
Copeland (1993a, 1993b) has described a process in which desulfurization occurs in two reactors connected in series. The first contains SnO₂ sorbent while the second contains a zinc-based sorbent. 90 to 99% H₂S removal is achieved using SnO₂ while the zinc sorbent is used to lower the H₂S content to less than 20 ppm. In the regeneration cycle, sulfided zinc ferrite is regenerated with air to produce SO₂ and the SO₂ is used to regenerate SnS and produce elemental sulfur. Thermodynamic analysis confirms that elemental sulfur can be produced by the reaction of SnS and SO₂, and we believe that tin is a viable candidate. However, we question the process concept of coupling the zinc and tin beds during regeneration. The SO₂ content of the product gas from ZnS regeneration must be low to avoid overheating the zinc sorbent. Using low SO₂ concentrations for regeneration of SnS will reduce the reaction rate and increase heat duty on the sulfur condenser. Use of a secondary zinc sorbent reactor may be necessary if product gas H₂S concentration is to be reduced to the 10 to 20 ppm level, but coupling the regeneration step within the two reactors is not part of our plan. Instead, we propose to recycle SO₂-containing gas from ZnS regeneration directly to the gasifier so that SnS regeneration can be carried out independently.

Anderson and Berry (1987) have reported on a similar two-reactor concept. Cobalt titanate sorbent in the first reactor is designed to remove 2/3 of the H₂S while a zinc-based sorbent in the second reactor will reduce the H₂S concentration to approximately 20 ppm. The ZnS is to be regenerated to SO₂ using O₂, and the product SO₂ is to be combined with recirculating SO₂ to regenerate the sulfided cobalt titanate and produce elemental sulfur. In addition to the previously mentioned problem of coupling the two regeneration reactions, this approach is limited since only 2/3 of the H₂S is removed in the first bed. It is our feeling that the first reactor should achieve approximately 90% or greater H₂S removal so that the second zinc sorbent bed would operate in more of a polishing mode. Under this scenario, the size of the second reactor and/or the frequency of regeneration could be greatly reduced.

Several papers on the regeneration of sulfided iron oxide to produce elemental sulfur have been identified. Schrodt and Best (1978) and Tseng et al. (1981) both studied a sorbent composed of Fe₂O₃ and SiO₂ (or fly ash) while Patrick et al. (1993) report the formation of elemental sulfur during regeneration of FeS on Al₂O₃. Questions concerning the rate of reaction with SO₂ and thermodynamic limitations on the maximum partial pressure of S₂(g) in the product were raised. Indeed, our thermodynamic analysis indicates that the reaction of FeS with SO₂ is less favored than the reaction of SnS with SO₂. Nevertheless, we feel that an iron-based sorbent should be considered as a possible candidate for elemental sulfur production by reaction with SO₂.

Partial Oxidation

A number of investigators have reported that significant amounts of elemental sulfur are released when metal sulfide is reacted with oxygen and steam under "O₂-starved" conditions. The net result is partial oxidation according to the stoichiometry



Although equation (4) represents the desired overall reaction, a number of simultaneous reactions such as listed in Table I for FeS regeneration would probably occur. Both gas-solid and gas phase reactions are included. Iron has been identified as a prime candidate sorbent for this regeneration concept based both on literature reports and thermodynamic analysis. The literature suggests that elemental sulfur yields improve at low temperature. Iron sulfate is significantly less stable than the sulfate of other candidate metals, so that lower temperature regeneration should be possible.

The basic approach would be to identify reaction conditions which promote those reactions which produce S₂ (reactions 1, 4, 6, 7, and 8) and retard those reactions which produce SO₂ (reactions 2 and 9). Thermodynamic analysis shows that the only significant gaseous sulfur product would be SO₂ when excess O₂ is present. Thus it will be desirable to operate in an "O₂-starved" atmosphere and at conditions where kinetics rather than thermodynamics controls the product distribution.

The concept is similar in many respects to a number of partial oxidation processes used in the chemical industry. A relevant example is the production of phthalic anhydride from o-xylene (Froment and Bischoff, 1990). The general reaction sequence is

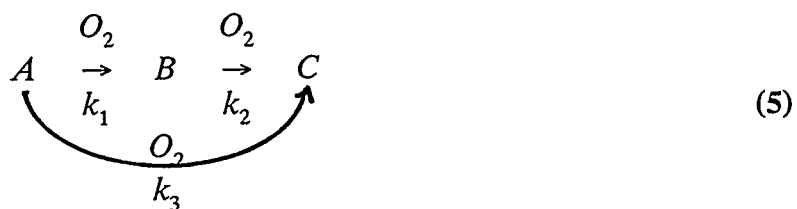


Table I. Simultaneous Reactions Involved
in the Partial Oxidation of FeS to Produce
Elemental Sulfur

Gas - Solid Reactions

1. $2\text{FeS(s)} + \frac{3}{2}\text{O}_2\text{(g)} \rightarrow \text{Fe}_2\text{O}_3\text{(s)} + \text{S}_2\text{(g)}$
2. $2\text{FeS(s)} + \frac{7}{2}\text{O}_2\text{(g)} \rightarrow \text{Fe}_2\text{O}_3\text{(s)} + 2\text{SO}_2\text{(g)}$
3. $3\text{FeS(s)} + 4\text{H}_2\text{O(g)} \rightarrow \text{Fe}_3\text{O}_4\text{(s)} + 3\text{H}_2\text{S(g)} + \text{H}_2\text{(g)}$
4. $3\text{FeS(s)} + 2\text{SO}_2\text{(g)} \rightarrow \text{Fe}_3\text{O}_4\text{(s)} + \frac{5}{2}\text{S}_2\text{(g)}$
5. $2\text{Fe}_3\text{O}_4\text{(s)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow 3\text{Fe}_2\text{O}_3\text{(s)}$

Gas-Phase Reactions

6. $\text{SO}_2\text{(g)} + 2\text{H}_2\text{S(g)} \rightarrow 2\text{H}_2\text{O(g)} + \frac{3}{2}\text{S}_2\text{(g)}$
7. $\text{H}_2\text{S(g)} \rightarrow \text{H}_2\text{(g)} + \frac{1}{2}\text{S}_2\text{(g)}$
8. $\text{SO}_2\text{(g)} + 2\text{H}_2\text{(g)} \rightarrow 2\text{H}_2\text{O(g)} + \frac{1}{2}\text{S}_2\text{(g)}$
9. $\text{S}_2\text{(g)} + 2\text{O}_2\text{(g)} \rightarrow 2\text{SO}_2\text{(g)}$

A represents o-xylene, B phthalic anhydride, and C the total oxidation products CO and CO₂. In the presence of sufficient oxygen, thermodynamics favors total oxidation, and it is necessary to control reaction conditions in order to produce the partially oxidized phthalic anhydride.

Several references from the literature suggest that partial oxidation of sulfided sorbents to produce elemental sulfur may be possible. Joshi et al. (1979) studied the regeneration of a previously sulfided 40% Fe₂O₃ on silica sorbent at 538°C using 95% H₂O and 5 % air at a gas hourly space velocity of 600. 75% of the sulfur in the regeneration gas was reported to be in elemental form. Grindley and Steinfeld (1981) studied the regeneration of an approximately 42% Fe₂O₃ on SiO₂ sorbent using METC's two-inch fixed-bed reactor. At the same conditions used by Joshi et al. (1979), complete regeneration was possible with approximately 75% of the sulfur liberated in elemental form and the bulk of the remainder as H₂S. Increasing the O₂ content of the regeneration feed gas resulted in less elemental sulfur and increased quantities of SO₂. It is important to recognize that elemental sulfur production was not the primary objective in the studies of Joshi et al. (1979) and Grindley and Steinfeld (1981). No attempt was made to identify regeneration conditions which would optimize elemental sulfur yields. Indeed, in these studies the elemental sulfur was a nuisance as it tended to plug downstream lines and valves upon condensation.

Van der Waal (1987) performed extensive studies on the regeneration of iron-based sorbents using a micro-fixed-bed reactor. The effects of temperature, O₂ content of the regenerating gas, space velocity and sorbent structure were studied. Low temperature, low O₂ content, and high space velocity increased the yield of elemental sulfur. Also, the ratio of S₂ to SO₂ was higher for supported than for unsupported Fe₂O₃.

A recent patent (Kay and Wilson, 1989) describes a process in which CeO₂ sorbent is converted to an oxysulfide, Ce₂O₂S, during the desulfurization cycle. Elemental sulfur was reported during regeneration at 900°C using a regeneration gas of 20% O₂ and 80% N₂. A high regeneration temperature was required in this system to avoid formation of Ce₂(SO₄)₃. In a follow-up paper, Kay et al. (1993) mention that "O₂-starved" conditions are required for the formation of elemental sulfur.

Regeneration With H₂O/Claus Reaction

By reversing the primary desulfurization reaction, regeneration to H₂S is possible. If the H₂S can be produced in sufficiently high concentration, the regeneration product may be fed to a Claus process for recovery of elemental sulfur. Although elemental sulfur is not a direct product of regeneration, we have included this concept since Claus technology is currently utilized in many areas. Again, since the regeneration reaction is the reverse of the desulfurization reaction, it is obvious that those sorbents which have the greatest affinity for H₂S, for example zinc-based sorbents, will be the most difficult to regenerate using this concept. Instead, metal oxide sorbents which have an intermediate affinity for H₂S are the likely candidates.

Nielsen et al. (1991) have used steam at 930°F, 300 psi (500°C, 24 atm) and space velocity of 1100 hr⁻¹ to regenerate SnS. 30 moles of steam per mole of sulfur were required, and the mol fraction of H₂S in the regenerator effluent was as high as 0.25. This process requires a separation step to recover H₂S from the excess steam and H₂ by-product, with the H₂S sent to a sulfur recovery unit.

Iron and tin have similar affinities for H_2S and two studies on the regeneration of iron-based sorbents with steam have been identified. Tamhankar et al. (1985) used an electrobalance reactor to study the regeneration of sulfided sorbent originally consisting of 45% Fe_2O_3 on SiO_2 . H_2S , H_2 , and Fe_3O_4 on SiO_2 were the reaction products. The formation of Fe_3O_4 instead of the more highly oxidized Fe_2O_3 is desirable since this will reduce H_2 consumption during the subsequent regeneration cycle. The reaction rate, however, was slow compared to air oxidation. Wakker et al. (1993) studied the sulfidation of $FeAl_2O_4$ and $MnAl_2O_4$ sorbents and commented on the possibility of regeneration with steam to produce a high concentration of H_2S in the regeneration product gas.

Sohn and Kim (1987) have studied the regeneration of ZnS with steam to produce ZnO and H_2S in an electrobalance reactor over the temperature range 640-1200K at 38.5 Pa gage. At this low pressure the reaction was complete in 20 to 80 minutes at the higher temperatures and the reaction was found to be first order in steam concentration. There was no mention of the steam-to-sulfur ratio used; however, because of the strong affinity of ZnO for H_2S , one would expect that large steam flow rates were required.

Summary

From the literature, tin appears to be a strong candidate for the production of elemental sulfur during regeneration. The thermodynamic analysis to be described in the following section of this report supports the literature reports. Tin oxide is capable of exceeding 90% H_2S removal during desulfurization. Tin sulfide will react with SO_2 to free elemental sulfur, and with H_2O to produce H_2S . While we have found no reports of experimental studies involving partial oxidation with steam and O_2 , it is logical that this reaction would also be favored.

A number of papers report the use of iron oxide sorbent and subsequent regeneration of FeS to produce elemental sulfur. Experimental studies involving FeS with all three of the regeneration concepts have been published. Iron oxide is also capable of achieving 90% H_2S removal in the primary desulfurization step.

Other possibilities identified in the literature search were the oxides of zinc, cobalt, manganese, and cerium. Because of the strong affinity between zinc and sulfur, we do not feel that it is a viable candidate for producing elemental sulfur during regeneration. Instead, we visualize a zinc-based sorbent in the secondary desulfurization reactor where the H_2S content would be lowered from approximately 500 ppm to the range of 10 to 20 ppm. This zinc sulfide would be regenerated to SO_2 and recycled to the gasifier.

The thermodynamic analysis which follows evaluates each of the metal oxide sorbents identified in the literature search, as well as other oxides, for suitability with each of the regeneration concepts.

THERMODYNAMIC ANALYSIS

The purpose of the thermodynamic analysis was to evaluate candidate sorbents for their ability to remove H_2S from Texaco and KRW coal gases, and the feasibility of producing elemental sulfur by one of the concepts previously described during the regeneration phase. An extensive thermodynamic analysis of H_2S removal capability has been reported by Westmoreland

and Harrison (1976); however, the composition of the coal gas and evaluation criteria were different in that study. Although limited thermodynamic analyses of the regeneration phase have been published, no comprehensive study is available.

Two general methods may be used for reaction equilibrium analysis--the equilibrium constant approach and free-energy minimization. In complex systems such as encountered in the desulfurization of coal gas and subsequent sorbent regeneration, the free energy minimization approach is favored. Free energy minimization evaluates the global equilibrium of the overall system. It is not necessary to specify individual chemical reactions. Only the elemental composition of the initial mixture and the Gibbs free energy of all possible equilibrium species are needed to calculate the equilibrium composition at a specified temperature and pressure.

CHEMQ

The free energy minimization program, CHEMQ, was used in the thermodynamic analysis. The computational method utilized by CHEMQ was originally developed at LSU (del Valle et al., 1967) for use by NASA to study equilibrium compositions produced from ablation heat shields during space vehicle re-entry. Westmoreland and Harrison (1976) used an earlier version of CHEMQ in their examination of 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 that the user 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 initially consisted of 1322 species, is then searched and all species whose elements are present initially are considered as possible components of the equilibrium mixture. The number of mols of each component which minimizes the free energy of the system subject to the elemental material balance constraint established by the initial mixture is then calculated. The gas phase is assumed to be ideal and condensed species are assumed to form pure phases having an activity of 1.0.

The data for each specie consist of the constants, A_1 through A_7 , required to calculate the Gibbs free energy from the equation

$$\frac{F_T^\circ}{RT} = A_1 (1 - \ln T) - \frac{A_2 T}{2} - \frac{A_3 T^2}{6} - \frac{A_4 T^3}{12} - \frac{A_5 T^4}{20} + \frac{A_6}{T} - A_7 \quad (6)$$

While the initial CHEMQ data base contained many of the compounds of interest to this study, data for some important species were missing. For example, the original data base considered gaseous sulfur to be present only as S , S_2 , and S_8 . Some metal compounds of potential interest, e.g., manganese, were completely missing from the data base. Nonlinear regression analysis has been performed on the free energy data from Barin (1993) to determine the constants A_1 through A_7 , and the data base has been enlarged. As examples, gaseous sulfur species S_3 , S_4 , S_5 , S_6 , and S_7 as well as thirteen manganese compounds have been added to the data base.

CHEMQ has been used to analyze both the reduction/desulfurization and regeneration cycles. Obviously, a metal sulfide from which elemental sulfur can be produced during regeneration is of no value if the corresponding oxide is unsuitable for desulfurization.

Coal Gas Characteristics

Two coal gas compositions representing the product from a Texaco oxygen-blown gasifier and from a KRW air-blown gasifier have been considered. Compositions of these gases, as specified by METC (Dorchak, 1994) are summarized in Table II. The mol fractions of H_2 and CO are greater in the Texaco gas, thus making it more highly reducing. In addition, there is a greater tendency for carbon deposition from the Texaco gas. The ratio of $[(H_2 + CO)/(H_2O + CO_2)]$ found at the bottom of Table II provides a measure of the reducing strength of the gas while the elemental ratio $[C/(O + H)]$ provides a measure of the carbon deposition tendency. Both ratios are considerably higher for the Texaco gas.

Free energy minimization using the initial Texaco and KRW coal gas compositions in the absence of sorbent was carried out to define the possible range of temperatures and pressures at which carbon deposition is favored, and to illustrate that the equilibrium gas composition is not static, but is also a function of temperature and pressure. The operating temperature limits established by equilibrium carbon deposition should not be considered as an absolute operating barrier. Since the thermodynamic tendency for carbon deposition decreases with increasing temperature, it is possible, particularly in fluidized-bed reactors having short residence times, that the rate of carbon deposition at temperatures somewhat lower than the thermodynamic limit would be small enough to allow operation.

Equilibrium carbon deposition tendencies for both the Texaco and KRW gases (Figure 1) increase with increasing pressure and decrease with increasing temperature. The Texaco gas exhibits a stronger tendency to carbon deposition because of the higher ratio of carbon to hydrogen plus oxygen. Temperature and pressure combinations in Area I of Figure 1 are such that carbon deposition may occur with both gas compositions. Area II temperatures and pressures are outside the carbon deposition region for the KRW gas but carbon deposition should remain a concern when using the Texaco gas. Temperatures and pressures falling in Area III are outside the carbon deposition range for both coal gases.

Figure 2 shows the mol fractions of the five dominant gas species in a Texaco gas as a function of temperature at 1 atm. At this pressure, carbon deposition might be expected at temperatures less than about 950K. CO_2 and H_2O mol fractions are high at low temperatures because the ratio of oxygen to hydrogen plus carbon remaining in the gas phase is high. As the temperature is increased, the quantity of solid carbon decreases, the mol fractions of CO and H_2 in the gas phase increase, and the gas becomes more reducing. Above 950K, the equilibrium gas composition is reasonably constant and is reasonably close to the initial Texaco coal gas composition. The equilibrium methane concentration decreases with increasing temperature and becomes quite small above 950K.

Table II. Composition of the Texaco Oxygen-Blown
and KRW Air-Blown Gasifier Products

	Composition, mol %	
	Texaco	KRW
H ₂	31.06	10.0
CO	39.87	15.0
H ₂ O	16.81	15.0
CO ₂	10.62	5.0
H ₂ S	1.04	1.0
N ₂	-----	54.0
NH ₃	0.21	-----
CH ₄	0.31	-----
$\frac{H_2 + CO}{H_2O + CO_2}$	2.59	1.25
$\frac{C}{O + H}$	0.29	0.22

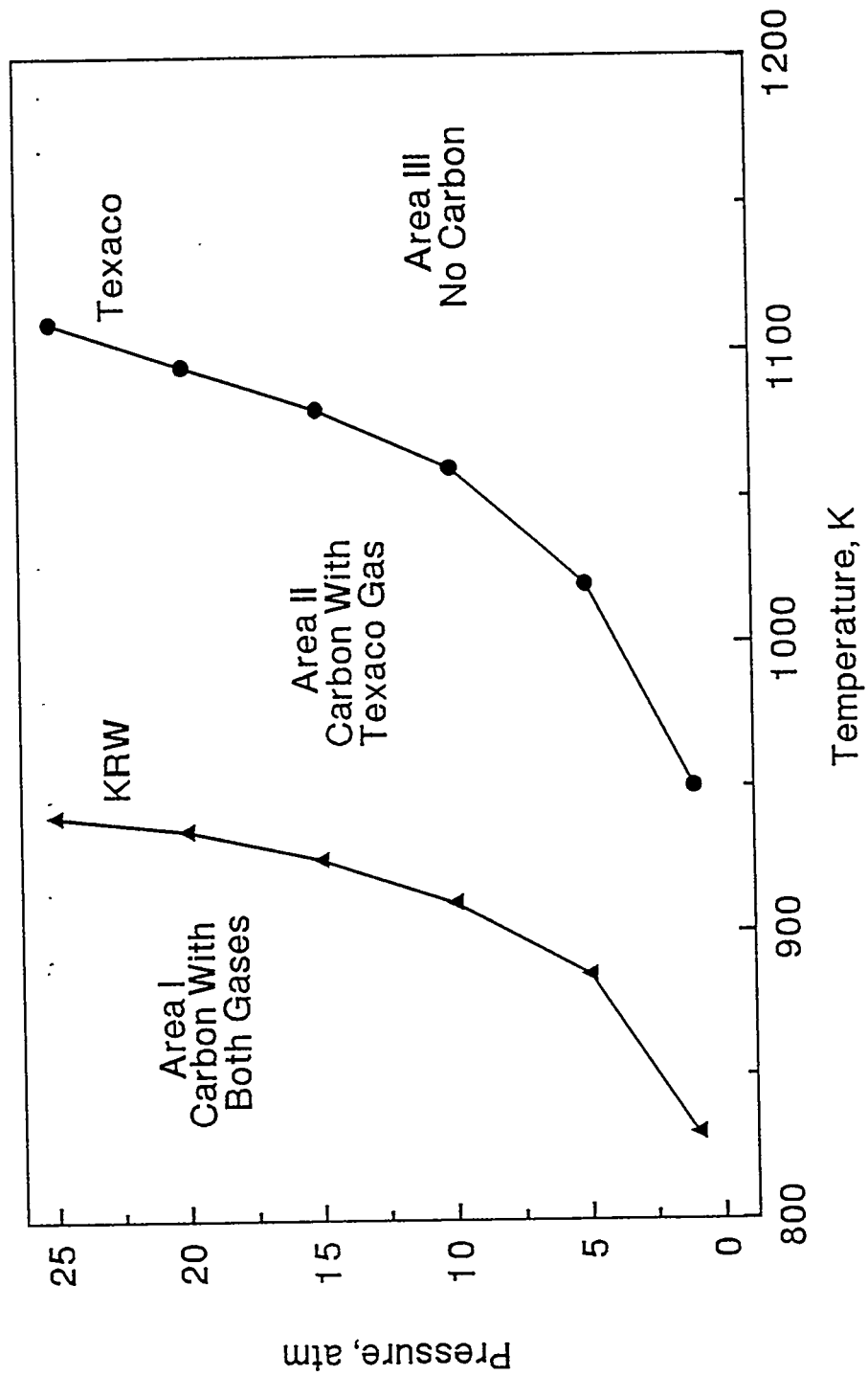


Figure 1. Carbon Deposition Tendencies of Texaco and KRW Gases

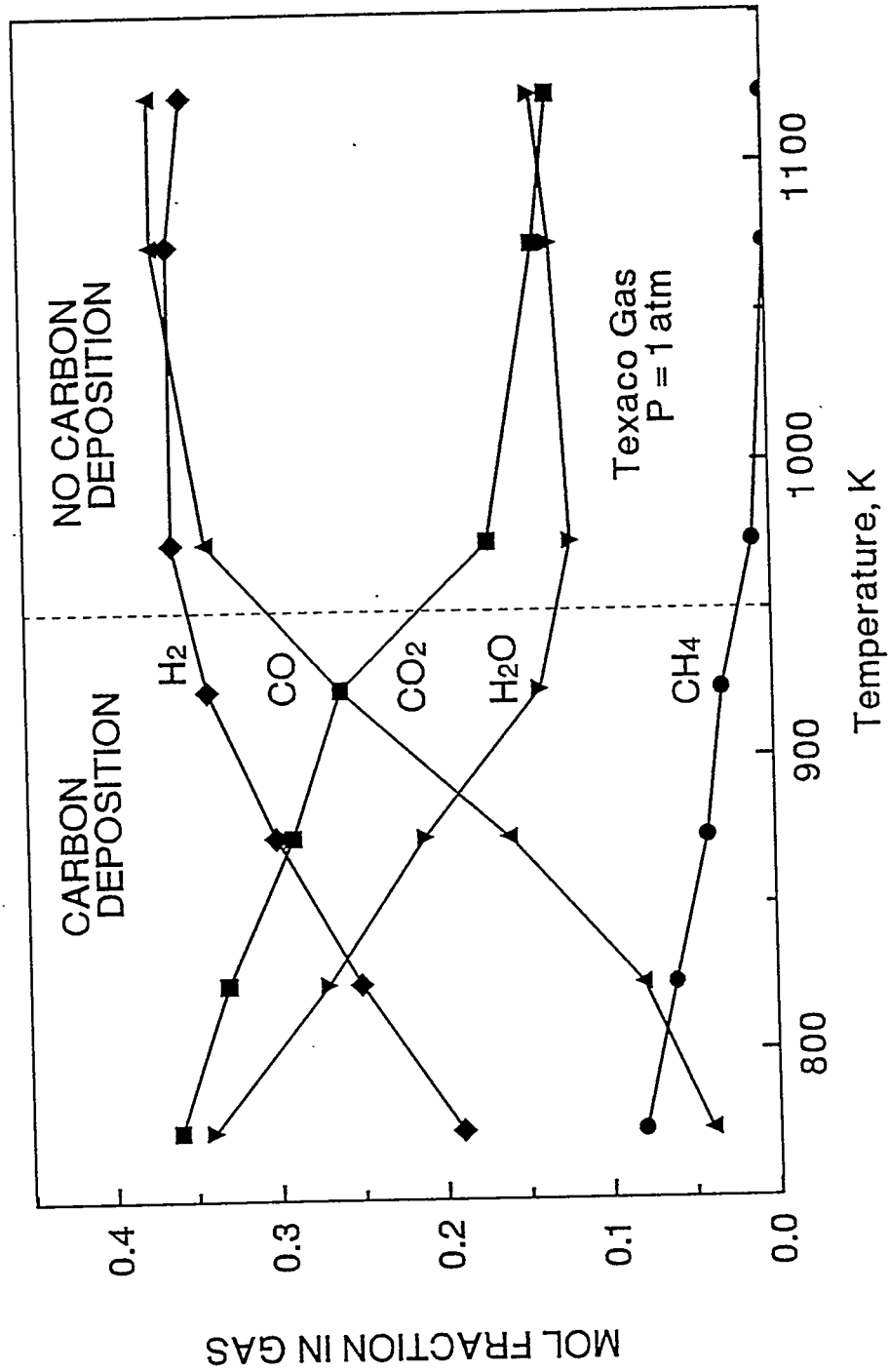


Figure 2. Equilibrium Mol Fraction of the Principal Gas Phase Components of Texaco Gas at $P = 1 \text{ atm}$

The effect of pressure is illustrated in Figure 3 where the equilibrium H_2 and H_2O mol fractions of a KRW gas are plotted as a function of temperature at both 1 and 25 atm. The maximum temperature at which carbon should be formed is about 830K at 1 atm and 940K at 25 atm. Below these temperatures the H_2 mol fraction increases and the H_2O mol fraction decreases with increasing temperature as the fixed quantity of oxygen in the gas phase must be divided between increasing amounts of carbon plus hydrogen. The smaller mol fraction of H_2 at high pressure is due primarily to increased quantities of CH_4 , particularly at low temperature. At temperatures above the carbon deposition region, the equilibrium gas composition becomes reasonably constant, and independent of both temperature and pressure.

Reduction-Desulfurization Analysis

Answers to several important questions can be obtained from the thermodynamic analysis of the reduction-desulfurization cycle. The most important question, of course, is the ability of the sorbent of interest to remove H_2S from the gas phase. Other questions concern the oxidation state of the excess sorbent in the reducing gas, the nature of the sulfided species, and possible formation of molten or volatile metal species. In order to answer all of the questions, a careful choice of the initial ratio of coal gas to sorbent is required.

We begin by considering one mol of metal oxide sorbent in its highest oxidation state. The quantity of coal gas to be equilibrated with the sorbent must be such that there is an excess of metal oxide with respect to H_2S and excess reducing gas with respect to metal oxide. Having more metal oxide than required to react with H_2S is necessary if one is to determine the oxidation state of the excess sorbent. If the sorbent is reduced in the coal gas, e.g. MnO_2 to MnO , it is necessary that the quantity of coal gas be sufficiently large to permit reduction without significantly altering the reducing character of the coal gas. As a general rule, these constraints are satisfied by choosing an initial molar ratio of coal gas to sorbent of 10 to 1. As a final check, the composition of the equilibrium gas phase of the sorbent-gas mixture should be compared to the equilibrium gas composition of the coal gas without sorbent being present.

Candidate sorbent systems which have been analyzed are listed in Table III. These systems were selected on the basis of the previous study of Westmoreland and Harrison (1976), and on their known ability to remove H_2S . Free-energy minimization analysis was carried out over a temperature range of 600 to 1150K (327 to 877°C; 620 to 1610°F) and pressure range of 1 to 25 atmospheres. Fractional removal of H_2S from the gas phase is only a weak function of pressure, particularly at temperatures above the carbon deposition region. Three types of temperature effects were found. With most sorbents, the fractional sulfur removal decreased monotonically with increasing temperature. Tin oxide, however, behaved differently, and the maximum fractional sulfur removal occurred at an intermediate temperature. Cerium oxide exhibited a still different pattern with equilibrium sulfur removal increasing with increasing temperature.

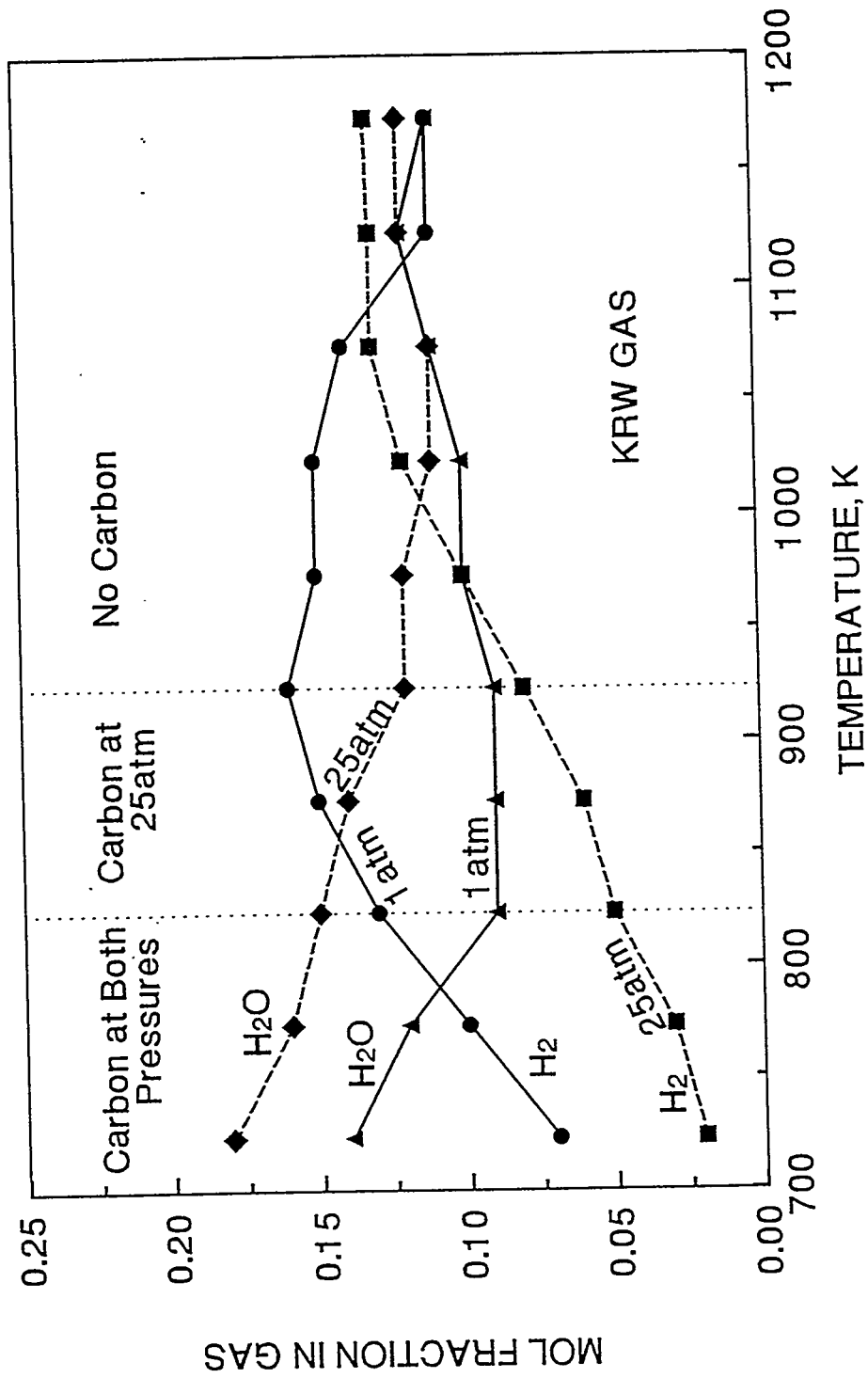


Figure 3. Variation in the Equilibrium H₂ and H₂O Mol Fractions of KRW Gas

Table III. Candidate Metal Oxide Sorbents
Considered in the Reduction/Desulfurization
Analysis

Metal	Highest Oxidation State
Cerium	CeO_2
Cobalt	Co_3O_4
Copper	CuO
Iron	Fe_2O_3
Manganese	MnO_2
Molybdenum	MoO_3
Tin	SnO_2
Zinc	ZnO

The normal behavior of decreasing sulfur removal efficiency with increasing temperature is illustrated in Table IV for manganese oxide. One mol of MnO_2 was equilibrated with 10 mols of Texaco gas (part A) and with 10 mols of KRW gas (part B). Equilibrium fractional sulfur removal is tabulated as a function of temperature and pressure. The limit of carbon deposition is indicated by the horizontal line in each column. Carbon deposition may occur at temperatures above the line (lower temperatures) but not below. Fractional sulfur removal decreases with increasing temperature and is almost independent of pressure, particularly at temperatures above the carbon deposition limit. MnO_2 should be reduced to MnO at all temperature and pressure combinations and no problem with the formation of volatile or molten manganese species is indicated. Fractional sulfur removals well in excess of 0.90 are possible at temperatures as low as 1000K (727°C, 1340°F) in the Texaco gas and as low as 850K (577°C, 1070°F) in the KRW gas, both at 1 atm. At 25 atm, the temperature limits are 1150K (877°C, 1610°F) in the Texaco gas and 1050K (777°C, 1430°F) in the KRW gas. The final point to be observed from Table IV is the small difference in the fractional sulfur removal potential between the Texaco and KRW gases.

The equilibrium analysis of tin oxide sorbent in contact with KRW gas is summarized in Table V. Once again, temperatures above the horizontal line in each column are in the carbon deposition region. For this system the fractional sulfur removal potential reaches a maximum at an intermediate temperature in the range of 870K (597°C, 1106°F). The maximum values, which range from 0.944 at 25 atm to 0.982 at 1 atm are appreciably smaller than obtained with manganese sorbent (Table IV). The tin system is complicated by the volatility of the sulfided product, SnS , and by the tendency of SnO_2 to be reduced to low melting metallic tin. SnS(g) and Sn(l) become significant at about the same temperature, which varies from about 850K at 1 atm to 975 K at 25 atm. Careful study of Table V shows that there are no conditions which simultaneously satisfy the requirement of no carbon deposition and no formation of SnS(g) or Sn(l) . A similar situation exists with tin oxide sorbent in contact with Texaco gas.

Therefore, if the thermodynamic analysis is correct, and if an operating system closely approached equilibrium, tin oxide would not be a satisfactory sorbent. However, because favorable experimental results have been reported using tin oxide, and because of favorable regeneration characteristics to be presented subsequently, we feel that tin oxide should be retained as a candidate sorbent. The analysis shows, however, that careful control of a tin oxide desulfurization reactor would be required. Positive temperature excursions would almost certainly result in the formation of SnS(g) and/or Sn(l) , while negative temperature excursions would result in carbon deposition.

Cerium oxide (CeO_2), as shown in Table VI, will not react with H_2S at low temperature. However, as the temperature is increased, formation of cerium oxysulfide, $\text{Ce}_2\text{O}_2\text{S}$, becomes favored. Although the maximum equilibrium fractional sulfur removal never achieves the desired level of 0.9, we feel that cerium oxide should be investigated further since its fractional sulfur removal-temperature response is unique, since no problems with the formation of molten or volatile species are indicated, and, since, as will be shown subsequently, cerium exhibits unique regeneration properties which favor the formation of elemental sulfur. The thermodynamic data

Table IV. Reduction/Desulfurization Analysis
of Manganese Oxide (MnO₂)

Part A: Initial Mixture, 1 mol MnO₂ plus 10 mols of Texaco Gas

Fractional Sulfur Removal

T(K)	P = 1 atm	P = 5 atm	P = 25 atm
600	0.999	0.997	0.985
650	0.998	0.998	0.994
700	0.997	0.996	0.996
750	0.994	0.993	0.993
800	0.992	0.990	0.989
850	0.989	0.986	0.984
900	0.987	0.982	0.978
950	0.981	0.977	0.970
1000	<u>0.972</u>	<u>0.971</u>	0.964
1050	0.960	0.960	0.955
1100	0.944	0.945	<u>0.943</u>
1150	0.926	0.926	<u>0.925</u>
Sulfided Product	MnS	MnS	MnS
Excess Mn	MnO	MnO	MnO
Molten/Volatile Species	None	None	None

Part B: Initial Mixture, 1 mol MnO₂ plus 10 mols of KRW Gas

Fractional Sulfur Removal

T(K)	P = 1 atm	P = 5 atm	P = 25 atm
600	0.999	0.999	0.997
650	0.999	0.999	0.999
700	0.998	0.998	0.998
750	0.997	0.996	0.996
800	<u>0.995</u>	0.994	0.993
850	0.990	0.990	0.989
900	0.986	0.986	0.984
950	0.979	<u>0.978</u>	0.978
1000	0.968	0.968	<u>0.968</u>
1050	0.957	0.957	0.957
1100	0.943	0.943	0.943
1150	0.925	0.925	0.925
Sulfided Product	MnS	MnS	MnS
Excess Mn	MnO	MnO	MnO
Molten/Volatile Mn Species	None	None	None

Table V. Reduction/Desulfurization Analysis of
Tin Oxide (SnO₂) With KRW Gas

Initial Mixture: 1 mol of SnO₂ and 10 mols of KRW gas

T(K)	Fractional Sulfur Removal		
	P = 1 atm	P = 5 atm	P = 25 atm
600	.532	.000	.000
650	.805	.552	.017
700	.911	.785	.512
750	.956	.888	.737
800	<u>.979</u>	.939	.849
850	.980	.967	.909
900	.959	.969	.943
950	.919	<u>.943</u>	.958
1000	.820	.905	<u>.924</u>
1050	.565	.832	.885
1100	.000	.679	.827
1150	.000	.351	.732
Sulfided Product	SnS	SnS	SnS
Excess Sn	SnO ₂ and Sn (ℓ) at T ≥ 850K	SnO ₂ and Sn (ℓ) at T ≥ 900K	SnO ₂ and Sn (ℓ) at T ≥ 975K
Volatile Species	SnS(g) at T ≥ 850K	SnS(g) at T ≥ 900K	SnS(g) at T ≥ 975K

Table VI. Reduction/Desulfurization Analysis of
Cerium Oxide (CeO_2) With Texaco Gas

Initial Mixture: 1 mol of CeO_2 and 10 mols of Texaco Gas

T(K)	Fractional Sulfur Removal		
	P = 1 atm	P = 5 atm	P = 25 atm
600	0.000	0.000	0.000
650	0.000	0.000	0.000
700	0.000	0.000	0.000
750	0.000	0.000	0.000
800	0.000	0.000	0.000
850	0.000	0.000	0.000
900	0.540	0.000	0.000
950	<u>0.818</u>	0.318	0.000
1000	0.848	<u>0.720</u>	0.000
1050	0.862	0.828	0.500
1100	0.870	0.859	<u>0.760</u>
1150	0.878	0.874	0.825
Sulfided Product	$\text{Ce}_2\text{O}_2\text{S}$	$\text{Ce}_2\text{O}_2\text{S}$	$\text{Ce}_2\text{O}_2\text{S}$
Excess Ce	CeO_2	CeO_2	CeO_2
Volatile Species	None	None	None

for Ce_2O_2S was obtained from the paper of Kay et al. (1993) since the general tabulation of Barin et al. (1993) does not contain data for this compound. It should be noted that there is some discrepancy between the Ce_2O_2S data from Kay et al. (1993) and that tabulated by Knacke et al. (1991), which is based upon original data of Fruehan (1979). We are uncertain as to which of the data sources is correct. Although the data of Kay et al. (1993) produces somewhat larger equilibrium fractional sulfur removal at temperatures equal to or greater than 900K, both data sets predict that equilibrium sulfur removal increases with increasing temperature.

Similar tables summarizing results of the reduction-desulfurization analysis for other sorbents may be found in the Appendix, and an overall summary of results is presented in Table VII. Reduction of excess oxide to a lower oxidation state occurs with the cobalt, copper, iron, manganese, and molybdenum systems. Cobalt and copper are reduced to the metallic state at all temperatures and pressures considered. SnO_2 is stable throughout most of the temperature and pressure range of interest, but, when reduction occurs, the product is elemental tin liquid. The lower oxide, SnO , is not stable at any of the conditions studied. The majority of the excess zinc is present as ZnO , but, as is well known, a small amount of elemental zinc vapor may be formed, with its formation favored at low pressure and high temperature. The only other volatile species encountered in the analysis was $SnS(g)$ whose formation is also favored by low pressures and high temperatures.

All systems except cerium and tin are thermodynamically capable of exceeding an arbitrarily established target of 90% desulfurization at conditions where carbon deposition is not favored. The maximum fractional sulfur removal for these two systems is slightly less than 90%, but because of their unique thermodynamic regeneration properties, both systems are considered as strong candidates. Although cobalt and copper are capable of high fractional sulfur removal, the fact that both are easily reduced to the metal makes them unsuitable sorbents.

Regeneration Analysis

The regeneration properties of the remaining candidate sorbents were analyzed using each of the regeneration concepts identified previously. As in the reduction/desulfurization analysis, answers to a number of questions were sought. Can the metal sulfide be regenerated and, if so, does the gaseous regeneration product contain substantial quantities of elemental sulfur? Fractional regeneration is defined as the fraction of sulfur originally present in the solid which is transferred to the gas phase; obviously this number should approach 1.0. In addition, substantial portions of the gas phase sulfur should be in elemental form (except for the third regeneration concept where H_2S is the desired product). Both fractions should be as large as possible.

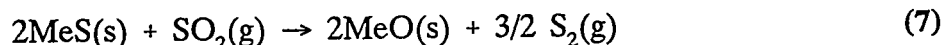
Other questions which can be answered by the thermodynamic analysis include the range of temperatures and pressures at which the metal sulfate may be formed, the oxidation state of the regenerated metal oxide, and the possible formation of molten or volatile regeneration products.

Table VII. Reduction/Desulfurization Analysis Summary

Sorbent System	Highest Oxidation State	Sulfided Product	Excess Metal	Volatile Species	90% Desulfurization w/o Carbon Deposition
Cerium	CeO ₂	Ce ₂ O ₂ S	CeO ₂	None	Slightly Below
Cobalt	Co ₃ O ₄	Co ₃ S ₄	Co(s)	None	Yes
Copper	CuO	Cu ₂ S	Cu(s)	None	Yes
Iron	Fe ₂ O ₃	FeS	FeO, Fe ₃ O ₄	None	Yes
Manganese	MnO ₂	MnS	MnO	None	Yes
Molybdenum	MoO ₃	MoS ₂	MoO ₂	None	Yes
Tin	SnO ₂	SnS	SnO ₂ , Sn(ℓ)	SnS(g)	Slightly Below
Zinc	ZnO	ZnS	ZnO, Zn(g)	Zn(g)	Yes

Concept 1: Reaction With SO₂

The desired reaction is represented generically by



The free energy minimization analysis was carried out by "mixing" one mol of metal sulfide with three mols of SO₂ and determining the equilibrium product composition as a function of temperature and pressure. Since the SO₂ is in excess, complete fractional regeneration is possible. If the reaction proceeded cleanly as written, the gaseous product would contain equal molar quantities of SO₂ and S₂. Thus, ideal performance would correspond to fractional regeneration of 1.0 and 50% of the gas phase sulfur would be in elemental form. While the conditions of this analysis do not match actual regeneration conditions, the results provide a valid relative comparison of sorbent regeneration properties.

MnS, MoS₂, and ZnS were effectively nonreactive with SO₂ over the temperature and pressure ranges of potential interest. Iron sulfide exhibited moderate reactivity while both SnS and Ce₂O₂S are capable of extensive reaction. Table VIII summarizes results when 1 mol of Ce₂O₂S is allowed to equilibrate with 3 mols of SO₂ at selected temperatures and pressures. The first requirement for achieving complete regeneration is that the temperature be above the sulfate decomposition temperature at the pressure of interest. All conditions in Table VIII satisfy this requirement except for 800K and 5 atm, where small amounts of Ce₂(SO₄)₃ are stable. The fractional regeneration at this condition is 0.95, but regeneration is complete at all other conditions illustrated in the table. Some of all of the gas phase sulfur compounds S₂ through S₈ are present at equilibrium. However, as the temperature is increased, S₂ becomes the dominant sulfur species. The distribution of gas phase sulfur between elemental and oxidized forms is reasonably close to the ideal fifty-fifty split at conditions where total regeneration is achieved, ranging only from 46% elemental sulfur at 1100K and 25 atm to 50% elemental sulfur at 750K and 1 atm. In order to maximize the elemental sulfur yield, regeneration should be carried out at the lowest possible temperature consistent with sulfate decomposition.

Regeneration of SnS with SO₂ produces results which are qualitatively similar to the Ce₂O₂S regeneration results of Table VIII. Complete regeneration is possible when the temperature exceeds the sulfate decomposition temperature, and the fraction of elemental sulfur in the gas phase is in the range of 0.46 to 0.48 at these conditions. However, tin sulfate (SnSO₄) is somewhat more stable than Ce₂(SO₄)₃, so that higher decomposition temperatures are required. Also, gas phase SnS may be formed at high temperatures and low pressures.

The performance of one mol of FeS with three mols of SO₂ is summarized in Table IX. At the lower temperatures, equilibrium would result in sulfur actually being added to the solid phase since FeS₂ is the dominant solid product. FeSO₄ may also be formed at high pressure and low temperature (25 atm and 773K). As the temperature is increased, FeS₂ is no longer stable and the original sulfided product FeS appears in the condensed phase. At this point, reaction

Table VIII. Equilibrium Analysis for the Regeneration of $Ce_2O_2S(s)$
With Three Mols of $SO_2(g)$ at Selected T and P

Temp., K	750	1100	800	850	1100	900	1100
Press., atm	1	1	5	5	5	25	25
Gas Phase Composition, mol fraction							
CeO_2	1.00	1.00	0.97	1.00	1.00	1.00	1.00
$Ce_2(SO_4)_3$	0.00	0.00	0.03	0.00	0.00	0.00	0.00
Condensed Phase Composition, mol fraction							
SO_2	0.84	0.66	0.82	0.81	0.67	0.82	0.69
S_2	0.04	0.31	0.04	0.07	0.28	0.05	0.23
S_3	0.01	0.01	0.01	0.01	0.02	0.01	0.03
S_4	0.00	0.00	0.00	0.01	0.00	0.01	0.01
S_5	0.01	0.00	0.01	0.01	0.00	0.01	0.00
S_6	0.04	0.00	0.04	0.03	0.00	0.03	0.00
S_7	0.03	0.00	0.04	0.03	0.00	0.03	0.00
S_8	0.03	0.00	0.04	0.01	0.00	0.03	0.00
S_2O	0.01	0.02	0.01	0.02	0.03	0.01	0.03
Sulfur Distribution (as S), fraction							
Condensed Phase	0.00	0.00	0.05	0.00	0.00	0.00	0.00
Gas Phase	1.00	1.00	0.95	1.00	1.00	1.00	1.00
Sulfur Distribution Within Gas Phase, fraction							
Elemental	0.50	0.48	0.53	0.49	0.47	0.49	0.46
Oxide	0.50	0.52	0.47	0.51	0.53	0.51	0.54

Table IX. Regeneration Analysis For
the Reaction Between Iron Sulfide
(FeS) and SO₂

		Initial Conditions: One Mol of FeS With Three Mols of SO ₂						
Temp., K		873	973	1173	773	873	1073	1173
Press., atm		1	1	1	25	25	25	25
Condensed Phase Composition, mol fraction								
FeS		0.00	0.97	0.93	0.00	0.00	0.97	0.96
FeS ₂		0.82	0.00	0.00	0.67	0.83	0.00	0.00
Fe ₃ O ₄		0.18	0.03	0.07	0.00	0.17	0.03	0.04
FeSO ₄		0.00	0.00	0.00	0.33	0.00	0.00	0.00
Gas Phase Composition, mol fraction								
SO ₂		0.99	0.98	0.95	1.00	1.00	0.98	0.97
S ₂		0.01	0.02	0.05	0.00	0.00	0.02	0.03
Sulfur Distribution (as S), fraction								
Condensed Phase		0.30	0.24	0.20	0.42	0.31	0.23	0.22
Gas Phase		0.70	0.76	0.80	0.58	0.69	0.77	0.78
Sulfur Distribution Within Gas Phase, fraction								
Elemental		0.02	0.04	0.09	0.00	0.00	0.04	0.05
Oxidized		0.98	0.96	0.91	1.00	1.00	0.96	0.95

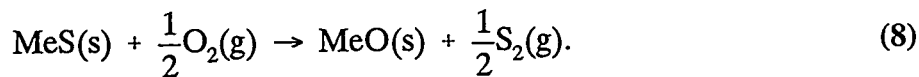
between FeS and SO₂ becomes possible, but the extent of regeneration is small even at the highest temperature. At 1 atm and 1173K (900°C, 1651°F), FeS remains the dominant condensed phase specie and 20% of the sulfur remains in the condensed phase (as contrasted to 25% of the sulfur in the condensed phase of the initial mixture). The only gaseous sulfur products are SO₂ and S₂; 9% of the gas phase sulfur is present as S₂, compared to 50% under ideal regeneration conditions.

While the regeneration of FeS with SO₂ to form S₂ is possible at high temperature, extremely large quantities of SO₂ would be required to achieve complete conversion of FeS to Fe₃O₄ and the regenerator off-gas will contain only a small concentration of elemental sulfur. Thus, the energy requirements associated with sulfur condensation and SO₂ reheat and recycle will be large.

In summary, we conclude that regeneration of SnS and Ce₂O₂S with SO₂ to produce elemental sulfur may be attractive. Regeneration of FeS using this concept is technically possible, but not economically feasible. Regeneration of MnS, MoS₂, and ZnS are even less feasible than FeS regeneration.

Concept 2: Partial Oxidation

The desired reaction is represented generally by



However, we anticipate that the regeneration inlet gas would contain steam as well, and the reactor would operate in an O₂-starved regime. Multiple gas-solid and gas phase reactions such as listed in Table I would be expected under these conditions.

In order to compare the feasibility of regenerating the various sorbents using the partial oxidation approach, the thermodynamic analysis was carried out by "mixing" one mol of sulfided sorbent with one mol of O₂ and one mol of H₂O, and calculating the equilibrium composition as a function of temperature and pressure. The questions of interest were essentially the same as those asked for regeneration concept 1. What is the extent of regeneration (transfer of sulfur from solid to gas) and what fraction of the sulfur in the gas phase is in elemental form? What temperatures and pressures are required to avoid sulfate formation, and what is the oxidation state of the metal oxide product? What volatile or molten metal compounds may be formed and at what conditions?

All sulfided sorbents will react, at least to some extent, in the oxygen-steam atmosphere. However, effectively no elemental sulfur can be formed from either MoS₂ or ZnS. A small amount of elemental sulfur can be produced during the regeneration of MnS, and a somewhat larger amount with FeS. Once again, SnS and Ce₂O₂S are most reactive at these conditions, and the quantities of elemental sulfur which can be formed are quite significant.

Table X summarizes the results for the regeneration of Ce_2O_2S . $Ce_2(SO_4)_3$ formation can be avoided at all pressures if the regeneration temperature is equal to or greater than about 700K (427°C, 800°F). All sorbent would be regenerated to the original CeO_2 when sulfate formation is avoided. The quantity of elemental sulfur produced is sufficient, however, that condensation of sulfur in the regeneration reactor at low temperature and high pressure is of concern.

The equilibrium gas phase consists primarily of H_2O and effectively all O_2 has reacted. Elemental sulfur (S_2 through S_8), oxidized sulfur (predominantly SO_2), and reduced sulfur species (predominantly H_2S) are formed. The fraction of the sulfur in elemental form is greatest just above the sulfate decomposition temperature. At the optimum conditions represented in Table X, 75% of the total sulfur can be converted to elemental form at 700K (427°C, 800°F) and 1 atm. The fact that the ratio H_2S to SO_2 is approximately 2 at several conditions raises the possibility of sending the regeneration product gas, after elemental sulfur condensation, to a Claus reactor where much of the remaining sulfur compounds could be converted to additional elemental sulfur.

The behavior of SnS is similar in many respects to the behavior of Ce_2O_2S , although, as shown in Table XI, higher temperatures are required if complete regeneration is to be approached. $SnSO_4$ is somewhat more stable than $Ce_2(SO_4)_3$, and SnS_2 and Sn_2S_3 may be formed at certain conditions. At the highest temperatures in Table XI, between 6% and 11% of the sulfur would remain in the solid phase, as SnS at 1 atm and as Sn_2S_3 at 5 and 25 atm. Because of the higher temperatures required to approach complete regeneration, the elemental sulfur content in the gas phase is not as large as with Ce_2O_2S . At best, 56% of the gas phase sulfur is in elemental form at 1 atm and 1050K (777°C, 1430°F). Once again, significant quantities of gaseous SnS may be formed at high temperature.

The partial oxidation concept may also be used to regenerate FeS and selected results of the equilibrium analysis are shown in Table XII. No serious problems with $FeSO_4$ are indicated since its decomposition temperature is relatively low. However, regeneration temperature should be sufficiently high to prevent the formation of FeS_2 , approximately 900K (627°C, 1160°F) for the conditions represented in Table XII. Fe_3O_4 is the stable oxide product at all conditions illustrated. Complete regeneration cannot be achieved at these conditions, as between 33% and 48% of the sulfur remains in the solid phase. In addition, the vast majority of sulfur in the gas phase would be present in oxidized form (SO_2). Elemental sulfur is favored at high temperature and low pressure where 10% of the gas phase sulfur is in elemental form.

The fact that the maximum concentration of elemental sulfur in the gas phase is far below levels which have been reported experimentally should not be of concern. It is impossible for thermodynamic analysis to duplicate actual conditions in a fixed-bed reactor. Instead, the initial conditions of one mol of metal sulfide, one mol of O_2 , and one mol of steam for the thermodynamic analysis were chosen to permit the relative performance of various sorbent systems to be compared.

Table X. Equilibrium Analysis for the Regeneration of One Mol of $Ce_2O_2S(s)$
 With One Mol of $O_2(g)$ and One Mol of $H_2O(g)$

Temp., K	650	700	750	850	1100	750	850	1100	750	850	1100
Press., atm	1	1	5	5	5	5	5	5	5	5	25
Condensed Phase Composition, mol fraction											
$CeO_2(s)$	0.99	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
$Ce_2(SO_4)_3(g)$	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$S(l)$	0.00	0.00	0.00	0.00	0.00	0.15	0.00	0.00	0.19	0.00	0.00
Gas Composition, mol fraction											
H_2	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
H_2O	0.74	0.69	0.52	0.68	0.50	0.78	0.63	0.50	0.79	0.63	0.48
H_2S	0.13	0.14	0.17	0.15	0.20	0.16	0.18	0.20	0.12	0.18	0.23
SO_2	0.03	0.07	0.09	0.07	0.10	0.01	0.09	0.10	0.04	0.09	0.11
S_2	0.00	0.01	0.21	0.01	0.18	0.00	0.02	0.18	0.00	0.02	0.15
S_6	0.03	0.03	0.00	0.03	0.00	0.01	0.03	0.00	0.01	0.02	0.00
S_7	0.02	0.02	0.00	0.02	0.00	0.01	0.02	0.00	0.01	0.02	0.00
S_8	0.04	0.03	0.00	0.03	0.00	0.03	0.03	0.00	0.00	0.02	0.00
S_2O	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.02	0.00	0.01
Sulfur Distribution (as S), fraction											
Condensed	0.03	0.00	0.00	0.00	0.00	0.41	0.00	0.00	0.48	0.00	0.00
Gas	0.97	1.00	1.00	1.00	1.00	0.59	1.00	1.00	0.52	1.00	1.00
Sulfur Distribution Within Gas Phase, fraction											
Elemental	0.82	0.75	0.63	0.73	0.55	0.70	0.66	0.55	0.65	0.66	0.49
Oxidized	0.03	0.08	0.14	0.09	0.16	0.01	0.12	0.16	0.09	0.12	0.19
Reduced	0.15	0.17	0.23	0.18	0.29	0.29	0.22	0.29	0.26	0.22	0.33

Table XI. Equilibrium Analysis for the Regeneration of One Mol SnS(s) With One Mol of O₂(g) and One Mol of H₂O(g) at Selected Conditions Near the Sulfate Decomposition Temperature

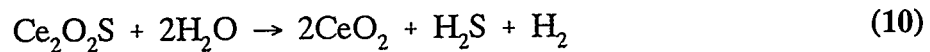
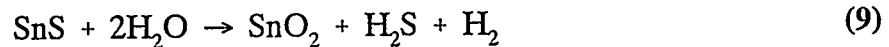
Temp., K	875	900	975	1050	900	975	1050	975	1050	975	1050	1125
Press., atm	1	1	1	1	5	5	5	5	5	25	25	25
Condensed Phase Composition, mol fraction												
SnO ₂ (3)	0.76	0.91	0.96	0.94	0.53	0.74	0.97	0.51	0.58	0.51	0.58	0.96
SnS(B)	0.00	0.00	0.00	0.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SnSO ₄ (s)	0.10	0.00	0.00	0.00	0.28	0.14	0.00	0.30	0.31	0.30	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	0.19	0.00	0.00
Sn ₂ S ₃ (s)	0.00	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.11	0.00	0.11	0.04
Gas Composition, mol fraction												
H ₂ O	0.60	0.54	0.52	0.53	0.71	0.60	0.51	0.71	0.65	0.71	0.65	0.51
H ₂ S	0.18	0.17	0.18	0.15	0.22	0.21	0.19	0.25	0.25	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	0.02	0.04	0.15
S ₂	0.09	0.13	0.17	0.18	0.03	0.09	0.15	0.02	0.05	0.02	0.05	0.13
S ₂ O	0.00	0.01	0.01	0.01	0.00	0.00	0.01	0.00	0.00	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	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	0.68	0.57	0.11
Gas Phase	0.63	0.82	0.93	0.94	0.34	0.61	0.92	0.32	0.43	0.32	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	0.12	0.23	0.42
Oxidized	0.25	0.27	0.19	0.20	0.12	0.21	0.23	0.07	0.12	0.07	0.12	0.27
Reduced	0.37	0.29	0.28	0.24	0.70	0.42	0.21	0.80	0.63	0.80	0.63	0.23
Metal Sulfide	0.00	0.00	0.00	0.00	0.00	0.01	0.08	0.01	0.02	0.01	0.02	0.08

Table XII. Equilibrium Analysis for the Regeneration of One Mol of FeS(s) With One Mol of O₂(g) and One Mol of H₂(g) at Selected T and P

Temp., K	873	973	1173	873	973	1173
Pres., atm	1	1	1	25	25	25
Condensed Phase Composition, mol fraction						
FeS	0.00	0.63	0.60	0.00	0.63	0.61
FeS ₂	0.48	0.00	0.00	0.49	0.00	0.00
Fe ₃ O ₄	0.52	0.37	0.40	0.51	0.37	0.39
Gas Composition, mol fraction						
H ₂ O	0.65	0.61	0.60	0.66	0.61	0.60
H ₂ S	0.01	0.01	0.02	0.01	0.02	0.02
SO ₂	0.33	0.36	0.35	0.33	0.37	0.36
S ₂	0.00	0.01	0.02	0.00	0.01	0.01
Sulfur Distribution (as S), fraction						
Condensed		0.36	0.33	0.48	0.36	0.34
Gas		0.64	0.67	0.52	0.64	0.66
Sulfur Distribution Within Gas Phase, fraction						
Elemental		0.05	0.10	0.01	0.03	0.06
Oxide		0.92	0.86	0.97	0.93	0.89
Reduced		0.03	0.04	0.02	0.05	0.05

Concept 3: Regeneration With Steam/Claus

Concept 3, involving sorbent regeneration with steam, is actually a reverse of the desulfurization reaction, and the direct product is H_2S instead of elemental sulfur. This is considered a viable concept, however, if sufficiently high concentrations of H_2S to permit direct feed to a Claus reactor can be produced. Since this concept represents a reversal of the desulfurization reaction, it is obvious that sorbents having the greatest affinity for sulfur will be the least amenable to regeneration with steam. For this reason, we have examined only the SnS and Ce_2O_2S systems. In both of these cases, H_2 as well as H_2S will be produced. The desired reactions are



The thermodynamic analysis shows that the reaction should proceed essentially as written. That is, no equilibrium products other than those represented by the stoichiometric equations should be formed in appreciable quantities. The questions which were examined in the thermodynamic analysis included the equilibrium fractional regeneration (fraction of the sulfur transferred to the gas phase), the H_2S content of the regeneration product gas, and the possible presence of volatile or molten species in the equilibrium product.

Table XIII summarizes results from the analysis of SnS regeneration with steam at selected temperatures, pressures, and steam to SnS ratios. The results are, for practical purposes, independent of pressure, since the reaction results in no change in the number of gas phase mols. The key parameter, as shown in the first four columns of Table XIII, is the steam to SnS ratio. While only two mols of steam per mole of SnS are required by stoichiometry, equilibrium requires that more than 20 mol of steam per mol of SnS be used if complete regeneration is to be achieved. Figure 4 shows the minimum steam to sorbent ratio required for complete regeneration of both SnS and Ce_2O_2S as a function of temperature at a pressure of 15 atm. The ratio is almost constant for SnS and increases with increasing temperature for Ce_2O_2S . Discussion of the regeneration of Ce_2O_2S will follow the SnS discussion. The mol fractions of the gaseous products H_2O , H_2 , and H_2S at $P = 15$ atm and $T = 850K$ do not change with the steam to SnS ratio until complete regeneration becomes theoretically possible at approximately 24 mols steam per mol SnS. Below this ratio, the only parameter which changes is the fractional distribution of sulfur between the gaseous and condensed phases. Temperature causes no significant change in the gas phase composition when a thermodynamic excess of steam is used (as shown by the last four columns of Table XIII). However, as the temperature is increased, trace quantities of SnS(g) and later SO_2 and S_2 may be formed.

Table XIII. Regeneration Analysis for the Reaction of Tin Sulfide (SnS) With Steam

Press., atm	15	15	15	15	15	15	15	15	15	15	15	15
Temp., K	850	850	850	850	850	850	850	850	750	950	1050	
Mol H ₂ O/Mol SnS	3	10	20	30	30	3	3	3	30	30	30	
Condensed Species, mol fraction												
SnO ₂	0.130	0.435	0.069	1.00	1.00	0.130	0.130	0.130	1.00	1.00	1.00	1.00
SnS	0.870	0.565	0.131	0.00	0.00	0.870	0.870	0.870	0.00	0.00	0.00	0.00
Gas Species, mol fraction												
H ₂	0.043	0.043	0.043	0.033	0.033	0.044	0.043	0.033	0.033	0.033	0.033	0.033
H ₂ O	0.913	0.913	0.913	0.933	0.933	0.912	0.913	0.933	0.933	0.933	0.933	0.933
H ₂ S	0.043	0.043	0.043	0.033	0.033	0.044	0.043	0.033	0.033	0.033	0.033	0.033
SnS	0.000	0.000	0.000	0.000	0.000	trace	trace	0.000	0.000	trace	trace	trace
SO ₂	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
S ₂	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Sulfur Distribution (as S), fraction												
Condensed Phase	0.87	0.57	0.13	0.00	0.00	0.87	0.87	0.00	0.00	0.00	0.00	0.00
Gas Phase	0.13	0.43	0.87	1.00	1.00	0.13	0.13	1.00	1.00	1.00	1.00	1.00
Sulfur Distribution Within Gas Phase, fraction												
Elemental	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	trace
Oxidized	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	trace
Reduced	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	0.99
Metal Sulfide	0.00	0.00	0.00	0.00	0.00	trace	trace	0.00	0.00	0.00	0.00	trace

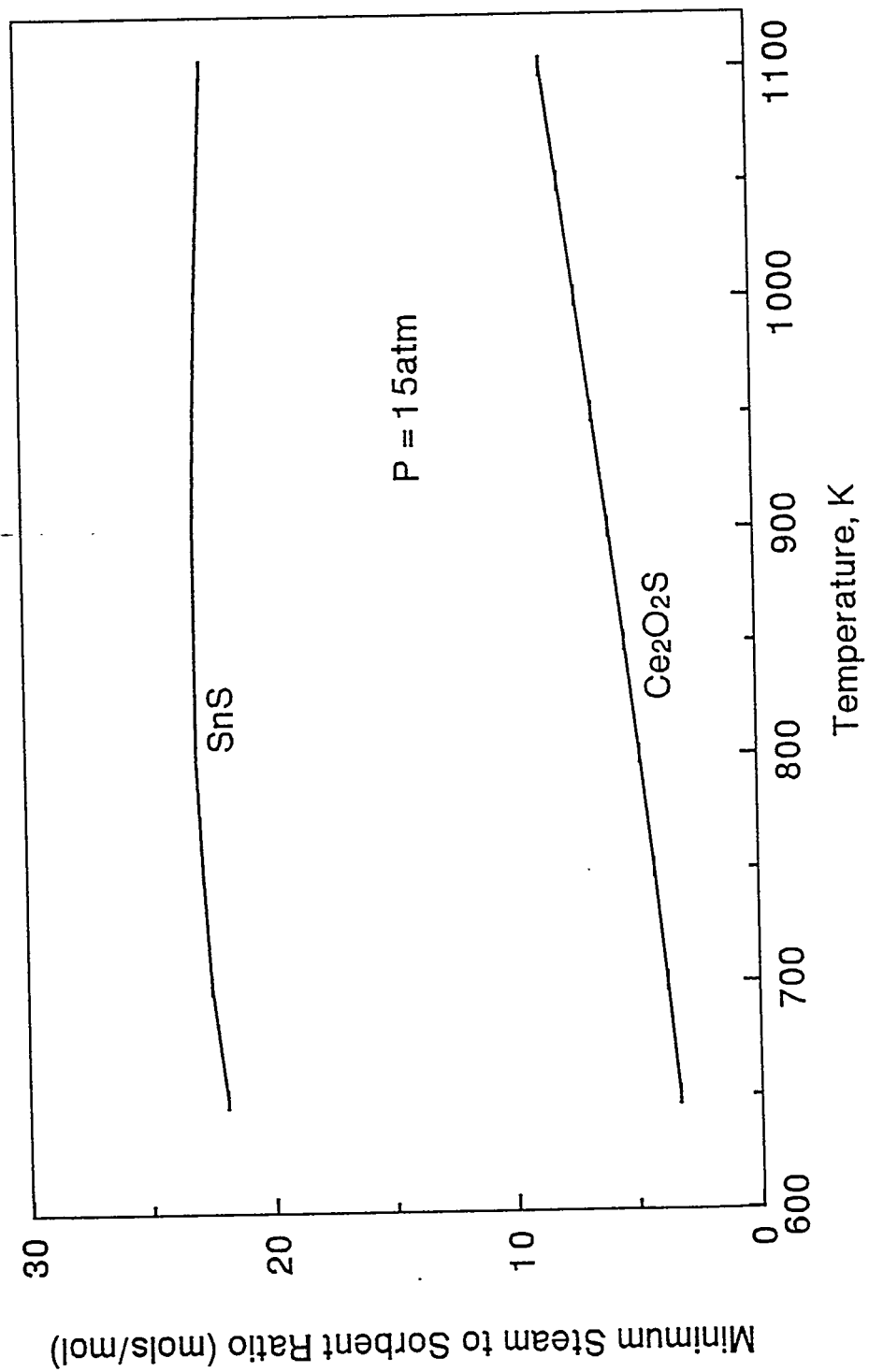


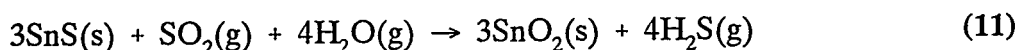
Figure 4. Minimum Ratio of Steam to Sulfided Sorbent Required for Complete Regeneration

The remaining questions regarding the possible regeneration of SnS with steam relate to the kinetics. Are the kinetics sufficiently fast to allow equilibrium to be approached without using large amounts of steam beyond the thermodynamic minimum? Similarly, are the kinetics sufficiently fast so that regeneration can be achieved at temperatures and pressures where the formation of SnS is not important?

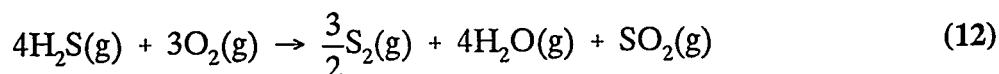
From a thermodynamic standpoint, Ce_2O_2S is more amenable to regeneration with steam than is SnS. This property has already been illustrated in Figure 4, which shows that the minimum steam requirement varies between about 3 and 9 mols per mol of Ce_2O_2S , depending on temperature. More detailed results of the thermodynamic analysis are presented in Table XIV. In addition to the fact that smaller quantities of steam are required, we see that no by-products are formed except at temperatures equal to or greater than 1050K, where trace quantities of elemental sulfur are predicted. Ce_2O_2S is regenerated to the original CeO_2 form and there is no indication that volatile cerium compounds may be formed. Effectively all of the sulfur is converted to H_2S which may be produced at mol fractions ranging from 0.1 to 0.30.

The remaining questions concerning this regeneration concept are the same as those for SnS regeneration, and relate to the kinetics of the reaction. These questions can only be answered experimentally.

Nielsen and Rudbeck (1993) have recently proposed a modification of the concept involving steam regeneration of SnS to produce H_2S . In the modification, both H_2O and SO_2 are fed in stoichiometric ratios for the reaction



H_2S is converted in a modified Claus reactor to produce elemental sulfur, SO_2 and H_2O by the reaction :



The H_2O to SO_2 ratio of 4 to 1 is the same as that needed for sorbent regeneration. By recycling this H_2O and SO_2 there would be little net consumption of steam or SO_2 .

We have also examined the thermodynamics of the steam- SO_2 regeneration reaction and selected results are presented in Table XV. A stoichiometric ratio of 1 represents 3 mols of SnS per 1 mol SO_2 and 4 mols H_2O as required by the stoichiometric equation. At the lower temperatures, either SnS_2 or Sn_2S_3 is favored, and it is not until 1100K that SnO_2 and SnS becomes the only equilibrium solid species. At these conditions the fractional regeneration increases with increasing temperature but complete regeneration is not possible using stoichiometric feed ratios. At most, 50% of the sulfur ends up in the gas phase

Table XIV. Regeneration Analysis for the Reaction of Cerium Oxysulfide ($\text{Ce}_2\text{O}_2\text{S}$) With Steam

Press., atm	15	15	15	15	15	15
Temp, K	650	850	1050	650	850	1050
Mol H_2O /Mol $\text{Ce}_2\text{O}_2\text{S}$	3	3	3	10	10	10
Condensed Species, mol fraction						
CeO_2	0.95	0.72	0.55	1.00	1.00	1.00
$\text{Ce}_2\text{O}_2\text{S}$	0.05	0.28	0.44	0.00	0.00	1.00
Gas Species						
H_2	0.30	0.19	0.13	0.10	0.10	0.10
H_2O	0.39	0.62	0.74	0.80	0.80	0.80
H_2S	0.30	0.19	0.13	0.10	0.10	0.10
S_2	0.00	0.00	trace	0.00	0.00	trace
Sulfur Distribution (as S), fraction						
Condensed	0.09	0.43	0.61	0.00	0.00	0.00
Gas	0.91	0.57	0.39	1.00	1.00	1.00
Sulfur Distribution Within Gas Phase, fraction						
Elemental	0.00	0.00	trace	0.00	0.00	trace
Oxidized	0.00	0.00	0.00	0.00	0.00	0.00
Reduced	1.00	1.00	1.00	1.00	1.00	1.00

Table XV. Regeneration Analysis for the Reaction of SnS With SO₂ and H₂O

Temp., K	800	900	1000	1100	800	950	1000	1050	800	850	900	1050	1050	1050
Press., atm	1	1	1	1	1	1	1	1	1	1	1	1	1	1
Stoichiometric Ratio	1	1	1	1	2	2	2	2	5	5	5	5	5	5
Condensed Species, mol fraction														
SnO ₂	0.48	0.53	0.45	0.32	0.46	0.86	0.91	0.73	0.00	0.40	1.00	1.00	1.00	1.00
SnS	0.00	0.00	0.47	0.68	0.00	0.06	0.00	0.27	0.00	0.00	0.00	0.00	0.00	0.00
SnSO ₄	0.00	0.00	0.00	0.00	0.20	0.00	0.00	0.00	1.00	0.60	0.00	0.00	0.00	0.00
SnS ₂	0.52	0.39	0.00	0.00	0.33	0.14	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sn ₂ S ₃	0.00	0.08	0.08	0.00	0.00	0.00	0.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Gas Species, mol fraction														
H ₂	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00
H ₂ O	0.78	0.74	0.65	0.68	0.75	0.64	0.65	0.66	0.78	0.76	0.72	0.73	0.71	0.71
H ₂ S	0.21	0.23	0.20	0.13	0.20	0.22	0.20	0.16	0.16	0.13	0.10	0.08	0.11	0.11
SO ₂	0.00	0.01	0.05	0.08	0.03	0.05	0.05	0.07	0.03	0.08	0.13	0.13	0.14	0.14
S ₂	0.00	0.02	0.09	0.09	0.02	0.08	0.09	0.10	0.02	0.03	0.04	0.05	0.03	0.03
Sulfur Distribution (as S), fraction														
Condensed	0.79	0.71	0.49	0.50	0.52	0.17	0.15	0.16	0.38	0.22	0.00	0.00	0.00	0.00
Gas	0.21	0.29	0.51	0.50	0.48	0.83	0.85	0.84	0.62	0.78	1.00	1.00	1.00	1.00
Distribution of Gas Phase Sulfur, fraction														
Elemental	0.01	0.13	0.42	0.46	0.18	0.40	0.43	0.46	0.16	0.24	0.27	0.35	0.23	0.21
Oxidized	0.00	0.03	0.12	0.20	0.11	0.12	0.12	0.16	0.15	0.28	0.42	0.39	0.44	0.44
Reduced	0.99	0.84	0.46	0.32	0.71	0.49	0.44	0.37	0.69	0.48	0.31	0.24	0.33	0.35
Metal Sulfide	0.00	0.00	trace	0.02	0.00	trace	trace	0.01	0.00	0.00	trace	trace	trace	trace

at 1100K. This represents a fractional regeneration of only 0.33 since some sulfur was in the gas phase initially.

Doubling the quantities of SO_2 and H_2O to give a stoichiometric ratio of 2 (100% excess SO_2 and H_2O) increases the transfer of sulfur to the gas phase but does not result in complete regeneration. At 1050K, 84% of the sulfur is in the gas phase, which corresponds to 0.78 fractional regeneration. SnSO_4 , SnS_2 , and Sn_2S_3 are stable solid products below 1050K. Further increases in the quantities of SO_2 and H_2O to produce a stoichiometric ratio of 5 (400% excess) results in complete regeneration at temperatures of 900K and above. SnSO_4 is stable to 850K, but SnS_2 and Sn_2S_3 are not favored. At 900K, the fractional distribution of sulfur in the gas phase is 0.27 as elemental sulfur (primarily S_2), 0.42 as oxidized sulfur (primarily SO_2), and 0.31 as reduced sulfur (primarily H_2S), and a trace of $\text{SnS}(\text{g})$. If the temperature is increased to 1050K, regeneration to SnO_2 is complete, the fraction of elemental sulfur is increased, and less SO_2 and H_2S are formed. More $\text{SnS}(\text{g})$ is also formed but the quantity is still small. An increase in pressure at conditions corresponding to complete regeneration will cause the distribution of gas phase compounds to change and will extend the stability of SnSO_4 to higher temperatures. As indicated in the last three columns of Table XV, 1050K and a stoichiometric ratio of 5 should result in complete regeneration even at 25 atmospheres. Increased pressure, however, reduces the proportion of elemental sulfur and increases the proportions of oxidized and reduced sulfur.

Nielsen and Rudbeck (1993) suggest that this process should operate near 400°C and that the gas products from the Claus reactor should contain H_2O and SO_2 in the 4 to 1 molar ratio required for the regeneration reaction. No steam or SO_2 make-up would be required since these two components react in the 4 to 1 ratio in the regenerator and are reformed in the same ratio in the modified Claus system. However, the thermodynamic analysis using a stoichiometric ratio of 5 indicates that SnSO_4 would be formed and that no regeneration would occur at this temperature. At higher temperatures required for regeneration of SnS to SnO_2 , side reactions would likely upset the required 4 to 1 H_2O to SO_2 ratio, thus requiring purge and make-up streams to re-establish to the stoichiometric ratio.

Discussion

Thermodynamic analysis of each of the regeneration concepts has shown that sorbents which possess the greatest affinity for H_2S in the reduction/desulfurization cycle will be the most difficult to regenerate with elemental sulfur as a direct product. For practical purposes, elemental sulfur cannot be produced during the regeneration of zinc, manganese, and molybdenum sorbents. Each of these systems is thermodynamically capable of H_2S removal efficiencies which approach 100%.

Iron-based sorbents are somewhat less effective for removal of H_2S , but are more amenable to elemental sulfur production. The most promising concept for the production of elemental sulfur during FeS regeneration seems to be partial oxidation in which the regeneration reactor feed would consist of a limited amount of O_2 and an excess of H_2O . Numerous simultaneous reactions such as listed in Table I would occur. The primary objective, therefore,

would be to determine reactor conditions which maximize the rate of the reactions which produce elemental sulfur relative to the rate of the reactions which produce SO_2 . The feasibility of this objective is supported by literature reports (Joshi et al., 1979, Grindley and Steinfeld, 1981) indicating that complete regeneration is possible with as much as 70% of the liberated sulfur produced in elemental form.

Direct regeneration of FeS with SO_2 (concept 1) is feasible although the thermodynamic analysis indicates that a large excess of SO_2 would be required to obtain complete regeneration. Separating the elemental sulfur by condensation and then reheating and recycling the excess SO_2 will likely be prohibitively expensive. Similarly, the regeneration of FeS using steam to produce H_2S will require large excesses of steam which will also be costly.

The thermodynamic properties of both SnS and $\text{Ce}_2\text{O}_2\text{S}$ make these systems uniquely suited to elemental sulfur production during regeneration. They are, however, not as efficient for H_2S removal, and two-step desulfurization such as shown in Figure 5 would be required to reduce the H_2S concentration to the 10 to 20 ppm level. At desulfurization conditions of interest, i.e., outside the carbon deposition region and at temperatures and pressures such that volatile or molten metal species will not be formed, the H_2S removal capability of both SnO_2 and CeO_2 is from 85 to 90%. A primary desulfurization reactor containing either SnO_2 or CeO_2 would be followed by a secondary reactor containing a zinc sorbent. Regeneration of the sulfided zinc sorbent would be accomplished in the traditional manner and product gas containing low SO_2 concentrations would be recycled to the gasifier. Regeneration of sulfided cerium or tin sorbent from the primary reactor would use one of the concepts outlined previously. Figure 5 illustrates the dual-bed desulfurization-regeneration concept. Elemental sulfur would be condensed from the regeneration product and excess SO_2 would be reheated and recycled. Because the reaction between SO_2 and either SnS or $\text{Ce}_2\text{O}_2\text{S}$ is more favorable than the reaction with FeS, the amount of excess SO_2 required would be much less and the energy and cost penalty associated with reheat and recycle would be correspondingly reduced. Although the general thermodynamic characteristics of SnS and $\text{Ce}_2\text{O}_2\text{S}$ are similar with respect to elemental sulfur production, there are significant differences in other respects.

The condensed phase products of SnS regeneration are more complex. Under appropriate conditions either SnS_2 or Sn_2S_3 may be produced from SnS. SnSO_4 is moderately stable and high temperatures are required to prevent its formation, particularly at high pressure. The reduction of SnO_2 to liquid metallic Sn may occur if SnO_2 is exposed to a coal gas having sufficiently high reducing strength. Finally, the sulfided product, SnS, may be transformed to SnS(g) at appropriate conditions. This is a potential problem in both the desulfurization and regeneration cycles. Avoidance of all of these problems may leave only a small window, or no window at all, at which the tin sorbent can operate.

In contrast, the condensed phase of the cerium system is less complex. Cerium oxysulfide, $\text{Ce}_2\text{O}_2\text{S}$, is the only product of desulfurization. $\text{Ce}_2\text{O}_2\text{S}$ is not volatile and there is no danger of reducing CeO_2 to the metal. Indeed, the desulfurization performance of CeO_2 improves

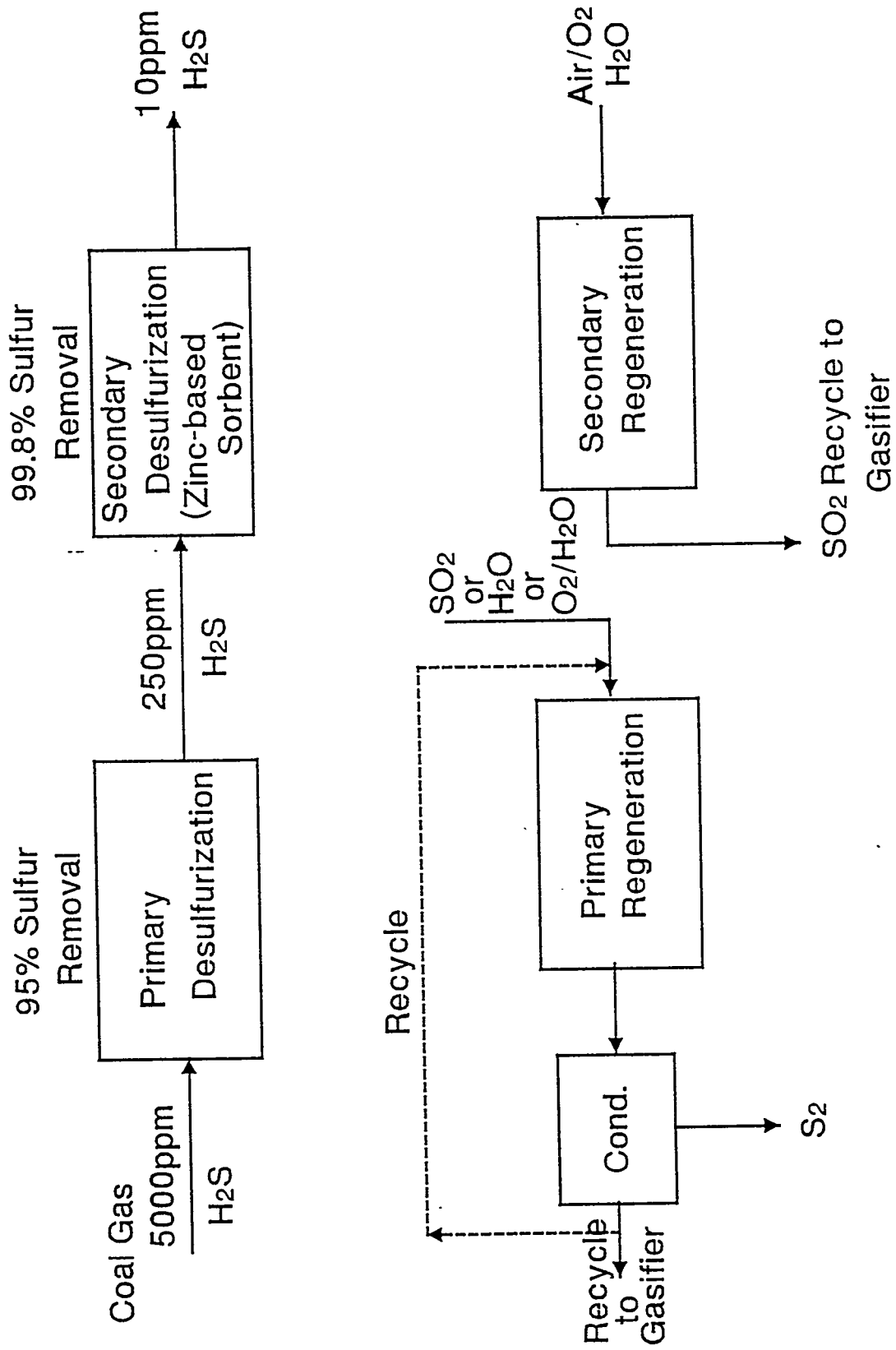


Figure 5. Two-Stage Desulfurization-Regeneration Concept

with increasing temperature and in more highly reducing coal gas. The permissible operating window for cerium desulfurization and regeneration is larger than the operating window of the tin system. The drawbacks of cerium are its limited theoretical capacity of 0.093g sulfur per gram of sulfided sorbent, and its availability and cost.

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Appendix

Summary of Results of the Equilibrium Reduction- Desulfurization Analysis of Candidate Sorbents With Texaco and KRW Gases

Table A-1. Reduction/Desulfurization Analysis of
Cerium Oxide (CeO₂) With KRW Gas

Initial Mixture: 1 mol of CeO₂ With 10 mols of KRW Gas

T(K)	Fractional Sulfur Removal		
	P = 1 atm	P = 5 atm	P = 25 atm
600	0.000	0.000	0.000
650	0.000	0.000	0.000
700	0.000	0.000	0.000
750	0.000	0.000	0.000
800	0.000	0.000	0.000
850	<u>0.447</u>	0.000	0.000
900	0.590	0.377	0.000
950	0.647	<u>0.579</u>	0.236
1000	0.682	0.664	<u>0.500</u>
1050	0.709	0.705	0.639
1100	0.733	0.732	0.709
1150	0.754	0.754	0.746
Sulfided Product	Ce ₂ O ₂ S	Ce ₂ O ₂ S	Ce ₂ O ₂ S
Excess Ce	CeO ₂	CeO ₂	CeO ₂
Volatile Species	None	None	None

Table A-2. Reduction/Desulfurization Analysis of
Cobalt Oxide (Co_3O_4) With Texaco Gas

Initial Mixture: 1 mol of Co_3O_4 With 10 mols of Texaco Gas

T(K)	Fractional Sulfur Removal		
	P = 1 atm	P = 5 atm	P = 25 atm
600	1.000	1.000	1.000
650	1.000	1.000	1.000
700	1.000	1.000	1.000
750	1.000	1.000	1.000
800	1.000	1.000	1.000
850	1.000	1.000	1.000
900	1.000	1.000	1.000
950	<u>0.999</u>	0.999	1.000
1000	0.999	<u>0.999</u>	0.999
1050	0.998	0.998	0.999
1100	0.998	0.998	<u>0.998</u>
1150	0.997	0.997	0.997
Sulfided Product	Co_3S_4	Co_3S_4	Co_3S_4
Excess Co	Co(s)	Co(s)	Co(s)
Volatile Species	None	None	None

Table A-3. Reduction/Desulfurization Analysis of Cobalt Oxide (Co_3O_4) With KRW Gas

Initial Mixture: 1 mol of Co_3O_4 With 10 mols of KRW Gas

T(K)	Fractional Sulfur Removal		
	P = 1 atm	P = 5 atm	P = 25 atm
600	1.000	1.000	1.000
650	1.000	1.000	1.000
700	1.000	1.000	1.000
750	1.000	1.000	1.000
800	<u>1.000</u>	1.000	1.000
850	1.000	1.000	1.000
900	1.000	1.000	1.000
950	1.000	<u>1.000</u>	1.000
1000	1.000	1.000	<u>1.000</u>
1050	1.000	1.000	1.000
1100	0.999	1.000	1.000
1150	0.997	1.000	1.000
Sulfided Product	Co_3S_4	Co_3S_4	Co_3S_4
Excess Co	Co(s), all T Co_3O_4 , T \leq 850 CoO, T \geq 900	Co(s), all T Co_3O_4 , T \leq 850 CoO, T \geq 900	Co(s), all T Co_3O_4 , T \leq 850 CoO, T \geq 900 CoCO_3 , T \leq 650
Volatile Species	None	None	None

Table A-4. Reduction/Desulfurization Analysis of
Copper Oxide (CuO) With Texaco Gas

Initial Mixture: 1 mol CuO With 10 mols of Texaco Gas

T(K)	Fractional Sulfur Removal	
	P = 1 atm	P = 25 atm
600	1.000	1.000
650	1.000	1.000
700	0.999	1.000
750	0.998	1.000
800	0.997	0.999
850	0.995	0.998
900	0.990	0.998
950	<u>0.986</u>	0.995
1000	0.979	0.992
1050	0.977	0.986
1100	0.973	<u>0.980</u>
1150	0.970	0.973
Sulfided Product	Cu ₂ S	Cu ₂ S
Excess Cu	Cu(s)	Cu(s)
Volatile Species	None	None

Table A-5. Reduction/Desulfurization Analysis of
Copper Oxide (CuO) With KRW Gas

Initial Mixture: 1 mol CuO With 10 mols of KRW Gas

T(K)	Fractional Sulfur Removal	
	P = 1 atm	P = 25 atm
600	1.000	1.000
650	1.000	1.000
700	0.999	1.000
750	0.998	1.000
800	<u>0.997</u>	0.999
850	0.995	0.998
900	0.990	0.998
950	0.986	0.995
1000	0.980	<u>0.992</u>
1050	0.977	0.986
1100	0.973	0.980
1150	0.969	0.973
Sulfided Product	Cu ₂ S	Cu ₂ S
Excess Cu	Cu(s)	Cu(s)
Volatile Species	None	None

Table A-6. Reduction/Desulfurization Analysis of
Iron Oxide (Fe_2O_3) With Texaco Gas

Initial Mixture: 1 mol Fe_2O_3 With 10 mols of Texaco Gas

T(K)	Fractional Sulfur Removal	
	P = 1 atm	P = 15 atm
823	0.958	-----
873	0.950	0.926
923	<u>0.941</u>	0.906
973	0.915	0.886
1023	0.881	0.869
1073	0.838	<u>0.831</u>
1123	0.754	0.782
Sulfided Product	FeS	FeS
Excess Fe	FeO	FeO
Volatile Species	None	None

Table A-7. Reduction/Desulfurization Analysis of
Iron Oxide (Fe_2O_3) With KRW Gas

Initial Mixture: 1 mol Fe_2O_3 With 10 mols of KRW Gas

T(K)	Fractional Sulfur Removal	
	P = 1 atm	P = 15 atm
623	.988	.982
673	.988	.980
723	.988	.978
773	.981	.976
823	<u>.971</u>	.967
873	.957	.954
923	.938	.936
973	.881	<u>.907</u>
1023	.912	.881
1073	.843	.844
1123	.801	-----
Sulfided Product	FeS	FeS
Excess Fe	Fe_3O_4 , $T \leq 723$ K FeO, $T \geq 773$ K	Fe_3O_4 , $T \leq 773$ FeO, $T \geq 823$
Volatile Species	None	None

Table A-8. Reduction/Desulfurization Analysis of Molybdenum Oxide (MoO_3) With Texaco Gas

Initial Mixture: 1 mol MoO_3 With 10 mols of Texaco Gas

T(K)	Fractional Sulfur Removal		
	P = 1 atm	P = 5 atm	P = 25 atm
600	1.000	1.000	1.000
650	0.999	0.999	0.999
700	0.999	0.999	0.999
750	0.998	0.997	0.998
800	0.996	0.996	0.996
850	0.995	0.994	0.993
900	0.991	0.990	0.989
950	<u>0.984</u>	0.984	0.984
1000	0.975	<u>0.973</u>	0.976
1050	0.964	0.959	0.958
1100	0.949	0.942	<u>0.937</u>
1150	0.931	0.920	0.911
Sulfided Product	MoS_2	MoS_2	MoS_2
Excess Mo	MoO_2	MoO_2	MoO_2
Volatile Species	None	None	None

Table A-9. Reduction/Desulfurization Analysis of Molybdenum Oxide (MoO_3) With KRW Gas

Initial Mixture: 1 mol MoO_3 With 10 mols of KRW Gas

T(K)	Fractional Sulfur Removal		
	P = 1 atm	P = 5 atm	P = 25 atm
600	1.000	1.000	1.000
650	1.000	1.000	1.000
700	0.999	0.999	0.999
750	0.999	0.999	0.999
800	<u>0.998</u>	0.998	0.997
850	0.996	0.996	0.995
900	0.992	0.992	0.993
950	0.988	<u>0.988</u>	0.987
1000	0.981	0.981	<u>0.980</u>
1050	0.970	0.970	0.970
1100	0.957	0.957	0.957
1150	0.941	0.941	0.941
Sulfided Product	MoS_2	MoS_2	MoS_2
Excess Mo	MoO_2	MoO_2	MoO_2
Volatile Species	None	None	None

Table A-10. Reduction/Desulfurization Analysis of Tin Oxide (SnO₂) With Texaco Gas

Initial Mixture: 1 mol SnO₂ With 10 mols of Texaco Gas

T(k)	Fractional Sulfur Removal		
	P = 1 atm	P = 5 atm	P = 25 atm
600	.000	.000	.000
650	.467	.000	.000
700	.750	.417	.000
750	.874	.690	.285
800	.935	.828	.585
850	.966	.901	.746
900	.928	.942	.840
950	<u>.849</u>	.903	.897
1000	.698	<u>.800</u>	.888
1050	.386	.636	.772
1100	.000	.372	<u>.583</u>
1150	.000	.000	.310
Sulfide Product	SnS	SnS	SnS
Excess Sn	SnO ₂ , T ≤ 850 Sn(ℓ), T ≥ 900	SnO ₂ , T ≤ 900 Sn(ℓ), T ≥ 950	SnO ₂ Sn(ℓ), T ≥ 975
Volatile Species	SnS, T ≥ 850	SnS, T ≥ 900	SnS, T ≥ 975

Table A-11. Reduction/Desulfurization Analysis of
Zinc Oxide (ZnO) With Texaco Gas

Initial Mixture: 1 mol ZnO With 10 mols Texaco Gas

T(K)	Fractional Sulfur Removal	
	P = 1 atm	P = 15 atm
773	1.000	1.000
823	1.000	1.000
873	0.999	0.999
923	<u>0.999</u>	0.998
973	0.999	0.998
1023	0.998	0.997
1073	0.997	<u>0.996</u>
Sulfided Product	ZnS	ZnS
Excess Zn	ZnO Zn(g), T ≥ 923	ZnO Zn(g), T ≥ 1023
Volatile Species	Zn(g), T ≥ 923	Zn(g), T ≥ 1023

Table A-12. Reduction/Desulfurization Analysis of
Zinc Oxide (ZnO) With KRW Gas

Initial Mixture: 1 mol ZnO With 10 mols KRW Gas

T(K)	Fractional Sulfur Removal	
	P = 1 atm	P = 25 atm
723	1.000	1.000
823	<u>1.000</u>	1.000
923	1.000	-----
973	-----	<u>0.998</u>
1023	0.998	-----
1073	0.996	0.996
1173	0.992	0.992
Sulfided Product	ZnS	ZnS
Excess Zn	ZnO	ZnO
	Zn(g), T ≥ 923	Zn(g), T ≥ 1023
Volatile Species	Zn(g), T ≥ 923	Zn(g), T ≥ 1023