Thermodynamic Analysis of Sorption Reactions for the Removal of Sulfur from Hot Gases

J.H. Swisher and K. Schwerdtfeger

Both coal combustion and coal gasification processes now require careful control of sulfur-bearing efflu-ents. These needs have stimulated an extensive amount of research and development (R & D) on simple and complex sulfur sorbent materials. The application of thermodynamics in the study of the perform-ance of these materials can and should be an effective approach. Examples are described to show its effec-tiveness as an analytical tool and to point out some misconceptions that have been created in the published literature.

1. Introduction

MANY elements and their compounds react readily with sulfur, and this tendency is used to advantage in the removal of nox-ious sulfur species from hot coal-derived gases. A review arti-cle, published recently by the current authors, discusses the properties of metals and binary oxide compounds as sulfur sor-bents.[1] The purpose of the present article is to supplement the first article with a thermodynamic analysis of sorbent reactions. This review and analysis will begin with metals and simple ox-ide compounds, then extend into a discussion of mixed oxide compounds, which are receiving the most attention in the cur-rent R & D projects. As will be discussed in more detail later, a number of authors have created misconceptions about the equilibria involved in the sulfidation reactions they studied.

2. General Thermodynamics

It has been found through experience that the products formed during sorption reactions are generally those that would be expected from thermodynamic calculations. This observa-tion is not surprising because of the high temperature at which the reactions occur. In various coal gasification and combus-tion processes, sulfur sorbents are exposed to a wide range of temperatures and gas compositions. Therefore, it is not feasible to analyze the complete range of conditions of interest. Instead, one appropriate example of gasification conditions and another of combustion conditions will be presented.

For the gasification example, the exit gas composition was obtained from tests of a Kellogg-Rust-Westinghouse (KRW) air-blown gasifier.[2] Because the exit gas composition corre-sponds to ambient temperature and because the composition changes as the gas is cooled, the composition of the gas at 1000 K was determined by calculation. The computer program used for this calculation, which minimized the free energy of the sys-tem, was EQUIMET.[3] The results are given in Table 1. The pa-rameters p_{O_2}, p_{S_2}, and a_C are keys to determining what sorbent reactions should occur.

J.H. Swisher, Department of Mechanical Engineering and Energy Processes, Southern Illinois University at Carbondale, Illinois; and **K. Schwerdtfeger,** Institut fur Allgemeine Metallurgie, Technische Universitat Clausthal, Clausthal-Zellerfeld, Germany.

For the combustion example, recent literature was not very helpful in providing gas compositions to which sulfur sorbents are exposed. In an older reference,[4] data are reported from tests that show the variation of flue gas composition with the amount of combustion air provided. Data for air provided at 100% of the stoichiometric requirement are reproduced in the second column of Table 2. The third column in this table lists the calculated equilibrium gas composition at 2000 K, assum-ing that 3000 ppm of SO_2 was also present. The temperature of 1200 K is in the upper range for fluidized bed combustion and somewhat below the temperature reached in pulverized coal combustors. Therefore, the results apply, to a good approxima-tion, to both fluidized bed and conventional combustion proc-esses.

Table 1 **Equilibrium Gas Composition at 1000 K and 1 atm Pressure for a KRW Air-Blown Gasifier**[2]

| Species | Partial pressure, atm, at: | |
	298 K	1000 K
H_2	0.132	0.177
CO^+	0.150	0.117
CO_2+	0.104	0.137
N_2	0.422	0.422
CH_4	4.3×10^{-3}	2×10^{-4}
H_2S	2.6×10^{-3}	2.6×10^{-3}
H_2O	0.185	0.144
O_2	...	5×10^{-21}
S_2	...	1×10^{-8}

Note: ^+CO-CO_2 corresponds to carbon activity, a_C, of 0.06 at 1000 K.

Table 2 **Equilibrium Gas Composition at 1200 K and 1 atm Pressure for Coal Combustion**[4]

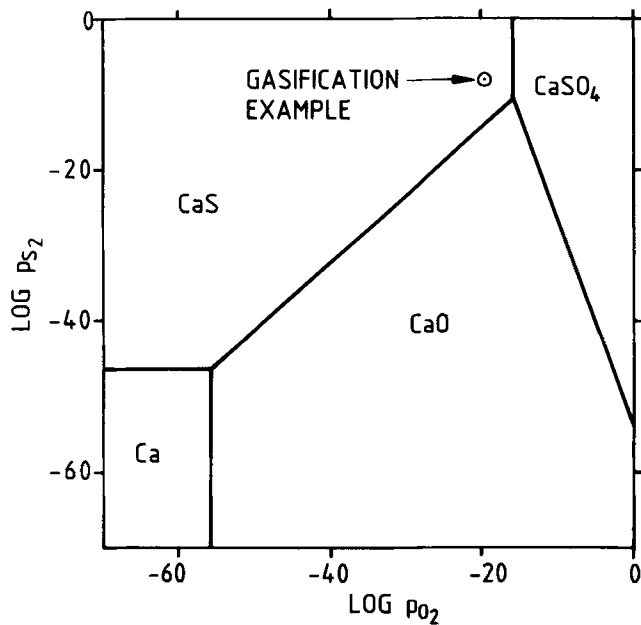| Species | Partial pressure, atm, at: | |
	298 K	1200 K
H_2	~0	1.6×10^{-6}
CO^+	~0	1.6×10^{-6}
CO_2	0.093	0.093
N_2	0.699	0.699
CH_4	~0	~0
H_2O	0.208	0.208
SO_2	...	3×10^{-3}
O_2	...	2×10^{-6}

Fig. 1 Phase predominance area diagram for calcium compounds at 1000 K.

Table 3 Summary of Equilibrium Products Formed during Sulfur Sorption Reactions

Sorbent category	Reaction products at equilibrium Gasification	Combustion
Calcium compounds	CaS	$CaSO_4$
Sodium compounds	Na_2S	Na_2SO_4 (liquid)
Iron oxide	FeS	Fe_2O_3
Zinc oxide	ZnS	ZnO
Zinc ferrite	FeS, (Zn,Fe)S	$ZnFe_2O_4$
Copper/copper oxide	Cu_2S	Cu_2O
Manganese/manganese oxide	MnS	Mn_3O_4
Nickel/nickel oxide	Ni-S (liquid)	NiO
Molybdenum/molybdenum oxide	Mo_2S_3	MoO_3 (liquid), MoO_3 (gas)
Chromium/chromium oxide	Cr_2O_3	Cr_2O_3

The next step in the analysis was to select categories of potential sorbent materials and carry out thermodynamic calculations to determine which compounds are the most stable under the conditions specified in Tables 1 and 2. In these calculations, free energy values compiled by Barin[5] for sulfates, ZnO, and ZnS were used. For carbides and all other oxides and sulfides, the compilation by Elliott and Gleiser[6] was used. Data for the free energy of formation of zinc ferrite, $ZnFe_2O_4$, were taken from a paper by Wang, Choi, and Honig.[7]

Because there are a number of possible reaction paths a potential sorbent can take, the best approach for analyzing the reactions is to construct so-called phase predominance area diagrams. Two of these diagrams were constructed as examples for reactions involving calcium compounds. Figure 1 shows an example for 1000 K, in which the conditions for stability of various phases or compounds are plotted as functions of the oxygen and sulfur partial pressures. The same phase will be present at
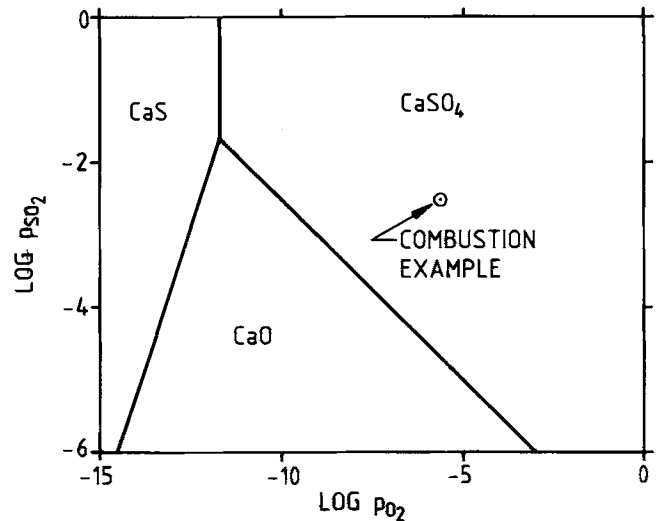

Fig. 2 Phase predominance area diagram for calcium compounds at 1200 K.

equilibrium regardless of which phase or phases are present in the starting material. The point on the figure that corresponds to the coal gasification example falls within the CaS phase field. Note, however, that the point is rather close to the regions where $CaSO_4$ and CaO are stable. Consequently, if the gas composition or perhaps temperature were very different from those given in Table 1, a phase other than CaS could form.

A slightly different type of diagram was constructed to show regions of stability at 1200 K. In Fig. 2, the partial pressures of SO_2 and O_2 are plotted instead of S_2 and O_2. This type of diagram is more suitable when conditions are more oxidizing, as is the case with combustion. The coordinates of the point corresponding to combustion fall in the $CaSO_4$ phase field. This result, along with the result in Fig. 1 for coal gasification, is consistent with practical experience. A study was conducted by Nagarajan et al. on comparisons of thermodynamic predictions with observed behavior for calcium-base sorbents.[8] They analyzed experimental data obtained by others in the areas of coal devolatilization, gasification, and combustion and found what they termed qualitative agreement in all three areas.

Calculations of the type used to construct Fig. 1 and 2 were carried out for a number of potential sorbent materials. A summary of the results in the form of a list of sorption reaction products for the gasification and combustion examples is presented in Table 3. Examining results for the gasification example first, note that the reaction products are sulfides for all the materials except chromium or chromium oxide. Chromium is one of the few reactive elements that does not form a very stable sulfide. Hence, Cr_2O_3 is nearly always the stable phase present after exposure to sulfur- and oxygen-bearing gases. The same situation exists for aluminum and Al_2O_3; neither chromium nor aluminum is useful as a sulfur sorbent.

All of the other materials will reduce sulfur concentrations in hot gases to low or very low levels by forming sulfides. Selection of the best material for coal gasification processes is complicated, because there are trade-offs between the sulfur level attainable, regenerability, cost, mechanical properties,
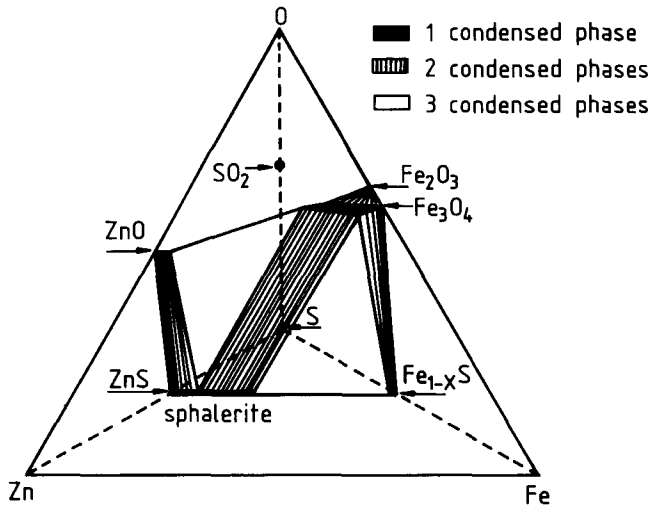
Fig. 3 Schematic representation of phase equilibria in the Zn-Fe-S-O system at 900 °C with $p_{SO_2} = 1$ atm.[17]

Fig. 4 Phase predominance area diagram for iron-zinc compounds with Fe/Zn = 2 at 1000 K.

and other considerations. Note that zinc ferrite reacts under coal gasification conditions to form two sulfide phases. Prior published articles generally refer to FeS and ZnS as the common products, but they do not mention that ZnS can dissolve as much as 30 mol.% FeS at 1000 K.[9] Thus, it is more appropriate to specify (Zn,Fe)S as one of the reaction products.

Note also in Table 3 that nickel and nickel oxide are somewhat unique in that they can form a liquid sulfide at 1000 K. The formation of liquid sulfide can be advantageous because of rapid mass transport within the sorbent. However, a mechanism must be found for containing the liquid sulfide product. In a prior study by the current authors, nickel dispersed in a porous Al_2O_3 matrix was found to be attractive as a sorbent.[10]

Turning now to the combustion example in Table 3, note that the choice of materials for sulfur sorption is very limited under oxidizing conditions. Calcium and sodium compounds both form sulfates, but none of the other materials forms sulfur compounds. Because Na_2SO_4 is a liquid at 1200 K, calcium compounds are the only materials that have been studied extensively for combustion processes. The calcium compounds include lime (CaO), limestone ($CaCO_3$), and dolomite ($CaCO_3 \cdot MgCO_3$).

One other detail regarding Table 3 should be mentioned. Some potential sorbents react to form volatile species that limit their utility. For zinc compounds, zinc vapor can form at relatively high partial pressures, and one of the oxides of molybdenum, MoO_3, is also volatile.

3. Mixed Oxide Sorbents

During the last 10 years, by far the most research on sulfur sorption reactions in reducing atmospheres has been conducted on mixed oxide compounds. The principal sponsor of this research has been the U.S. Department of Energy, and documentation of the results can be found in proceedings of annual contractor review meetings. Reference 11 is such an example.
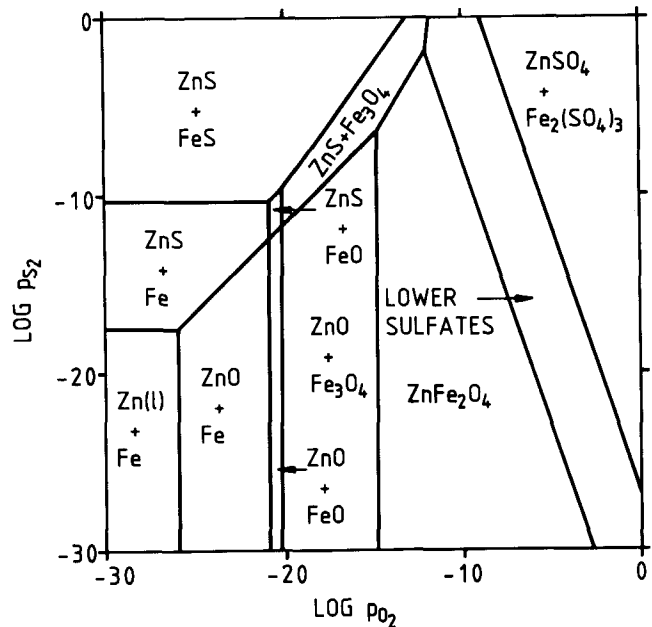
Another publication that contains numerous articles on mixed oxide sorbents is Ref 12. Most of the published articles on this subject do not provide a good scientific rationale for why various mixed oxide sorbents were selected for study. In the remainder of this section, an attempt is made to provide more insight on the sorbents that should and should not be attractive by application of thermodynamic and materials science principles.

3.1 Zinc Ferrite

Research, development, and testing of zinc ferrite, $ZnFe_2O_4$, have grown over the past 10 years into a large program. The pioneering work was conducted by Grindley and Steinfeld,[13] who found that the compound has a high reactivity and can reduce the H_2S concentration in hot gas streams to the low parts-per-million level. However, if one analyzes thermodynamic properties and phase equilibria in the Zn-Fe-S-O system, a number of potential problems emerge, and these problems are now being faced in development projects.

There is a wealth of information available on $ZnFe_2O_4$ as a result of research on zinc extraction processes and on magnetic materials, and desulfurization research investigators do not appear to be aware of this information. For example, it is known that $ZnFe_2O_4$ and Fe_3O_4 are mutually soluble, forming a continuous series of spinel solid solutions, at least in the temperature range from 850 to 1050 °C.[14-19] One of the reasons for the large number of publications on this subject is that there is disagreement on thermodynamic activity values. Graydon and Kirk[20] give evidence that spinel solid solutions separate into two phases at temperatures below 827 °C. One of the phases contains 0.12 mole fraction and the other contains 0.30 mole fraction Fe_3O_4. The high mutual solubility of $ZnFe_2O_4$ and Fe_3O_4 means that large amounts of iron can be added to $ZnFe_2O_4$ without causing a phase transformation. Additions of

iron would reduce the thermodynamic activity of zinc in the spinel phase, which can be denoted as $Zn_{1-x}Fe_{2+x}O_4$. The lower zinc activity would, in turn, reduce the vapor pressure of zinc over the compound. Additions of iron would also expand the oxygen pressure range over which the compound is stable. Of course, other properties of $Zn_{1-x}Fe_{2+x}O_4$ sorbents could be affected in either a positive or negative way by increasing the iron content. In some of the projects on sulfur sorption, variations in iron content were made, but they appeared to have been made on a strictly empirical basis.

Concerning phase equilibria more generally, Espelund and Jynge[17] prepared a diagram that shows some of the important phenomena quite well; it is reproduced in Fig. 3. The diagram was prepared for a temperature of 900 °C and for $P_{SO_2} = 1$ atm, so the metal and FeO phases do not appear. It shows the spinel phase as a solid solution projecting into the diagram from the Fe_3O_4 point, and it shows that ZnS (sphalerite) can dissolve a large quantity of $Fe_{1-x}S$. The latter feature could also have an impact on the performance of $Zn_{1-x}Fe_{2+x}O_4$ sorbents.

To analyze phase equilibria in the Zn-Fe-O-S system in more detail, the phase predominance area diagram shown in Fig. 4 was constructed. Normally, such diagrams are prepared to describe reactions of a single metal. Here, because two metals are considered, it is necessary to specify the ratio of their concentrations. In this case Fe/Zn = 2, which corresponds to stoichiometric $ZnFe_2O_4$. A temperature of 1000 K was used, and the range of S_2 and O_2 partial pressures corresponds to the range of practical interest in coal gasification.

For clarity, a few simplifications were made in constructing the diagram. Individual lines showing the stability regions of the lower sulfates, $FeSO_4$ and $ZnO \cdot 2ZnSO_4$, were not drawn because they are close together and cross within a narrow band. Therefore, the band where these lines fall is labeled "lower sulfates." The mutual solubility of ZnS and FeS is not indicated. Including this feature would have required additional calculations using assumptions of unknown validity. The mutual solubility of Fe_3O_4 and $ZnFe_2O_4$ does not show on this diagram because of the fixed ratio of iron to zinc that was assumed.

In carrying out the calculations, data on the free energy of formation of $ZnFe_2O_4$ published by Gilbert and Kitchener[14] were used. Wang, Choi, and Honig[7] analyzed the literature on this subject very carefully and favor Gilbert and Kitchener's results over those of Tretyakov[15] and Fitzner.[18] For the reaction, $ZnFe_2O_4 = ZnO + Fe_2O_3$, Ref 7 and 14 give $\Delta G° = -4140 + 7.48T$ (calories).

At 1000 K, $\Delta G° = 3340$ cal/mole. Because this value is not very high, it follows that the $ZnFe_2O_4$ should not be stable in strongly reducing atmospheres, a prediction that has been found to be true in experiments on the use of $ZnFe_2O_4$ as a sorbent in coal gasification atmospheres. This conclusion can also be drawn from Fig. 4. The oxygen partial pressure in coal gasification processes is frequently 10^{-20} atm or less. Consequently, the stable phase of iron could be Fe_3O_4, FeO, or iron.

Other observations that can be made in Fig. 4 are that sulfidation and regeneration of $ZnFe_2O_4$ involve numerous solid phase transformations and that special procedures may be needed during regeneration to prevent the formation of undesirable iron and zinc sulfates.

Characterizing the tendency of $ZnFe_2O_4$ to decompose in reducing atmospheres was the objective of the project carried out by Lamoreaux et al.[2] Realizing that zinc loss by vaporization is a limitation of $ZnFe_2O_4$, they also calculated the vapor pressure of zinc for various compositions, temperatures, and total pressures. The authors concluded correctly that zinc losses should be lower at lower temperatures, higher total gas pressures, and more oxidizing conditions. However, there were several shortcomings in their report that should be noted. Their information on the free energy of formation of $ZnFe_2O_4$ was taken from rather old calorimetric data, and they did not reference publications describing more direct determinations. Fortunately, this oversight did not lead to significant errors in their zinc vapor pressure calculations. It was stated that values such as 0.23 at.% sulfur in the gas phase are too low to affect the phase equilibria. As shown in Tables 1 and 3, this statement is incorrect, because both FeS and ZnS should form. Another problem was their analysis of carbon deposition and the formation of Fe_3C. It is not common for Fe_3C, which is a metastable compound, to form by gas-solid reaction. It is far more likely in reducing atmospheres that carbon would dissolve in iron; then Fe_3C would form by a phase transformation during cooling.

Returning to the question of zinc losses due to vaporization, a calculation showed that the zinc vapor pressure over $ZnFe_2O_4$ at 1000 K in air may be up to ten times lower than the vapor pressure over ZnO under the same conditions. However, the vapor pressure over both compounds under oxidizing conditions is too low to be of practical importance. The zinc loss problem arises because the ferrite is readily reduced to ZnO and either Fe_3O_4, FeO, or iron when exposed to gasifier conditions. Starting with the ferrite therefore provides no significant benefit in reducing zinc losses.

No attempt will be made to review details of the progress and problems in the development of $ZnFe_2O_4$ as a sorbent, as covered in Ref 11 and 12 and other publications. The two main problems are zinc loss by vaporization, as discussed above, and attritioning of particles during many sulfidation/regeneration cycles. The latter is not surprising because, as illustrated in Fig. 4, numerous phase transformations occur as the material is cycled between the right and left parts of the diagram.

Some comments should be made on the general outlook for $ZnFe_2O_4$ as a sorbent. The goals that have been set for the material are very ambitious. It must desulfurize hot gas streams to very low levels of H_2S and COS. Regeneration in air or another oxidizing gas mixture must produce a product with the same desulfurization characteristics as the starting material. Loss of zinc by vaporization must be small, as must loss of sorbent by attrition.

In the authors' opinion, these goals are unrealistic for $ZnFe_2O_4$ in bulk form and for monolithic ceramic materials in general. The number of phase transformations the material must withstand and the mechanical damage that can occur in gasification reactors are too demanding for ceramic materials. There is a greater chance for success if the sorbent is used in pulverized form, or as a dispersoid in a porous support material that has good mechanical properties. Partly for this reason, some of the more recent projects have entailed evaluation of $ZnFe_2O_4$ in pulverized form. Another reason is that there is increasing interest in fluidized bed processes, which make pellet-

ized sorbents more vulnerable to attritioning than in fixed bed processes.

3.2 Zinc Titanates

During the past few years, zinc titanate compounds have emerged as sorbents with most of the advantages and few of the limitations of $ZnFe_2O_4$. Unfortunately, published phase diagram and thermodynamic stability information on zinc titanates is not comprehensive. The free energy of formation of Zn_2TiO_4 as a function of temperature is given by Barin.[5] Similar data are not available for $ZnTiO_3$ and $ZnTi_3O_8$. All three compounds were identified in various sorbent formulations studied by Flytzani-Stephanopoulos, et al.[12,21] Results from this and other recent studies show that zinc titanates react more slowly than $ZnFe_2O_4$, but they are less susceptible to zinc vaporization loss and attritioning.

Sulfidation of Zn_2TiO_4 occurs by the reaction:

$$Zn_2TiO_4 + 2H_2S = ZnS + TiO_2 + 2H_2O$$
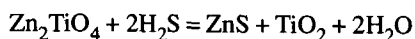
In a simulated coal gasification atmosphere, titanium does not react with sulfur, nor is TiO_2 reduced. Therefore, because TiO_2 is relatively inert, it has a beneficial effect on mechanical properties of the sorbent.

A phase predominance area diagram was constructed for Zn-Ti-O-S compounds at 1000 K (see Fig. 5). The results are for Zn/Ti = 2, which corresponds to the composition of Zn_2TiO_4. An important conclusion that can be drawn by com-
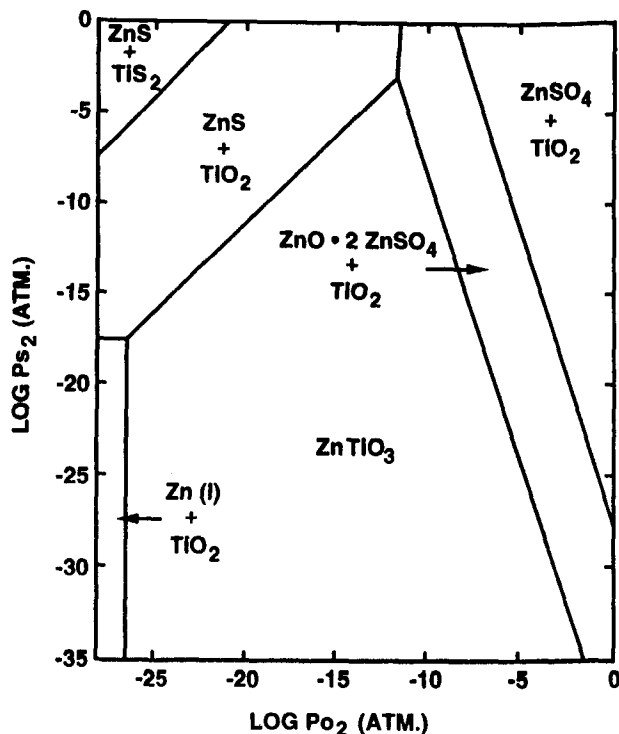
paring this figure with Fig. 4 for $ZnFe_2O_4$ is that Zn_2TiO_4 is stable to a lower P_{O_2} than $ZnFe_2O_4$. The greater stability means that vaporization losses of zinc in a coal gasifier should be less for Zn_2TiO_4, which agrees with experimental observations. For the same reason, one would expect the reactivity of $ZnTiO_4$ with H_2S to be lower than for $ZnFe_2O_4$. Experimental results confirm this prediction, and it is a penalty that must be accepted if vaporization losses of zinc are to be reduced.

The titanate is also subjected to fewer phase transformations than the ferrite during sulfidation/regeneration cycles. This characteristic should favor the titanate over the ferrite in attrition resistance. However, in the authors' opinion, more involvement of materials scientists is needed in sorbent development projects if both mechanical property and chemical reactivity goals are to be met.

3.3 Other Mixed Oxides

A large number of other oxides containing two or more metallic elements have been evaluated as sulfur sorbents. Formulations containing copper and/or manganese have been studied by several investigators.[11,12] Because the purpose of this article is to increase the understanding of sorption reactions, a limited number of examples that suit this purpose will be discussed.

In an article by Lew, Jothimurgeson, and Flytzani-Stephanopoulos,[21] one of the materials studied was copper ferrite dispersed in a porous Al_2O_3 matrix. The compounds identified in sulfided samples were CuS, FeS, $CuFe_2S_3$, and $CuFeS_2$. The question might be asked, "What controls the concentration of H_2S leaving a fixed bed reactor before the reagents are spent, i.e., break-through condition?" The formation of a ternary sulfide like $CuFe_2S_3$ should correspond to a lower H_2S effluent concentration than if only CuS and FeS were present. The author did not mention this point, but stated that having copper ferrite present in the sorbent should produce a lower H_2S level than if copper metal were present. A similar statement was made by Gangwal et al.[22] They reported that CuO in their starting material was better than copper because it should have produced a lower H_2S concentration. These statements are believed to be incorrect. To explain the error, consider a hypothetical analog for desulfurization with $ZnFe_2O_4$. Assume that the product from a coal gasifier is passed through a $ZnFe_2O_4$ bed at 1000 K and that the desulfurized gas exiting the bed contains 2 ppm H_2S, 20% H_2, and 2% H_2O. This gas composition corresponds to $P_{S_2} = 10^{-14}$ atm and $P_{O_2} = 10^{-22}$ atm. Referring to Fig. 4, these conditions exist in an area of the diagram where metallic iron is the only stable form of iron and where ZnS is in equilibrium with ZnO. When ZnS and ZnO coexist, the sulfur content of the gas will be fixed by the reaction:

$$ZnO + H_2S = ZnS + H_2O$$

or, equivalently:

$$ZnO + 1/2\ S_2 = ZnS + 1/2\ O_2$$
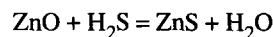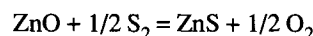
Thus, the exit gas composition does not depend on whether or not $ZnFe_2O_4$ was present in the bed initially. A similar analysis would lead to the same conclusion for a copper ferrite bed or a bed containing CuO. Reduction of copper from the oxidized

Fig. 5 Phase predominance area diagram for zinc-titanium compounds with Zn/Ti = 2 at 1000 K.

state to metallic copper would occur rapidly in a coal gasification atmosphere.

There is a consensus in this field that recyclable sorbents are preferred over once-through, cheaper sorbents. Both economic and waste disposal arguments are made in support of this opinion. Thus, sorbent regeneration chemistry is just as important as sulfidation chemistry in sorbent development. With this principle in mind, Anderson and Berry[23] developed a two-step process using metal oxide sorbents that was quite innovative. Two beds were used; one contained zinc oxide on the surface of zinc aluminate, and the other contained cobalt titanate on the surface of TiO_2. The unique feature of the process was the regeneration method. The first regeneration reaction was:

$$ZnS + 3/2\ O_2 = ZnO + SO_2$$
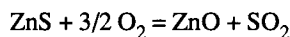
The SO_2 produced in the first bed was then passed through the second bed, causing the following reaction to occur:

$$Co_9S_8 + 9/2\ SO_2 + 9\ TiO_2 = 9CoTiO_3 + 25/4\ S_2$$

The exit gas from the second bed contained both SO_2 and S_2. The S_2 was separated as a by-product by cooling and condensation, and the remaining SO_2 was recycled.

Development work on the Anderson-Berry process was discontinued in 1987 mainly because the cost of reagents was judged to be higher than for $ZnFe_2O_4$ processes. In retrospect, this decision may have been premature, because $ZnFe_2O_4$ sorbents are not durable and would have to be replaced frequently.

The last project to be discussed is another example of an innovative approach to combined sulfidation reactions. Most investigators regenerated mixed oxide sorbents in air, which sometimes caused sulfates to form instead of the original mixed oxide. Wakker and Gerritsen published two papers in Ref 12 that describe an approach that prevents sulfate formation during regeneration. Mixed oxide sorbents were prepared by impregnating porous Al_2O_3 with salt solutions. The salts were then converted to dispersed metal aluminates in the pores of the Al_2O_3 support structure. Aluminates of nickel, zinc, cobalt, manganese, and iron were produced for evaluation.

From this set, $MnAl_2O_4$ and $FeAl_2O_4$ were selected after preliminary experiments for in-depth R & D. With thermodynamic calculations, the authors demonstrated that regeneration in a steam atmosphere prevents sulfate formation. They believed that having manganese and iron present in aluminate compounds instead of simple oxides was the key to successful regeneration with steam.

Laboratory experiments were conducted in a fixed bed reactor at temperatures between 400 and 800 °C. Only slight deactivation was reported with both compounds after hundreds of sulfidation/regeneration cycles. It was stated, but without presentation of many results, that H_2S was removed to a level of 10 to 50 ppm, depending on gas composition. Although this claim is not surprising for $MnAl_2O_4$, it is difficult to see how such low levels are possible with $FeAl_2O_4$.

In a second phase of their project, Wakker and Gerritsen evaluated their sorbents in a coal gasification pilot plant. These tests permitted larger quantities of the sorbents to be used, and they involved exposure to the complex gas mixtures generated during coal gasification. During the tests, which consisted of 4 weeks of cycling, the cleaned fuel gas contained less than 40

ppm H_2S. The only problem encountered was a significant reduction in breakthrough capacity. This problem was more severe for $MnAl_2O_4$ than for $FeAl_2O_4$.

4. Summary

Thermodynamics is believed to be a good tool for predicting and analyzing the performance of sulfur sorbents. When the active agent is a metal or binary oxide, thermodynamic calculations are simple, and data are readily available for performing the calculations. In recent years, mixed oxide compounds have been receiving the most attention in sulfur sorbent R & D. Analyzing the reactions involving these compounds is more complex because sequential and/or parallel reactions occur, and the thermodynamic database is sometimes inadequate. Consequently, many investigators are not making effective and correct use of thermodynamic calculations in their research. The construction of four component phase predominance area diagrams is considered to be a good approach in analyzing sulfidation and sorbent regeneration reactions with mixed oxide compounds.

Acknowledgment

References

1. J.H. Swisher and K. Schwerdtfeger, "Review of Metals and Binary Oxides as Sorbents for Removing Sulfur from Coal-Derived Gases," *J. Mater. Eng. Perform.*, Vol. 1(3), 399-407 (1992).
2. R.M. Lamoreaux, R.D. Brittain, J. Zeigher, and S.C. Leach, Report No. DOE/MC/21096-2192, U.S. Dept. of Energy, Washington, DC (1986).
3. A.E. Morris, General Mineral Technology for Pyrometallurgy, University of Missouri at Rolla, Rolla, MO (1989).
4. L. Shnidman, in *Chemistry of Coal Utilization*, Vol 2, H.H. Lowry, Ed., John Wiley & Sons, New York, 1252-1286 (1945).
5. I. Barin, *Thermochemical Data of Pure Substances*, VCH Verlagsgesellschaft, Weinheim, Germany (1989).
6. J.F. Elliott and M. Gleiser, *Thermochemistry for Steelmaking*, Vol 1, Addison-Wesley, Reading, MA (1960).
7. P. Wang, Q.W. Choi, and J.M. Honig, *Z. Anorg. Alleg. Chem.*, 550, 91-101 (1987).
8. R. Nagarajan, M.R. Khan, H.N. Pham, R.J. Anderson, and L.C. Headley, *Preprint Papers, Am. Chem. Soc., Div. Fuel Chemistry*, 33(2), 197-207 (1988).
9. G. Kullerud, *Fortschritte der Mineralogie*, 41, 259 (1963) (in German).
10. J.H. Swisher and K. Schwerdtfeger, *Proc. 8th Annual Int. Pittsburgh Coal Conf.*, Pittsburgh, PA 646-653 (1991).
11. V.P. Kothari and J.L. Beeson, Ed., *Proc. Tenth Annual Gasification and Gas Stream Cleanup Systems Contractor Review Meeting*, Report No. DOE/METC-90/6115, U.S. Dept. of Energy, Washington, DC (1990).

12. *Preprint Papers, Am. Chem. Soc., Div. Fuel Chemistry, 35*(1), (1990).

13. T. Grindley and G. Steinfeld, Report No. DOE/METC-16545-1125, U.S. Dept. of Energy, Washington, DC (1981)

14. I.G.F. Gilbert and J.A. Kitchener, *J. Chem. Soc.,* London, Oct-Dec, 3924-3926 (1956).

15. Y.D. Tretyakov, *Termodynamika Ferritov,* Chapt. 10, Izdatel-istva Khimija, Leningrad (1967) in Russian.

16. I. Katayama, J. Shibata, M. Aoki, and Z. Kozuka, *Trans. Jpn. Inst. Metals, 18,* 743-749 (1977).

17. A.W. Espelund and H.J. Jynge, *Scan. J. Metall., 6,* 256-262 (1977).

18. K. Fitzner, *Thermochem. Acta, 31,* 227-236 (1979).

19. S.C. Schaefer and R.A. McCune, *Metall. Trans. B, 17,* 515-521 (1986).

20. J.W. Graydon and D.W. Kirk, *Metall. Trans. B, 19,* 919-925 (1988).

21. S. Lew, K. Jothimurgeson, and M. Flytzani-Stephanopoulos, *Ind. Eng. Chem. Res., 28,* 535-541 (1989).

22. S.K. Gangwal, J.M. Stogner, S.M. Harkins, and S.J. Bossart, *Environ. Prog., 8*(1), 26-34 (1989).

23. G.L. Anderson and F.O. Berry, *Proc. Seventh Annual Gasification and Gas Stream Cleanup Systems Contractors Review Meeting,* M.R. Ghate, K.E. Markel, L.A. Jarr, and S.J. Bossart, Ed., Report No. DOE/METC-87/6079, U.S. Dept. of Energy, Washington, DC 642-655 (1987).