

CALCULATIONS OF THE INFLUENCE OF ADDITIVES ON COAL COMBUSTION DEPOSITS

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INTRODUCTION

The complex chemistry of coal combustion involves hundreds of species in gaseous, solid, and liquid phases, with some of these being solution phases. We have developed new robust calculational techniques capable of defining the total chemistry of coal combustion and of the complex solid and liquid silicate and sulfate solutions involved.^{1,2} The results indicate that coal combustion chemistry is more complex than had been believed and that kinetic factors can enhance fouling and corrosion by liquid condensates. In this paper, we examine the changes in chemistry due to additions of CaCO_3 (to desulfurize the gaseous effluents) and of NaCl and CaCl_2 (which are recommended as deicers or to increase the conductivity of effluents in electrostatic precipitators).³ The results reveal the chemical changes due to these additives; these should be important in defining a strategy for making such additions. In addition, we also impose an expected kinetic constraint on the chemical reactions. Such constraints should, ultimately, prove to be very important in real systems. Ultimately, in order to take these into account in deducing the total chemistry of combustion, a coupled calculational-experimental study of combustion should be carried out to define the important kinetic factors.

CALCULATIONAL METHODS

A robust updated version of SOLGASMIX⁴ was used to perform these calculations using data on the large number of possible species in the F*A*C*T⁵ data base. In addition to the gaseous, solid, and liquid species in the data base, we incorporated a method for calculating the thermodynamic properties of liquid silicates^{6,7,8} and a method for calculations of the properties of sulfates using the data deduced in our analysis of the Na_2SO_4 - CaSO_4 - MgSO_4 ternary molten salt system and of the CaSO_4 - MgSO_4 and Na_2SO_4 - CaSO_4 - MgSO_4 solid solutions that crystallize from the sulfate melts. This analysis led to an assessed phase diagram for the ternary sulfate, which was necessary in order to define the chemical properties and the range of stability of the corrosive liquid sulfate phase that forms from the coal combustion condensates.

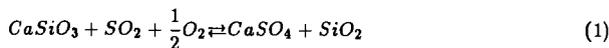
COMBUSTION OF ILLINOIS #6 COAL

We have previously examined the equilibrium combustion products of Illinois #6 coal and have imposed an expected kinetic constraint on the formation of $\text{NaAlSi}_3\text{O}_8$ and NaAlSiO_4 to illustrate the importance of kinetic factors.^{1,2} In this paper, we compare these constrained equilibrium calculations with calculations performed with the addition of CaCO_3 , NaCl , or CaCl_2 . These additions lead to changes in the total chemistry, and our results can be used to deduce strategies for making such additions. The overall composition of Illinois #6 coal is

given in Table I. In the calculations that follow, we combusted 100 grams of coal with an excess of oxygen (237 grams O₂ added as air). To this mixture, we added 6.25 grams of CaCO₃, or 0.4 grams of NaCl, or 0.4 grams of CaCl₂. The additives lead to complex changes in the total chemistry.

In Tables II, III, and IV, we present a selection of the results of our calculations of condensates with and without CaCO₃ addition that illustrate the important changes in chemistry brought about by the additive. In Table II, we give calculations for the composition of liquid silicates at temperatures where they are present. With no added CaCO₃, a molten silica-rich silicate exists down to about 1260 K, where a small amount of sulfate forms. With the addition of CaCO₃, the amount of molten silicate is increased significantly at the higher temperatures, mostly because of an increase in the CaO content. As a consequence, the liquid is not as silica rich and will be considerably less viscous than when no limestone is added. Because the activity coefficients of all the basic components of the slag are generally higher at low silica than at high silica contents, and also because of the high CaO concentration, this slag reacts more readily with SO₂ + $\frac{1}{2}$ O₂ (and SO₃) in the gas phase than does a high silica slag and forms a liquid sulfate phase between 1350 and 1400 K with CaCO₃ additions. This temperature is considerably higher than the temperature of first formation of liquid sulfate with no CaCO₃ addition, because the activities of the basic oxides (CaO, MgO, and Na₂O) in the silica saturated acid slag are significantly lower than in the less acid slags found with limestone addition and because the tendency to form sulfate increases with a decrease in temperature, i.e., the standard entropy of reaction of the oxides with gaseous SO₂ and O₂ is negative.

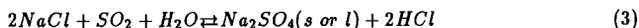
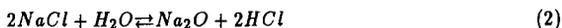
For the case with CaCO₃ addition, the decrease in the amount of slag at 1350 K (to 0.15 g) is accompanied by the appearance of a significant amount of sulfate, largely Na₂SO₄, as exhibited in Table III. These relative amounts remain essentially the same, at least down to 1300 K (Table III). The slag disappears by 1250 K (Table II) and somewhat more sulfate appears (Table III) at the expense of the slag constituents and CaSiO₃ (Table IV). The SO₃ (SO₂ + $\frac{1}{2}$ O₂) in the gas phase is a stronger "acid" at these temperatures than even SiO₂. Thus, one of the reactions that has taken place to a small extent between 1250 K and 1300 K is



with the product SiO₂ appearing as a new phase (Table IV). At yet lower temperatures, the liquid sulfate crystallizes to form two solid solutions and there is an increasing tendency for reactions of the remaining alkaline earth silicates or aluminosilicates with SO₂ + $\frac{1}{2}$ O₂ to form sulfates. Consequently, upon cooling, solid CaSiO₃ (wollastonite) disappears before 1150 K, and CaAl₂Si₂O₈ (anorthite) and CaMg(SiO₃)₂ (diopside) disappear before 1050 K, with a consequent increase in the amount of sulfate solid solutions and silica at both temperatures. Essentially, all of the alkali and alkaline earth oxides are thus converted to sulfate before 1050 K. This result holds with or without limestone additions because of the excess of oxides of sulfur in the gas. The total amount of sulfate is, of course, much larger with limestone additions because of an increased amount of CaSO₄ with a consequent decrease (relative to no limestone addition) in sulfur oxides of 68% at 1050 K and 1000 K. In real systems, kinetic factors could lead to desulfurization percentages less than this. The kinetics of reactions to form sulfates from solids such as CaAl₂Si₂O₈, CaSiO₃, or CaMg(SiO₃)₂ could be too slow to go to completion. If field data indicate this to be true, then our calculations can be used to define a strategy for improved

desulfurization. In addition, because a significant amount of SO_2 remains in the gas, greater desulfurization is possible in principle with larger additions of CaCO_3

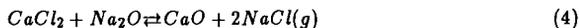
The addition of 0.4 grams of NaCl does not lead to large differences in the chemistry. NaCl is largely present in the vapor at high temperatures, which reacts at lower temperatures to form either the oxide or sulfate and HCl by the reactions



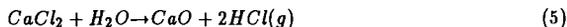
where the oxide in (2) could enter the slag or form a solid silicate. More HCl than NaCl is present in the vapor at 1300 K or lower with a liquid sulfate appearing between 1250 K and 1300 K.

For very large additions of NaCl (3.5 grams) to 100 grams of coal, the amount of Na_2O in the slag increases noticeably. However, most of the NaCl is in the vapor phase at the higher temperatures. In this case, the amount of HCl exceeds that of NaCl at 1250 K, at which temperature a liquid sulfate is also present. (There is no sulfate phase at 1300 K.)

With the addition of 0.4 grams of CaCl_2 , there is a significant decrease in the amount of slag (e.g., 0.49 grams at 1300 K), largely due to the formation of solid $\text{CaAl}_2\text{Si}_2\text{O}_8$ (anorthite) by the reactions



at high temperatures and



at low temperatures, where the CaO produced reacts with slag and aluminosilicates to form solid anorthite.

With no constraint on the formation of $\text{NaAlSi}_3\text{O}_8$ (albite), there is a similar effect on the amount of slag produced with NaCl additions. Removal of this constraint on albite formation with NaCl additions would be justified because albite forms at considerably higher temperatures with NaCl additions than without these additions, and the causes of the kinetic constraint would not hold at such temperatures. However, in order to explore this class of reactions more completely, we will have to perform analyses of alumina containing slag systems that are consistent with the liquidus temperatures of anorthite and albite and incorporate these analyses into our calculations. The possibility of reducing the amount of slag and the temperature range of liquid slag stability by suitable additives is important enough to expend an effort on the above analyses. Irrespective of the results of the above analyses, the volatility of sodium chloride and the increasing tendency of chlorides to form sulfates and HCl as temperature decreases partially controls the changes in the final products of combustion with chloride additives.

DISCUSSION

Our calculations provide information that could be useful for defining strategies for the use of additives. Two results of our calculations for limestone addition are clearly significant for desulfurization strategy. First, more slag is produced and it is considerably less viscous than those produced with no additives. Secondly, the CaO from the limestone forms silicates at high temperatures that react with sulfur oxides at lower temperatures to form sulfates. There is a good likelihood that this sulfate-forming reaction will not go to completion because of kinetic

barriers to reactions involving complex silicates. Consequently, addition of limestone at lower temperatures would avoid the complexity and kinetic problems involved in additions to the coal and if the additives can desulfurize effectively at temperatures of about 1200 K or below, the amount and temperature range of stability of the corrosive liquid sulfate would be minimized.

Additions of chlorides as deicers tend to produce gaseous HCl at low temperatures, and boiler designs and materials of construction should be chosen to minimize corrosion by this species. With large chloride additions, the stability and amount of molten slag produced will be very different from the case with no additions. Precise results require development of means to represent the slag chemistry with alumina as a constituent. Our calculations suggest that large additions of CaCl₂ and NaCl might decrease the amount and temperature range of stability of a liquid slag.

Further work is necessary to extend our slag model to incorporate alumina as a component to better define the total chemistry, especially for the case with chloride additions. In addition, a coupled experimental-calculational research program would help to define important kinetic factors to incorporate into our calculations as constraints and could ultimately permit us to define the total combustion chemistry of coal.

ACKNOWLEDGMENT

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REFERENCES

1. S. Sinha, K. Natesan, and M. Blander, "A New Calculational Method for Deducing the Complex Chemistry of Coal Ash Deposits," Proceedings of the Conference on Mineral Matter and Ash Deposition from Coal, Santa Barbara, California, February 21-26, 1988, in press.
2. M. Blander, S. Sinha, A. Pelton, and G. Eriksson, "Calculations of the Chemistry of Coal Combustion Effluents," Proceedings American Flame Research Committee 1988 Fall Meeting, Pittsburgh, Pennsylvania, October 4-6, 1988, Paper No. 25.
3. J. E. Radway, "All You Ever Want to Know About Additive Application and Testing," Proceedings of the Conference on Mineral Matter and Ash Deposition from Coal, Santa Barbara, California, February 21-26, 1988, in press.
4. G. Eriksson, *Chemica Scripta*, **8**, 100-103 (1975).
5. W. T. Thompson, C. W. Bale, and A. D. Pelton, *F*A*C*T Users Guide*, McGill University, Ecole Polytechnique, Montreal (1988).
6. M. Blander and A. D. Pelton, "Computer Assisted Analysis of the Thermodynamic Properties of Slags in Coal Combustion Systems," ANL/FE-83-19, Argonne National Laboratory, Argonne IL (1983).
7. A. D. Pelton and M. Blander, *Metall. Trans.* **17B**, 805-815 (1986).
8. M. Blander and A. D. Pelton, *Geochim. et Cosmochim. Acta*, **51**, 85-95 (1987).

Table I. Composition of High-Sulfur Illinois #6 Coal Used for the Present Work

Coal Constituents		Ash Constituents	
Species	Wt %	Species	Wt %
C	60.15	SiO ₂	46.77
H	4.26	Fe ₂ O ₃	16.22
N	0.97	Al ₂ O ₃	18.47
S	3.41	CaO	6.91
Cl	0.05	MgO	1.28
H ₂ O	10.54	SO ₃	4.35
O	7.30	Na ₂ O	4.96
Ash	13.32	Unknown	1.04
TOTAL	100.00		100.00

Table II. Calculated Slag Compositions
(Weight Percent)

	Temperature (K)					
	1800	1700	1600	1500	1400	1300
<u>w/o CaCO₃</u>						
SiO ₂	57.47	65.63	74.63	77.27	78.62	78.08
FeO	23.57	16.15	7.41	1.92	0.32	0.06
CaO	10.27	6.65	3.61	2.22	1.03	0.51
Na ₂ O	7.07	9.43	11.71	15.81	18.98	20.87
MgO	1.63	2.13	2.64	2.79	1.04	0.48
wt (g)	9.78	7.45	6.02	4.46	3.72	3.38
<u>6.25 g CaCO₃ added</u>						
SiO ₂	42.16	44.11	45.90	46.65	47.56	71.27
FeO	19.41	9.86	4.63	1.88	0.64	0.06
CaO	31.46	36.40	38.48	40.13	34.97	4.49
Na ₂ O	5.63	7.85	8.97	9.26	13.74	23.91
MgO	1.34	1.80	2.03	2.09	3.10	0.27
wt (g)	11.87	8.85	7.84	7.62	5.14	0.16

Table III. Molten and Solid Sulfate Condensates
(Weight Percent)

	1350		1300		1250		1150		1050	
	Without CaCO ₃	With CaCO ₃								
<u>Liquid</u>										
Na ₂ SO ₄	--	94.77	--	91.10	96.65	80.73	--	--	--	--
CaSO ₄	--	5.22	--	8.89	3.25	19.25	--	--	--	--
MgSO ₄	--	0.01	--	0.01	0.10	0.21	--	--	--	--
wt (g)	--	1.61	--	1.68	1.67	2.04	--	--	--	--
<u>Solid</u>										
Na ₂ SO ₄	--	--	--	--	--	--	50.29	45.78	50.32	49.58
CaSO ₄	--	--	--	--	--	--	49.47	54.11	44.72	48.88
MgSO ₄	--	--	--	--	--	--	0.25	0.12	4.96	1.54
wt (g)	--	--	--	--	--	--	3.22	3.53	3.22	3.26
<u>Solid</u>										
CaSO ₄	--	--	--	--	--	--	--	99.77	87.86	96.62
MgSO ₄	--	--	--	--	--	--	--	0.23	12.14	3.38
wt (g)	--	--	--	--	--	--	--	5.01	1.14	9.66

Table IV. Solid Condensates (in grams)

	w/o CaCO ₃				w/CaCO ₃			
	1350	1250	1150	1050	1350	1250	1150	1050
CaAl ₂ Si ₂ O ₈	4.85	4.87	1.73	--	7.16	7.16	7.16	--
Fe ₂ O ₃	2.56	2.56	2.56	2.56	2.56	2.56	2.56	2.56
SiO ₂	1.25	3.82	4.50	5.02	0.00	0.21	3.10	5.05
Al ₆ Si ₂ O ₁₃	1.18	--	--	--	--	--	--	--
MgSiO ₃	0.33	0.40	0.39	0.15	--	--	--	0.08
Al ₂ SiO ₅	--	1.34	3.17	4.17	--	--	--	4.17
CaSiO ₃	--	--	--	--	5.78	5.55	--	--
CaMg(SiO ₃) ₂	--	--	--	--	0.85	0.85	0.83	--