

SOLID-LIQUID-VAPOR INTERACTIONS IN ALKALI-RICH COAL SLAGS

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I. INTRODUCTION

Sodium and potassium are important constituents of the clay minerals found in most coals. As the coal is combusted these metals may be vaporized, transported and reabsorbed by slag in the cooler portions of the system, leading to the production of slags having concentrations of alkalis several times that of the primary mineral matter. Without doubt the most marked concentrations occur in slags from magnetohydrodynamic generators, where potassium is deliberately added to the combustion gases to enhance electrical conductivity of the plasma. Slags from MHD generators have K_2O concentrations approaching 20 wt%.

The corrosive effects of these high alkali slags on ceramic components of combustion systems are well known. Corrosion arises from the fact that such slags are good solvents for a wide range of materials. Furthermore, when many ceramics come into contact with high alkali slags, destructive reactions producing new solids may occur. For example, alumina, a widely used refractory, may react to produce $NaAlSiO_4$, $KAlSiO_4$, or beta alumina, depending upon the activities of silica and the alkalis. In most situations, reactions of this type would result in loss of structural integrity of the ceramic.

For these and related reasons, there is need for detailed knowledge of the physical chemistry of high alkali coal ash - derived slags. NBS has an ongoing theoretical and experimental program to systematically determine the nature of solid-liquid-vapor equilibria in high alkali coal slags. Given the wide variability of coal slag, this necessitates a close interaction between theory and experiment, if significant progress is to be made.

Experimentally, three principal methods are being utilized. Application of the high temperature quenching method, with examination of results by x-ray diffraction and electron microprobe methods, is facilitated by the fact that most silicate melts quench readily to glasses, preserving the textural and chemical relationships which prevailed under equilibrium at high temperatures. On the other hand, the relatively slow kinetics makes necessary great care in the determination of alkali vapor pressures by the Knudsen effusion/mass spectrometric method. Nonetheless the technique has been used successfully at NBS in determining vapor pressures by closely correlating effusion experiments with on-going quench experiments. Similarly, the application of the third principal experimental method, high temperature differential thermal-thermogravimetric analysis, requires a degree of caution.

There has long been interest in the development of models for the prediction of coal slag phase equilibria. While silicate phase diagrams of limited compositional range have been successfully modeled, a single model for accurate prediction of slag phase equilibria in general will require that considerably more progress be made not only in our understanding of the structural chemistry of slags but also in the availability of thermochemical data needed for such models. Progress to date is related to the realization that treatment of silicate liquids as polymerized melts may be necessary for very precise prediction of phase relationships. Also important is the discovery that alkali activities can be modeled over a wide range of compositions by treating slags as composed of mixtures of complex mineral melts such as $CaAl_2Si_2O_8$, $KAlSiO_4$, $NaAlSi_3O_8$, etc.

Thus coal slags, while not chemically ideal mixtures of the oxide components, appear to be much more ideal with respect to a choice of more complex components.

II. PHASE EQUILIBRIA IN COAL SLAGS

(A) Coal Slag As A 7-Component System

The variability of coal ash composition is directly related to variations in the proportions of mineral impurities such as SiO_2 , CaCO_3 , $\text{CaMg}(\text{CO}_3)_2$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, Fe_2O_3 , FeS_2 , and the clay minerals which comprise a complex group of hydrated alkali aluminosilicates. Coal ashes may vary widely in their contents of iron, calcium and magnesium, but do not vary as greatly in the amount of silica and alumina they contain. In fact, of the 323 coal ash analyses reported in U.S. Bureau of Mines Bull. 567 (1), the great majority have a $\text{SiO}_2/(\text{SiO}_2+\text{Al}_2\text{O}_3)$ mole ratio between .67 and .80, with a well defined maximum near .75 (2). The bulk chemistry of the ash is related to the conditions of formation of the coal. In general lignites and subbituminous coals of the western U.S.A. are high in calcium while bituminous coals of the eastern U.S.A. contain more iron. Table 1 gives typical analyses for ashes from these coals, and includes for comparison an analysis of coal slag from a magnetohydrodynamic generator. From this table, it can be seen that, in general, coal slag must be regarded as a seven component substance, if minor constituents such as TiO_2 and P_2O_5 are ignored and if sulfur is assumed to vaporize at high temperature.

Table 1. Typical Coal Ash Analyses (wt %).

	Montana Coal ⁽³⁾	Illinois Coal ⁽³⁾	MHD Slag ⁽⁴⁾
K_2O	0.4	1.4	20.2
Na_2O	0.4	1.6	0.5
CaO	11.9	8.2	3.9
MgO	3.9	0.8	1.1
Al_2O_3	21.4	16.2	12.4
Fe_2O_3	10.0	23.7	14.7
SiO_2	42.5	37.5	48.3
TiO_2	0.8	0.8	0.5
P_2O_5	0.3	0.1	-
SO_3	8.1	8.9	0.2

To account for the fact that Fe_2O_3 reduces partially to FeO with increasing temperature would require an added component. However this may be reduced again to seven if the oxygen partial pressure is included as an intensive variable along with temperature and composition. By doing this the need to specify both FeO and Fe_2O_3 in defining the bulk composition is eliminated; these are replaced by FeO_x , where x is determined by the oxygen partial pressure.

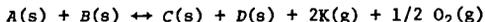
(B) Representation of Solid-Liquid-Vapor Equilibria

Ready visualization of a range of phenomena is one of the attributes making phase diagrams indispensable in understanding the chemistry of heterogeneous systems. However, although advanced multidimensional projective methods have been derived for the representation of n-component systems (5), these do not

in general lead to easily visualized diagrams. Thus for the seven component coal slag system, alternative methods must be used.

It is useful to subdivide the slag system into smaller systems. The system $\text{Al}_2\text{O}_3\text{-SiO}_2$ is perhaps the most fundamental system for all slags, and to this one may think of adding progressively combinations of the alkalis and CaO , MgO and FeO , until the desired degree of complexity is reached. Constituent systems making up the slag system are summarized in Table 2. Data are available for parts of many of these systems (6-10), but as the number of components increases, data become progressively fewer.

At NBS, experimental work is presently concentrating on the system $\text{K}_2\text{O-CaO-Al}_2\text{O}_3\text{-SiO}_2$. This along with $\text{K}_2\text{O-FeO-Al}_2\text{O}_3\text{-SiO}_2$ and $\text{K}_2\text{O-MgO-Al}_2\text{O}_3\text{-SiO}_2$, forms the basis for modeling potassium-rich slags. The approach has been to establish subsolidus equilibria (Figure 1) and then to combine these data with literature thermochemical data via solid state reactions of the type



At the temperature of minimum melting, such calculations provide direct links between the phase diagram and the measurements of potassium vapor pressure which are independent of any solution model (Figure 2). This approach aides greatly in the determination of an internally consistent set of thermochemical data.

As the systems investigated become more complex (more components), other techniques may be used to reduce the number of variables, so that results can be portrayed graphically. For example, in principle phase equilibria at 1 atm in the system $\text{K}_2\text{O-CaO-FeO-Al}_2\text{O}_3\text{-SiO}_2$ could be portrayed in three dimensions graphically as a tetrahedral diagram at constant $\mu_{\text{K}_2\text{O}}$ or $P_{\text{K}_2\text{O}}$, T and P_{O_2} .

Another way of reducing the dimensionality of the representational problem is to deal with saturation surfaces - this is actually a form of projection. For example by considering the equilibria in which Al_2O_3 participated as a phase, the need to use Al_2O_3 as a representational component would be eliminated.

(C) Role of Polymerization Theory

One of the major problems in prediction and calculation of phase equilibria is the formulation of accurate expressions for the free energy of mixing of silicate melts. Relatively few calorimetric measurements are available, and hence the importance of sound methods of estimation and prediction of mixing data to within the required degree of accuracy. Polymer theory, extended in the 1960's to include silicate melts by Masson (11) and others holds promise. It is perhaps the only general theory for silicate melts which deals quantitatively with the problem of melt structure. This has been used, with a surprising degree of success, to calculate phase equilibria in binary oxide systems (12,13). Preliminary calculations on multicomponent slags have shown that polymer theory, when treated in a quasicheical fashion, is highly flexible, and can accommodate seven component liquid immiscibility by making relatively few estimates and assumptions (Figure 3). However, attempts to fit liquidus surfaces in the system $\text{K}_2\text{O-CaO-Al}_2\text{O}_3\text{-SiO}_2$ have met with only partial success. Further applications and extensions of polymer theory in this quaternary system are hampered by a lack of experimental data, and an attempt is being made to rectify this situation.

Table 2. Breakdown of Lower Order Systems Comprising 7-Component Coal Slag System.

	(+CaO)	(+MgO)	(+FeO _x)	(+CaO +MgO)	(+CaO +FeO _x)	(+MgO +FeO _x)	(+CaO +MgO +FeO _x)
Al ₂ O ₃ -SiO ₂ BASE SYSTEM	CaO-Al ₂ O ₃ -SiO ₂	MgO-Al ₂ O ₃ -SiO ₂	FeO-Al ₂ O ₃ -SiO ₂	CaO-MgO-Al ₂ O ₃ -SiO ₂	CaO-FeO-Al ₂ O ₃ -SiO ₂	MgO-FeO-Al ₂ O ₃ -SiO ₂	CaO-MgO-FeO -Al ₂ O ₃ -SiO ₂ ^x
(+K ₂ O)	K ₂ O-CaO-Al ₂ O ₃ -SiO ₂	K ₂ O-MgO-Al ₂ O ₃ -SiO ₂	K ₂ O-FeO-Al ₂ O ₃ -SiO ₂	K ₂ O-CaO-MgO -Al ₂ O ₃ -SiO ₂	K ₂ O-CaO-FeO -Al ₂ O ₃ -SiO ₂ ^x	K ₂ O-MgO-FeO -Al ₂ O ₃ -SiO ₂ ^x	K ₂ O-CaO-MgO -FeO _x -Al ₂ O ₃ -SiO ₂
(+Na ₂ O)	Na ₂ O-CaO-Al ₂ O ₃ -SiO ₂	Na ₂ O-MgO-Al ₂ O ₃ -SiO ₂	Na ₂ O-FeO-Al ₂ O ₃ -SiO ₂	Na ₂ O-CaO-MgO -Al ₂ O ₃ -SiO ₂	Na ₂ O-CaO-FeO -Al ₂ O ₃ -SiO ₂ ^x	Na ₂ O-MgO-FeO -Al ₂ O ₃ -SiO ₂ ^x	Na ₂ O-CaO-MgO -FeO _x -Al ₂ O ₃ -SiO ₂
(+K ₂ O +Na ₂ O)	K ₂ O-Na ₂ O-CaO -Al ₂ O ₃ -SiO ₂	K ₂ O-Na ₂ O-MgO -Al ₂ O ₃ -SiO ₂	K ₂ O-Na ₂ O-FeO -Al ₂ O ₃ -SiO ₂ ^x	K ₂ O-Na ₂ O-CaO -MgO-Al ₂ O ₃ -SiO ₂	K ₂ O-Na ₂ O-CaO -FeO-Al ₂ O ₃ -SiO ₂ ^x	K ₂ O-Na ₂ O-MgO -FeO-Al ₂ O ₃ -SiO ₂ ^x	K ₂ O-Na ₂ O-CaO-MgO -FeO _x -Al ₂ O ₃ -SiO ₂ COAL SLAG SYSTEM

III. SOLUTION MODEL FOR THE PREDICTION OF ALKALI VAPOR PRESSURES

(A) Basis of the Model

The model employed for prediction of vapor pressures in multicomponent coal slags has been outlined in (14). Briefly, large negative deviations from ideal thermodynamic activity behavior are attributed to the formation of complex liquids and solids (actual components) such as K_2SiO_3 , $KAlSiO_4$, etc. The free energies of formation (ΔG_f) are either known or can be estimated for these liquids and solids. By minimizing the total system free energy, one can calculate the equilibrium composition with respect to these components. Thus, for instance the mole fraction of K_2O present ($X^*_{[K_2O]}$) in equilibrium with K_2SiO_3 , and other complex liquids (and solids) containing K_2O , is known. As has been shown previously for the ternary systems, the component activities can, to a good approximation, be equated to these mole fraction quantities (15). From this assumption it also follows that potassium partial pressures can be obtained from the relationship

$$P_K = \left\{ 2 \cdot X^*_{[K_2O]} K_p \right\}^{0.4},$$

where K is the stoichiometric dissociation constant for pure K_2O (liquid or solid) to K and O_2 . In the following discussion the model is tested by comparing predicted P_K data determined in this manner with experimental values. Thermodynamic activities and phase compositions were also calculated using this model. The experimental K -pressure data were obtained by Knudsen effusion mass spectrometry as discussed in detail elsewhere (16).

(B) Method of Calculation

The SOLGASMIX computer program (17) used for calculation of the equilibrium composition and hence activities utilizes a data base of the type given in (14). The coefficients to the ΔG_f equation were obtained by fitting ΔG_f vs T data available in JANAF (18), R6bie et al (19), Barin and Knacke (20), Rein and Chipman (21) and Kelley (22). In some cases no literature data were available and we estimated functions in the manner described earlier (16). Many of the compounds used in the calculation are mineral phases such as mullite ($Al_6Si_2O_{13}$), kaliophilite ($KAlSiO_4$), leucite ($KAlSi_2O_6$), feldspar ($KAlSi_3O_8$), and gehlenite ($Ca_2Al_2SiO_7$).

(C) Application to the K_2O - CaO - Al_2O_3 - SiO_2 System

Figure 4 shows results of calculations for potassium pressures made using the model. As can be seen these agree with experimental results within limits of experimental error over a wide range of temperature. The calculations also indicate temperatures of precipitation of various solids in the quaternary system. These predictions are being checked by experiment. Other potassium pressure calculations (not shown) show similarly good agreement with experiment in the system K_2O - CaO - Al_2O_3 - SiO_2 .

IV. SUMMARY

An integrated experimental/theoretical approach to the problem of non-condensed (solid-liquid-vapor) phase equilibria in multicomponent coal slags has been outlined, including methods for the presentation of results. This relies upon prediction as an important tool in planning experimental work. Theory in turn benefits from experimental feedback, resulting in a continual evolution of models. Hopefully this will lead to generalized solution models capable of predicting slag phase equilibria with a high degree of accuracy.

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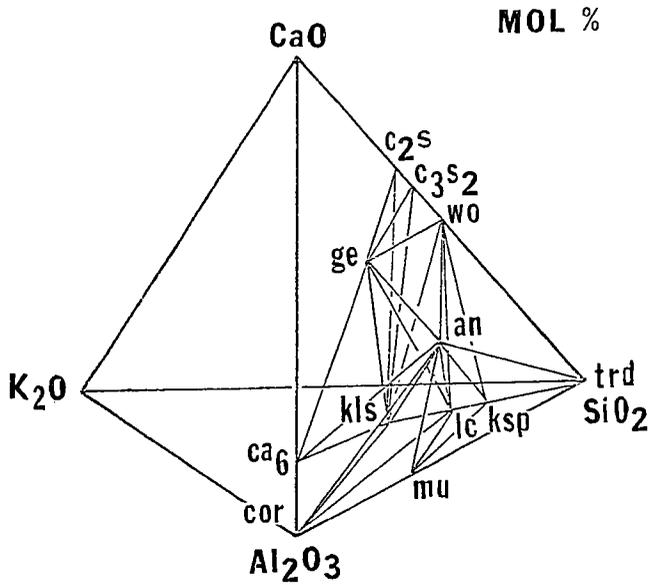


Figure 1. Experimentally determined subsolidus phase relations in the system $K_2O-CaO-Al_2O_3-SiO_2$.

$c_2s = Ca_2SiO_4$	$trd = SiO_2$
$c_3s_2 = Ca_3Si_2O_7$	$ksp = KAlSi_3O_8$
$wo = CaSiO_3$	$lc = KAlSi_2O_6$
$ge = Ca_2Al_2SiO_7$	$kl_s = KAlSiO_4$
$an = CaAl_2Si_2O_8$	$mu = 3Al_2O_3 \cdot 2SiO_2$
$ca_6 = CaAl_{12}O_{19}$	$cor = Al_2O_3$

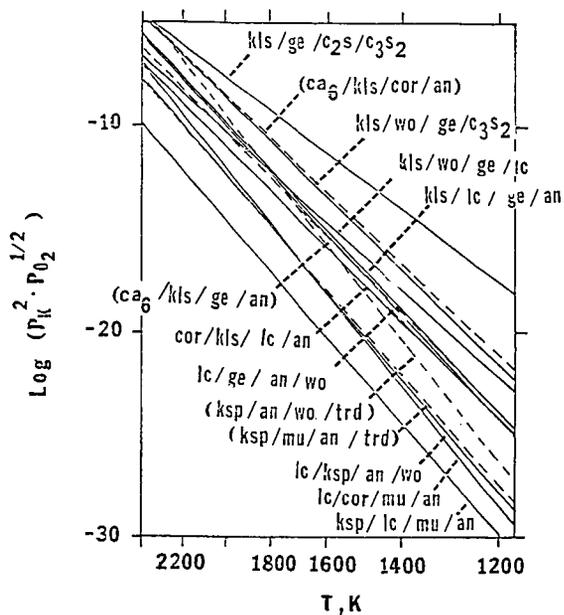


Figure 2. Calculated potassia pressures for solid assemblages in $\text{K}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ (see Figure 1). Thermochemical data used were from (19). Equilibria are metastable above the minimum melting temperatures.

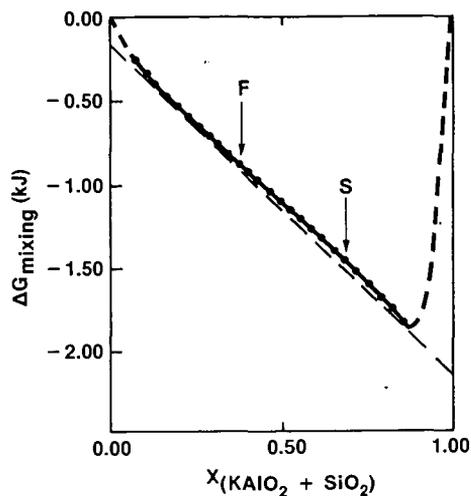


Figure 3. Calculated free energy of mixing along a compositional vector in the system $K_2O-CaO-MgO-FeO-Al_2O_3-SiO_2$ passing through experimentally determined compositions of immiscible melts (F and S). Calculations were made using the quasi-chemical melt polymerization theory (23). The compositions of predicted and observed immiscible melts can be made to agree reasonably well by adjustments in polymerization equilibrium constants and in the ratio $Fe^{+3}/(Fe^{+3} + Fe^{+2})$.

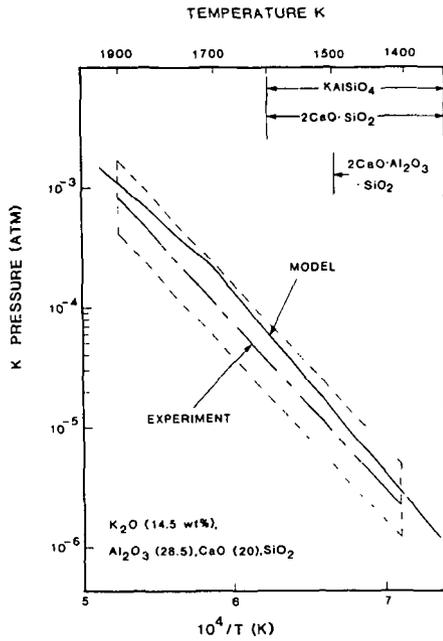


Figure 4. Comparison of ideal mixing of complex components solution model (solid curve) and experimental (broken curve) K-pressure data as a function of reciprocal temperature, for a composition in the $K_2O-CaO-Al_2O_3-SiO_2$ system. Compounds listed are solid precipitates formed over the temperature interval indicated.