

Corrosion of Alumina-Chromia Refractory by Alkali Vapors: I. Thermodynamic Approach

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Theoretical predictions were made for thermodynamically stable phases which formed when alkali (sodium and potassium) vapors reacted with the 90% Al_2O_3 -10% Cr_2O_3 refractory under coal gasifying atmosphere using the computer program of SOLGASMIX-PV.

The calculation results showed that the stable compounds that formed were $\text{X}_2\text{O} \cdot \text{Al}_2\text{O}_3$ and $\text{X}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$ ($\text{X} = \text{Na}^+$ or K^+), depending upon the alkali concentration. The presence of sulfur in gasifying atmospheres did not appear to affect the species of alkali reaction products. Alkali attack at high temperatures is likely to cause serious degradation at the hot face of the refractory, indicating that the alkali concentration is an important factor to affect the degradation of the refractory.

Key words: Thermodynamic calculation, SOLGASMIX-PV computer program, Alkali corrosion, Al_2O_3 - Cr_2O_3 refractory

I. Introduction

Alkali-attack is a common problem in many high temperature technologies where the presence of alkali is usually encountered. Coal gasification involves the production of synthetic or substitute natural gas (SNG) from coal. On combustion, alkali species are released from coal. When refractories are exposed to the alkali atmosphere, a series of reactions may occur, which either degrades the refractory materials, or leads to premature failure. For most refractory systems, the presence of alkali tends to lower the liquidus temperature and results in localized melting. Alternatively, compounds with lower densities often form when alkali reacts with refractory linings. These compounds tend to spall off when subjected to thermal cycling. In addition to alkali, sulfur is also constantly present in coal gasifiers. Presence of sulfur impurities can result in sulfur corrosion of non-slugging gasifier linings.¹⁾

The mechanism and the state of the release of alkali and sulfur impurities from coal are poorly understood due to the combined aggressive conditions of high temperature, high pressure, and high chemical reactivity in coal gasification atmosphere. In this paper, the equilibrium phases formed from the reactions of alkali and/or alkali-sulfur impurities with the 90% alumina - 10% chromia refractory were calculated in a given coal gasification atmosphere using the SOLGASMIX-PV computer program.²⁾

II. Calculation of Equilibrium Compositions

The calculation of equilibrium compositions in a given system is based on the minimization of free energy under the constraints of mass conservation and either constant pressure or constant volume. The computer program used for calculating thermodynamic equilibrium compositions in this study, SOLGASMIX-PV, can calculate equilibria in systems containing a gas mixture, condensed phase solutions, and condensed phases of invariant or variable stoichiometry. Either a constant total gas volume or a constant total pressure can be assumed. Basic equations and principles of calculations incorporated by the SOLGASMIX-PV to calculate equilibrium relationships in complex systems are discussed by Besmann.²⁾

The 90% alumina - 10% chromia refractory under study is a solid solution fired brick. Therefore, approximation of the solution model is needed to get reasonable computer calculation results. Although the regular solution model and the quasi-chemical solution model show better approximation of solution behavior than the ideal solution model, the ideal solution theory can be applied for some systems reasonably. According to Hildebrand and Scott,³⁾ some ceramics may be among the best test materials for the study of near ideal solution behavior. This is so because the activity coefficients (γ), which are direct measures of the deviations from the ideal behavior, are given by the relation

$$\ln \gamma = \left(\frac{A}{RT} \right) f(x) \quad (1)$$

where A = a constant, R = the Gas constant, T = temperature, and $f(x)$ = a simple function of the composition depending on temperature. Deviations from ideal behavior will tend to be quite small in high temperature stu-

Table 1. Composition of Gas Atmosphere (in mol%)

H ₂	CH ₄	CO	CO ₂	H ₂ O	N ₂	H ₂ S
12	18	17	12	20	20	0.7

Table 2. Chemical Species Considered in Calculations for Sodium

Gas Phases	Liquid Solutions	Solid Solutions	Solid Phases
H ₂ , CH ₄ , CO, CO ₂ H ₂ O, NH ₃ , O ₂ , N ₂ , Na, Na ⁺ , NaOH, NaO, NaO ⁻ , NaH, NaCN, Al ⁺ , Al, CrH, CrO, CrO ₂ , CrO ₃ , Cr	Al, Cr, Na ₂ CO ₃ , NaCN, NaOH, (Al, Cr) ₂ O ₃ , Na ₂ O, Na ₂ CrO ₄	(Al, Cr) ₂ O ₃ (ss)	C, Al, Cr, NaO ₂ , Na ₂ O, NaOH, Na ₂ CO ₃ , NaCH, Na ₂ O · 11Al ₂ O ₃ , Al ₄ C ₃ , AlN, Cr ₃ C ₂ , Cr ₇ C ₃ , Cr ₂₃ C ₆ , CrN,

Table 3. Chemical Species Considered in Calculations for Potassium

Gas Phases	Liquid Solutions	Solid Solutions	Solid Phases
H ₂ , CH ₄ , CO, CO ₂ H ₂ O, NH ₃ , O ₂ , N ₂ , Na, Na ⁺ , NaOH, NaO, NaO ⁻ , NaH, NaCN, Al ⁺ , Al, CrN, CrO, CrO ₂ , CrO ₃ , Cr	Al, Cr, Na ₂ CO ₃ , KCN, KOH, (Al, Cr) ₂ O ₃ , Na ₂ O, K ₂ CrO ₄	(Al, Cr) ₂ O ₃ (ss)	C, Al, Cr, KO ₂ , K ₂ O, KOH, K ₂ CO ₃ , KCH, K ₂ O · 11Al ₂ O ₃ , Al ₄ C ₃ , AlN, Cr ₃ C ₂ , Cr ₇ C ₃ , Cr ₂₃ C ₆ , CrN,

Table 4. Chemical Species Considered in Calculations for Sodium and Sulfur

Gas Phases	Liquid Solutions	Solid Solutions	Solid Phases
H ₂ , CH ₄ , CO, CO ₂ H ₂ O, NH ₃ , O ₂ , N ₂ , Na, Na ⁺ , NaOH, NaO, NaO ⁻ , NaH, NaCN, Al ⁺ , Al, CrH, CrO, CrO ₂ , CrO ₃ , Cr SO, S ₂ , H ₂ SO ₄ , H ₂ S, SO ₂ , Na ₂ SO ₄	Al, Cr, Na ₂ CO ₃ , NaCN, NaOH, (Al, Cr) ₂ O ₃ , Na ₂ O, Na ₂ CrO ₄ , Na ₂ S, Na ₂ SO ₄	(Al, Cr) ₂ O ₃ (ss)	C, Al, Cr, NaO ₂ , Na ₂ O, NaOH, Na ₂ CO ₃ , NaCH, Na ₂ O · 11Al ₂ O ₃ , Al ₄ C ₃ , AlN, Cr ₃ C ₂ , Cr ₇ C ₃ , Cr ₂₃ C ₆ , CrN, Cr ₂ N, Na ₂ O · Al ₂ O ₃ , Al ₂ S ₃ , CrS

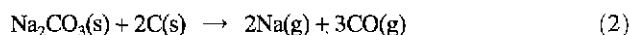
Table 5. Chemical Species Considered in Calculations for Potassium and Sulfur

Gas Phases	Liquid Solutions	Solid Solutions	Solid Phases
H ₂ , CH ₄ , CO, CO ₂ H ₂ O, NH ₃ , O ₂ , N ₂ , Na, Na ⁺ , NaOH, NaO, NaO ⁻ , NaH, NaCN, Al ⁺ , Al, CrN, CrO, CrO ₂ , CrO ₃ , Cr SO, S ₂ , H ₂ SO ₄ , H ₂ S, SO ₂ , K ₂ SO ₄	Al, Cr, K ₂ CO ₃ , KCN, KOH, (Al, Cr) ₂ O ₃ , K ₂ O, K ₂ CrO ₄ , K ₂ SO ₄ , K ₂ S	(Al, Cr) ₂ O ₃ (ss)	C, Al, Cr, KO ₂ , K ₂ O, KOH, K ₂ CO ₃ , KCH, K ₂ O · 11Al ₂ O ₃ , Al ₄ C ₃ , AlN, Cr ₃ C ₂ , Cr ₇ C ₃ , Cr ₂₃ C ₆ , CrN, Cr ₂ N, K ₂ O · Al ₂ O ₃ , Al ₂ S ₃ , CrS

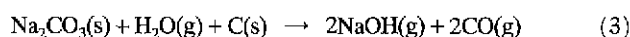
dies of ceramic systems. In 1953, Knapp⁴ calculated the free energy-composition curve for the Al₂O₃-Cr₂O₃ system by using the assumption of ideal solution behavior. The agreement between the calculated and experimental phase diagrams is fairly good. For these reasons, ideal solution theory was adopted for the present calculations. The calculations for the 90% Al₂O₃ - 10% Cr₂O₃ composition exposed to alkali and sulfur vapor phases at high temperature adopted thermodynamic data from various reference sources.⁵⁻¹⁶

In the calculations, the thermodynamic system con-

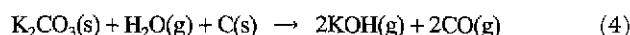
tained one gas mixture, one liquid solution, one solid solution, and various invariant condensed phases. The simulated coal gasification atmosphere composition used in the calculations is listed in Table 1. The stable alkali species in the gasifier up to 20 atm pressure were calculated. The results indicate that at low temperature, solid sodium and potassium carbonate are the stable species. When the temperature increases, sodium carbonate and potassium carbonate melt at roughly 1130K and 1170K, respectively. Above 1270K, sodium vapor may begin to form by the reaction



At 1340K, in addition to sodium vapor, sodium hydroxide vapor is predicted, along with carbon monoxide vapor, according to the reaction



In the case of potassium, potassium hydroxide starts to form above 1200K by the reaction



Above 1250K, in addition to potassium hydroxide vapor, potassium vapor is generated by the reaction

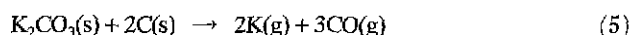


Table 2, 3, 4, and 5 provide a list of the important

species which were considered during the calculations. The thermodynamic calculations were performed to predict the stable phases at various Al_2O_3 to $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratios in the given coal gasification atmosphere containing 1 mol% sodium/potassium and 0.7 mol% sulfur. The calculations were carried out using ambient pressure, and temperatures ranging from 1000K to 1600K.

III. Results and Discussion

Results of thermodynamic calculations for sodium-refractory reactions summarized in Table 6 indicate that $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$ and $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$ (β -alumina) are stable phases at high temperatures (1000K to 1600K); these results are in reasonable agreement with the phase diagram¹⁷. When the $\text{Al}_2\text{O}_3:\text{Na}_2\text{O}$ ratio is 1:2, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3$ and Na_2CO_3 are the stable phases. At this alkali concentration, sodium oxide reacts with carbon dioxide to form sodium carbonate. When the $\text{Al}_2\text{O}_3:\text{Na}_2\text{O}$ ratio is 1:1, the calculations indicate that sodium aluminate is stable according to the reaction



For a range of $\text{Al}_2\text{O}_3:\text{Na}_2\text{O}$ ratios of 2:1 through 9:1, sodium aluminate and β -alumina are the stable phases. Finally, for an $\text{Al}_2\text{O}_3:\text{Na}_2\text{O}$ ratio of 18:1, β -alumina is predicted to become thermodynamically stable phase at

Table 6. Phases Predicted for Na and Alumina-Chromia Refractory Reactions

Temp. (K)	$\text{Al}_2\text{O}_3 : \text{Na}_2\text{O} = 1:2$	$\text{Al}_2\text{O}_3 : \text{Na}_2\text{O} = 1:1$	
1000	(Al, Cr) ₂ O ₃ (ss)*, NA [†] , Na ₂ CO ₃ (s)	(Al, Cr) ₂ O ₃ (ss), NA, Na ₂ CO ₃ (s)	
1100	(Al, Cr) ₂ O ₃ (ss), NA, Na ₂ CO ₃ (l)	(Al, Cr) ₂ O ₃ (ss), NA	
1200	(Al, Cr) ₂ O ₃ (ss), NA, Na ₂ CO ₃ (l)	(Al, Cr) ₂ O ₃ (ss), NA	
1300	(Al, Cr) ₂ O ₃ (ss), NA	(Al, Cr) ₂ O ₃ (ss), NA	
1400	(Al, Cr) ₂ O ₃ (ss), NA	(Al, Cr) ₂ O ₃ (ss), NA	
1500	(Al, Cr) ₂ O ₃ (ss), NA	(Al, Cr) ₂ O ₃ (ss), NA, NA ₁₁	
1600	(Al, Cr) ₂ O ₃ (ss), NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA ₁₁	
Temp. (K)	$\text{Al}_2\text{O}_3 : \text{Na}_2\text{O} = 2:1$	$\text{Al}_2\text{O}_3 : \text{Na}_2\text{O} = 9 :$	$\text{Al}_2\text{O}_3 : \text{Na}_2\text{O} = 18 : 1$
1000	(Al, Cr) ₂ O ₃ (ss), NA, NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA, NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA ₁₁
1100	(Al, Cr) ₂ O ₃ (ss), NA, NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA, NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA ₁₁
1200	(Al, Cr) ₂ O ₃ (ss), NA, NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA, NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA ₁₁
1300	(Al, Cr) ₂ O ₃ (ss), NA, NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA, NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA ₁₁
1400	(Al, Cr) ₂ O ₃ (ss), NA, NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA, NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA ₁₁
1500	(Al, Cr) ₂ O ₃ (ss), NA, NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA ₁₁
1600	(Al, Cr) ₂ O ₃ (ss), NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA ₁₁

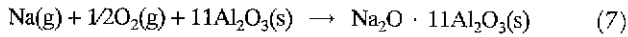
★ ss = solid solution, s = solid, l = liquid

† Conventional cement chemistry notation used

N = Na₂O

K = K₂O

all temperature according to the reaction



Results of the calculations for potassium-refractory reactions (Table 7) show that the compounds produced by the reaction between potassium and the $(\text{Al}, \text{Cr})_2\text{O}_3(\text{ss})$ refractory are $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$ and $\text{K}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$, analogous

to those produced by sodium degradation. When the ratio of $\text{Al}_2\text{O}_3:\text{K}_2\text{O} = 2:1$, K_2CO_3 and $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$ are the stable phases. When the ratio of $\text{Al}_2\text{O}_3:\text{K}_2\text{O} = 1:1$, only potassium aluminate is stable and when the ratio is 18:1, potassium- β -alumina is stable. Between the ratios of 1:1 and 18:1, both potassium aluminate and potassium- β -alumina are stable, equilibrium phases. Results of the cal-

Table 7. Phases Predicted for K and Alumina-Chromia Refractory Reactions

Temp. (K)	$\text{Al}_2\text{O}_3 : \text{K}_2\text{O} = 1 : 2$	$\text{Al}_2\text{O}_3 : \text{K}_2\text{O} = 1 : 1$	
1000	(Al, Cr) ₂ O ₃ (ss), KA, K ₂ CO ₃ (s)	(Al, Cr) ₂ O ₃ (ss), KA, K ₂ CO ₃ (s)	
1100	(Al, Cr) ₂ O ₃ (ss), KA, K ₂ CO ₃ (s)	(Al, Cr) ₂ O ₃ (ss), KA, K ₂ CO ₃ (s)	
1200	(Al, Cr) ₂ O ₃ (ss), KA, K ₂ CO ₃ (l)	(Al, Cr) ₂ O ₃ (ss), KA	
1300	(Al, Cr) ₂ O ₃ (ss), KA	(Al, Cr) ₂ O ₃ (ss), KA	
1400	(Al, Cr) ₂ O ₃ (ss), KA	(Al, Cr) ₂ O ₃ (ss), KA	
1500	(Al, Cr) ₂ O ₃ (ss), KA	(Al, Cr) ₂ O ₃ (ss), KA	
1600	(Al, Cr) ₂ O ₃ (ss), KA	(Al, Cr) ₂ O ₃ (ss), KA	
Temp. (K)	$\text{Al}_2\text{O}_3 : \text{K}_2\text{O} = 2 : 1$	$\text{Al}_2\text{O}_3 : \text{K}_2\text{O} = 9 : 1$	$\text{Al}_2\text{O}_3 : \text{K}_2\text{O} = 18 : 1$
1000	(Al, Cr) ₂ O ₃ (ss), KA, KA ₁₁	(Al, Cr) ₂ O ₃ (ss), KA, KA ₁₁	(Al, Cr) ₂ O ₃ (ss), KA ₁₁
1100	(Al, Cr) ₂ O ₃ (ss), KA, KA ₁₁	(Al, Cr) ₂ O ₃ (ss), KA, KA ₁₁	(Al, Cr) ₂ O ₃ (ss), KA ₁₁
1200	(Al, Cr) ₂ O ₃ (ss), KA, KA ₁₁	(Al, Cr) ₂ O ₃ (ss), KA, KA ₁₁	(Al, Cr) ₂ O ₃ (ss), KA ₁₁
1300	(Al, Cr) ₂ O ₃ (ss), KA, KA ₁₁	(Al, Cr) ₂ O ₃ (ss), KA, KA ₁₁	(Al, Cr) ₂ O ₃ (ss), KA ₁₁
1400	(Al, Cr) ₂ O ₃ (ss), KA, KA ₁₁	(Al, Cr) ₂ O ₃ (ss), KA, KA ₁₁	(Al, Cr) ₂ O ₃ (ss), KA ₁₁
1500	(Al, Cr) ₂ O ₃ (ss), KA, KA ₁₁	(Al, Cr) ₂ O ₃ (ss), KA, KA ₁₁	(Al, Cr) ₂ O ₃ (ss), KA ₁₁
1600	(Al, Cr) ₂ O ₃ (ss), KA, KA ₁₁	(Al, Cr) ₂ O ₃ (ss), KA, KA ₁₁	(Al, Cr) ₂ O ₃ (ss), KA ₁₁

Table 8. Phases Predicted for Na/S and Alumina-Chromia Refractory Reactions

Temp. (K)	$\text{Al}_2\text{O}_3 : \text{Na}_2\text{O} = 1 : 2$	$\text{Al}_2\text{O}_3 : \text{Na}_2\text{O} = 1 : 1$	
1000	(Al, Cr) ₂ O ₃ (ss), NA, Na ₂ CO ₃ (s), Na ₂ S(s)	(Al, Cr) ₂ O ₃ (ss), NA, Na ₂ S(s)	
1100	(Al, Cr) ₂ O ₃ (ss), NA, Na ₂ S(s)	(Al, Cr) ₂ O ₃ (ss), NA, Na ₂ S(s)	
1200	(Al, Cr) ₂ O ₃ (ss), NA, Na ₂ S(s)	(Al, Cr) ₂ O ₃ (ss), NA	
1300	(Al, Cr) ₂ O ₃ (ss), NA, Na ₂ S(s)	(Al, Cr) ₂ O ₃ (ss), NA	
1400	(Al, Cr) ₂ O ₃ (ss), NA	(Al, Cr) ₂ O ₃ (ss), NA	
1500	(Al, Cr) ₂ O ₃ (ss), NA	(Al, Cr) ₂ O ₃ (ss), NA, NA ₁₁	
1600	(Al, Cr) ₂ O ₃ (ss), NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA ₁₁	
Temp. (K)	$\text{Al}_2\text{O}_3 : \text{Na}_2\text{O} = 2 : 1$	$\text{Al}_2\text{O}_3 : \text{Na}_2\text{O} = 9 : 1$	$\text{Al}_2\text{O}_3 : \text{Na}_2\text{O} = 18 : 1$
1000	(Al, Cr) ₂ O ₃ (ss), NA, NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA, NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA ₁₁
1100	(Al, Cr) ₂ O ₃ (ss), NA, NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA, NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA ₁₁
1200	(Al, Cr) ₂ O ₃ (ss), NA, NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA, NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA ₁₁
1300	(Al, Cr) ₂ O ₃ (ss), NA, NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA, NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA ₁₁
1400	(Al, Cr) ₂ O ₃ (ss), NA, NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA, NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA ₁₁
1500	(Al, Cr) ₂ O ₃ (ss), NA, NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA ₁₁
1600	(Al, Cr) ₂ O ₃ (ss), NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA ₁₁	(Al, Cr) ₂ O ₃ (ss), NA ₁₁

Table 9. Phases Predicted for K/S and Alumina-Chromia Refractory Reactions

Temp. (K)	$\text{Al}_2\text{O}_3 : \text{K}_2\text{O} = 1 : 2$		$\text{Al}_2\text{O}_3 : \text{K}_2\text{O} = 1 : 1$
1000	(Al, Cr) ₂ O ₃ (ss), KA, K ₂ CO ₃ (s)		(Al, Cr) ₂ O ₃ (ss), KA, K ₂ CO ₃ (s)
1100	(Al, Cr) ₂ O ₃ (ss), KA, K ₂ CO ₃ (s), K ₂ S(l)		(Al, Cr) ₂ O ₃ (ss), KA, K ₂ CO ₃ (l), K ₂ S(l)
1200	(Al, Cr) ₂ O ₃ (ss), KA, K ₂ CO ₃ (s), K ₂ S(l)		(Al, Cr) ₂ O ₃ (ss), KA, K ₂ CO ₃ (l), K ₂ S(l)
1300	(Al, Cr) ₂ O ₃ (ss), KA, K ₂ S(l)		(Al, Cr) ₂ O ₃ (ss), KA
1400	(Al, Cr) ₂ O ₃ (ss), KA		(Al, Cr) ₂ O ₃ (ss), KA
1500	(Al, Cr) ₂ O ₃ (ss), KA		(Al, Cr) ₂ O ₃ (ss), KA
1600	(Al, Cr) ₂ O ₃ (ss), KA		(Al, Cr) ₂ O ₃ (ss), KA
Temp. (K)	$\text{Al}_2\text{O}_3 : \text{K}_2\text{O} = 2 : 1$	$\text{Al}_2\text{O}_3 : \text{K}_2\text{O} = 9 : 1$	$\text{Al}_2\text{O}_3 : \text{K}_2\text{O} = 18 : 1$
1000	(Al, Cr) ₂ O ₃ (ss), KA, KA ₁₁	(Al, Cr) ₂ O ₃ (ss), KA, KA ₁₁	(Al, Cr) ₂ O ₃ (ss), KA ₁₁
1100	(Al, Cr) ₂ O ₃ (ss), KA, KA ₁₁	(Al, Cr) ₂ O ₃ (ss), KA, KA ₁₁	(Al, Cr) ₂ O ₃ (ss), KA ₁₁
1200	(Al, Cr) ₂ O ₃ (ss), KA, KA ₁₁	(Al, Cr) ₂ O ₃ (ss), KA, KA ₁₁	(Al, Cr) ₂ O ₃ (ss), KA ₁₁
1300	(Al, Cr) ₂ O ₃ (ss), KA, KA ₁₁	(Al, Cr) ₂ O ₃ (ss), KA, KA ₁₁	(Al, Cr) ₂ O ₃ (ss), KA ₁₁
1400	(Al, Cr) ₂ O ₃ (ss), KA, KA ₁₁	(Al, Cr) ₂ O ₃ (ss), KA, KA ₁₁	(Al, Cr) ₂ O ₃ (ss), KA ₁₁
1500	(Al, Cr) ₂ O ₃ (ss), KA, KA ₁₁	(Al, Cr) ₂ O ₃ (ss), KA, KA ₁₁	(Al, Cr) ₂ O ₃ (ss), KA ₁₁
1600	(Al, Cr) ₂ O ₃ (ss), KA, KA ₁₁	(Al, Cr) ₂ O ₃ (ss), KA, KA ₁₁	(Al, Cr) ₂ O ₃ (ss), KA ₁₁

culations show good agreement with studies by Moya et al.¹⁸⁾ on the K₂O-Al₂O₃ system. The results of the thermodynamic calculations performed to predict the stable phases formed at various Al₂O₃ to Na₂O/K₂O ratios in the given coal gasification atmosphere containing 1 mol% of sodium and potassium and 0.7 mol% of sulfur are shown in Table 8 and 9 for sodium and potassium, respectively. The stable alkali phases at the given coal gasification conditions are sodium aluminate, potassium aluminate, and β-alumina (Na₂O · 11Al₂O₃/K₂O · 11Al₂O₃). The results of these calculations agree with studies by Weber et al.¹⁷⁾ and Brownmiller¹⁹⁾ who found stable phases to be X₂O · Al₂O₃ and X₂O · 11Al₂O₃ (X = Na, K).

When sulfur is present, the calculations show that K₂S is present as a liquid phase and Na₂S is present as a solid phase. At the ratio of Al₂O₃:Na₂O/K₂O = 1:2, sodium sulfide was calculated to be the stable phase between 1000K to 1300K. At the ratio of Al₂O₃:Na₂O/K₂O = 1:1, Na₂S appears to be stable from 1000K to 1100K, whereas K₂S appears to be stable from 1100K to 1200K. At the higher temperatures, both Na₂S and K₂S disappear. At the ratios of Al₂O₃:Na₂O/K₂O = 2:1, 9:1, and 18:1, calculation results show that alkali sulfides are not present.

At certain temperatures, the formation of alkali sulfide (Na₂S or K₂S) and alkali carbonate (Na₂CO₃ or K₂CO₃) may reduce the alkali concentration which cause Na₂O · Al₂O₃ or K₂O · Al₂O₃ to form and, therefore, mitigate the alkali attack of the alumina-chrome refractory. However, it is found that alkali sulfide and alkali carbonate exist only when excess alkali remains following alkali reaction with alumina-chrome refractory. If the amounts of alkali

are insufficient, e.g., Al₂O₃:Na₂O/K₂O = 2:1, 9:1, and 18:1, sulfide and carbonate compounds do not appear.

The thermodynamic calculations reveal that the phases formed by reactions of the alumina chromia refractory with both alkali and sulfur are the same as those formed by reactions with alkali alone; i.e., Na₂O · Al₂O₃/Na₂O · 11Al₂O₃ or K₂O · Al₂O₃/K₂O · 11Al₂O₃. Based on these calculation results, the 90% Al₂O₃-10% Cr₂O₃ refractory appears to be very resistance to corrosion by sulfur. However, alkali attack at high temperatures is likely to cause serious degradation at the hot face of the refractory providing alkali concentration is significant.

IV. Conclusions

The mechanism of alkali and/or alkali-sulfur attack on coal gasifier lining consists of two steps: (1) the release of the alkali and/or alkali-sulfur species from coal, and (2) the reactions with the gasifier lining. Theoretical calculations using the SOLGASMIX-PV computer program predict the alkali phases that form when alkali reacts with alumina-chromia refractories. Reaction of sodium and potassium vapors with an alumina-chromia refractory will form Na₂O · Al₂O₃/Na₂O · 11Al₂O₃, or K₂O · Al₂O₃/K₂O · 11Al₂O₃. The presence of sulfur in coal gasifying atmospheres does not appear to have any effect on phases that form when alkali reacts with alumina-chromia refractories. When refractories made by Al₂O₃-Cr₂O₃ system are exposed to alkali atmospheres, alkali reactions appear to be inevitable consequence from the view point of thermodynamic considerations.

References

1. J. B. Tak and D. J. Young, "Sulfur Corrosion of Calcium Aluminate Bonded Castables," *Am. Ceram. Soc. Bull.*, **61**[7], 725-727 (1982).
2. T. M. Besmann, "SOLGASMIX-PV, A Computer Program to Calculate Equilibrium Relationships in Complex Chemical Systems," ORNL/TM-5775, Contract No. W-7405-eng-26, (1977).
3. J. H. Hildebrand and R. L. Scott, "Solubility of Nonelectrolytes," 3rd ed., Reinhold Publishing Corp., New York (1950).
4. W. J. Knapp, "Use of Free Energy Data in the Construction of Phase Diagrams," *J. Am. Ceram. Soc.*, **36**[2], 43 (1953).
5. A. R. Richard, S. H. Bruce and R. F. James, "Thermodynamic Properties of Minerals and Related Substances at 298.15K and 1 Bar Pressure and at High Temperatures," U.S. Geol. Survey Bull., 1452 (1979).
6. O. Kubaschewski and C. B. Alcock, "Metallurgical Thermochemistry," Pergamon Press (1979).
7. E. T. Turdogan, "Physical Chemistry of High Temperature Technology," Academic Press (1980).
8. M. W. Chase, Jr., J. L. Curnutt, A. T. Hu, H. Prophet, A. N. Syverud and L. C. Walker, "JANAF Thermochemical Tables," 1974 Supplement, *J. Phys. Chem. Ref. Data*, **3**[2], 311 (1974).
9. M. W. Chase, Jr., J. L. Curnutt, H. Prophet, R. A. McDonald and A. N. Syverud, "JANAF Thermochemical Tables," 1975 Supplement, *J. Phys. Chem. Ref. Data*, **4**[1], 1 (1975).
10. M. W. Chase, Jr., J. L. Curnutt, R. A. McDonald and A. N. Syverud, "JANAF Thermochemical Tables," 1978 Supplement, *J. Phys. Chem. Ref. Data*, **7**[3], 793-940 (1978).
11. M. W. Chase, Jr., J. L. Curnutt, J. R. Downey, Jr., R. A. McDonald, A. N. Syverud and E. A. Valenzuela, "JANAF Thermochemical Tables," 1982 Supplement, *J. Phys. Chem. Ref. Data*, **11**[3], 695-940 (1982).
12. M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald and A. N. Syverud, "JANAF Thermochemical Tables, Third Edition," Am. Chem. Soc. and Am. Ins. Phys. for Nat. Bur. Stand., **14** (1985).
13. I. Barin, O. Knacke and O. Kubaschewski, "Thermochemical Properties of Inorganic Substances," Springer-Verlag, Berlin and New York (1977).
14. F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," Nat. Bur. Stand., Circ.500, Washington (1961).
15. L. G. Hepler, "Thermodynamics of Aqueous Hydrogen Chromate and Dichromate Ions. Heats of Formation of Chromates and Dichromates," *J. Am. Chem. Soc.*, **80**, 6181 (1958).
16. A. J. Bard, R. Parsons and J. Jordan, "Standard Potentials in Aqueous Solution," Marcel Dekker, Inc., New York and Basel (1985).
17. N. Weber and A. F. Venero, "Revision of the Phase Diagram $\text{NaAlO}_2\text{-Al}_2\text{O}_3$," *Am. Ceram. Soc. Bull.*, **49**[4], 491 (1970).
18. J. S. Moya, E. Criado and S. DeAza, "The $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3$ - Al_2O_3 System," *J. Mat. Sci.*, **17**, 2213-2217 (1982).
19. L. T. Brownmiller, "System Lime-Potash Alumina," *Am. J. Sci.*, **29**, 260 (1935).