Corrosion of Alumina-Chromia Refractories by Alkali Vapors; II. Experimental Approach

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Theoretical predictions for thermodynamically stable phases which formed when alkali (sodium and potassium) vapors reacted with alumina-chromia refractories under coal gasifying atmosphere were confirmed experimentally using a laboratory-scale coal gasifying reaction system and a commercial alumina-chromia refractory using SEM, XRD, and EDAX. Alkali concentration profiles in the refractory as a function of time were also determined. The results showed that the compounds that formed were $X_2O \cdot Al_2O_3$, $X_2O \cdot Cr_2O_3$, $X_2O \cdot 5Al_2O_3$, $X_2O \cdot 7Al_2O_3$, $X_2O \cdot 11Al_2O_3$ ($X=Na^+$ or K^+), depending upon the alkali concentration and time of exposure at high temperatures. The presence of sulfur in gasifying atmospheres did not appear to affect the alkali reaction products. Alkali penetration into the alumina-chromia refractory was deep and the formation of the Na_2O Al_2O_3/K_2O Al_2O_3 compounds resulted in the serious deformation of the refractory due to the large volume expansion at the reaction surface. The hot face of the alumina-chromia refractory in service under an alkali environment is prone to failure by alkali attack.

Key words : Alkali corrosion, Alumina-chromia refractory, Coal gasification atmosphere, Thermal spalling

I. Introduction

S ubstantial research has been conducted on the gaseous corrosion of refractories for dry-ash gasifiers and molten slag corrosion of slagging gasifier refractories. Sadler et al.[1] extensively evaluated the behavior of castable and brick refractories in dry-ash gasifier environments and found that intermediate and low-alumina refractories gave the best performance as liner materials. Test reported by Kennedy[2] and Kennedy and Poppel[3] indicate that chrome- and alumina-base refractories are the only commercial refractories that have stability at temperatures of ~1500°C with coal slags. However, little attention is found in the literature on the performance of refractories in the nonslagging, gaseous regions of the slagging gasifier.

It is well-known from experience in the glass, cement, and iron and steel industries that common alkali compounds and vapors react aggressively with refractory materials, often causing premature failure.[4-6] Alkali vapors are expecially damaging when they penetrate deeply into proes and cracks in the refractories and cause localized melting and/or undesirable compound formation. Differences in thermal expansion behavior and thermal shock resistance of the reaction products and the major phases of the refractory materials may cause severe thermal spalling. In some cases alkali compounds have been to known to condense in low temperature regions of a furnace structure, absorb moisture when cooled to ambient temperatues, and cause massive chemical spalling

of the refractories upon reheting because of the less dense structures formed. In many respects, blast furnace technology is similar to coal gasification technology. Alkali attack has been a continuing problem in the blast furnace with both fireclay and high alumina refractories showing considerable alkali attack and associated fracture parallel to the working face and general disintergration. Although alkali concentration in the blast furnace charge is low (comparable to htat in coal gasifiers), alkali concentrations up to 21% have been measured on the hot face. The alkali problems in blast rurnaces have never been completely solved and there is every reason to expect that some of these blast furnace experiences will repeat in coal gasifiers over long periods of operations.

Alkali vapors are almost will present in coal gasifiers because feed coals contain alkali compounds (typically 0.5 to 2.0% of the coal ash).[7] In general, alkali attack is regarded as a long-term phenomenon, with the refractory damage occurring over a period of many months or years of unit operation. Howere, a refractory lining in the Grand Forks Energy Technology Center slagging gasifier cracked and spalled after operating about 125 h due to alkali attack of the refractories in the slag-free sections of the reactor vessel,[8] demonstrating the severity of alkali-refractory reactions in these regions. Although research devoted to the study of gaseous alkali corrosion of slagging gasifier refractories has received little attention, the success of a coal gasification plant will depend upon the selection of refractory liner materials that

will offer an acceptalble service lifetime throughout all regions of the gasifier reactor.

The previous theoretical calculations[9] indicate that $X_2O \cdot Al_2O_3$ and $X_2O \cdot 11Al_2O_3$ (X=Na or K) are to be stable phases when alkali vapors react with the alumina-chromia refractory under the selected coal gasification atmosphere. Experimentation was used to confirm selected theoretical results and to understand the detrimental effects of alkali vapors on a commercial alumina-chromia refractory in service as a coal gasifying linner.

II. Experimental Test Procedure

1. Sample analysis

The 90% alumina-10% chromia solid solution fired refractory in the investigations was obtained from Harvison-Walker Refractory Co.. Slag compositions vary greatly for different coal, suggesting that a single refractory

Fig. 1. Scanning electron micrograph of as-received alumina-chromia refractory showing the fused alumina grains (regin A) surrounded by Cr_2O_3 reaction zone (region B) within the 70% Al_2O_3-30% Cr_2O_3 solid solution matrix (region C).
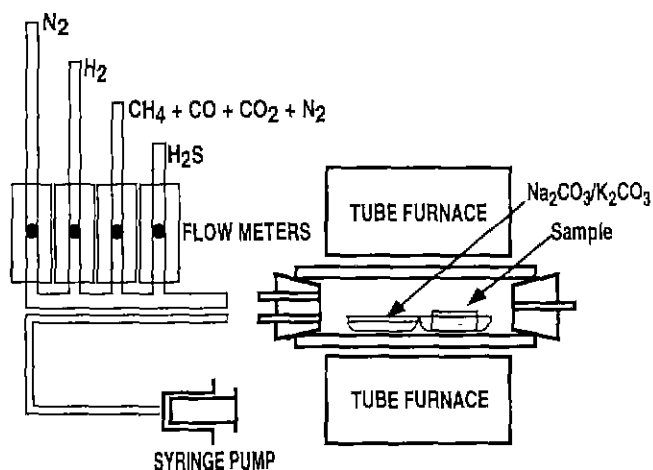

Fig. 2. Test apparatus for study of alkali and/or alkali-sulfur attack on the alumina-chromia refractory.

composition is unlikely to be equally effective against all slags. However the dense, fused grain alumina-chromia brick evaluated in this study is reported to have a high resistance to slag corrosions, particularly basic slags.[10] The as-received refractory was characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive x-ray analysis (EDAX). The SEM micrograph in Fig. 1 shows the fused alumina grains as white regions separated by the matrix phase. Dark regions surrounding the fused alumina grains indicate zones where Cr_2O_3 from the matrix has reacted with the alumina grains. Even though the initial weight ratio Al_2O_3 to Cr_2O_3 in the preparation of the refractory was 9 : 1, EDAX reveal that the matrix phase contains 70% Al_2O_3 and 30% Cr_2O_3. The dark region surrounding the Al_2O_3 grains has a Cr_2O_3 content that varies from over 30% to 0, typical of a reaction zone.

2. Test procedure

The schematic diagram of test apparatus is shown in Fig. 2. Test specimens approximately 1 cm × 1 cm × 7 cm were cut from the alumina-chromia refractory using a diamond cutting blade. During the test, the samples were placed in an alumina boat in the tube furnace along with a separate boat containing an identical weight of either sodium carbonate (Na_2CO_3) or potassium carbonate (K_2CO_3) located adjacent to, but upstream from, the test specimen. This arrangemnt provide exposure of the refractory specimens to alkali vapor phases only.

The refractory samples were exposed to the simulated coal gasifying atmosphere for 20 h at temperatures ranging from 1200 K to 1600 K at 100 K intervals. Individual gas composition to be combined in a glass tube prior to entering the test furnace. A gas flow was maintained throughout an exposure. Following exposure, samples were removed from the furnace and stored in a desiccator to prevent reaction with air prior to sample evaluation. The samples were examined by XRD to determine the phases present and reaction products in the refractories. In addition, EDAX and SEM were used to determine the alkali distribution in the exposed specimens.

III. Results and Discussion

1. Alkali-refractory reaction products

Phase identification results, both experimentally determined and theoretically calculated, in the alumina-chromia refractory following reaction with alkali (Na and K) are given in Tables 1 and 2 for sodium and potassium, respectively. Following experiments at 1200 K, only the primary phase (Al, Cr)$_2O_3$(ss) was detected by XRD. Apparently the 1200K heat treatment was not sufficient to form $Na_2O \cdot Al_2O_3/Na_2O \cdot 11Al_2O_3$ or $K_2O \cdot Al_2O_3/K_2O \cdot 11Al_2O_3$ even though the theoretical calculations and the phase diagrams suggest that $Na_2O \cdot Al_2O_3/Na_2O \cdot 11Al_2O_3$ or $K_2O \cdot Al_2O_3/K_2O \cdot 11Al_2O_3$ are stable phases at this

Table 1. Alumina-Chromia Refractory-Sodium Phases

Temp.(K)	Calculated	Experimentally Observed
1200K	$(Al,Cr)_2O_3(ss)$, NA_{11}, $NA^{\dagger}$	$(Al, Cr)_2O(ss)$
1300K	$(Al,Cr)_2O_3(ss)$, NA_{11}, NA	$(Al,Cr)_2O_3(ss)$, NA_{11}, NA, NC^{*}
1400K	$(Al,Cr)_2O_3(ss)$, NA_{11}, NA	$(Al,Cr)_2O_3(ss)$, NA_{11}, NA, NC
1500K	$(Al,Cr)_2O_3(ss)$, NA_{11}, NA	$(Al,Cr)_2O_3(ss)$, NA_{11}, NA, NC
1600K	$(Al,Cr)_2O_3(ss)$, NA_{11}	$(Al,Cr)_2O_3(ss)$, NA_{11}, NA, NC

†Conventional cement chemistry notationn used
$N=Na_2O$
$K=K_2O$
$A=Al_2O_3$
$C=Cr_2O_3$
*Metastable phase

Table 2. Alumina-Chromia Refractory-Potassium Phases

Temp.(K)	Calculated	Experimentally Observed
1200K	$(Al,Cr)_2O_3(ss)$, KA_{11}, KA	$(Al,Cr)_2O_3(ss)$
1300K	$(Al,Cr)_2O_3(ss)$, KA_{11}, KA	$(Al,Cr)_2O_3(ss)$, KA_{11}, KA
1400K	$(Al,Cr)_2O_3(ss)$, KA_{11}, KA	$(Al,Cr)_2O_3(ss)$, KA_{11}, KA
1500K	$(Al,Cr)_2O_3(ss)$, KA_{11}, KA	$(Al,Cr)_2O_3(ss)$, KA_{11}, KA
1600K	$(Al,Cr)_2O_3(ss)$, KA_{11}, KA	$(Al,Cr)_2O_3(ss)$, KA_{11}, KA

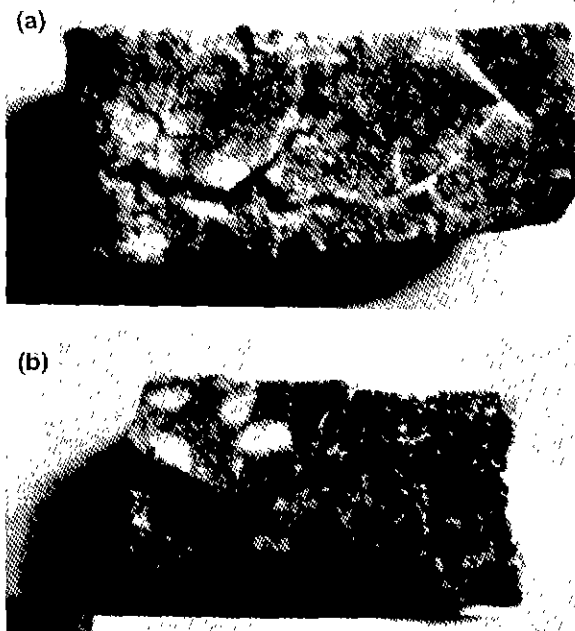**Fig. 3.** Deformed specimens after exposure to (a) Na and (b) K vapor at 1600K for 20h in the coal gasification atmosphere.
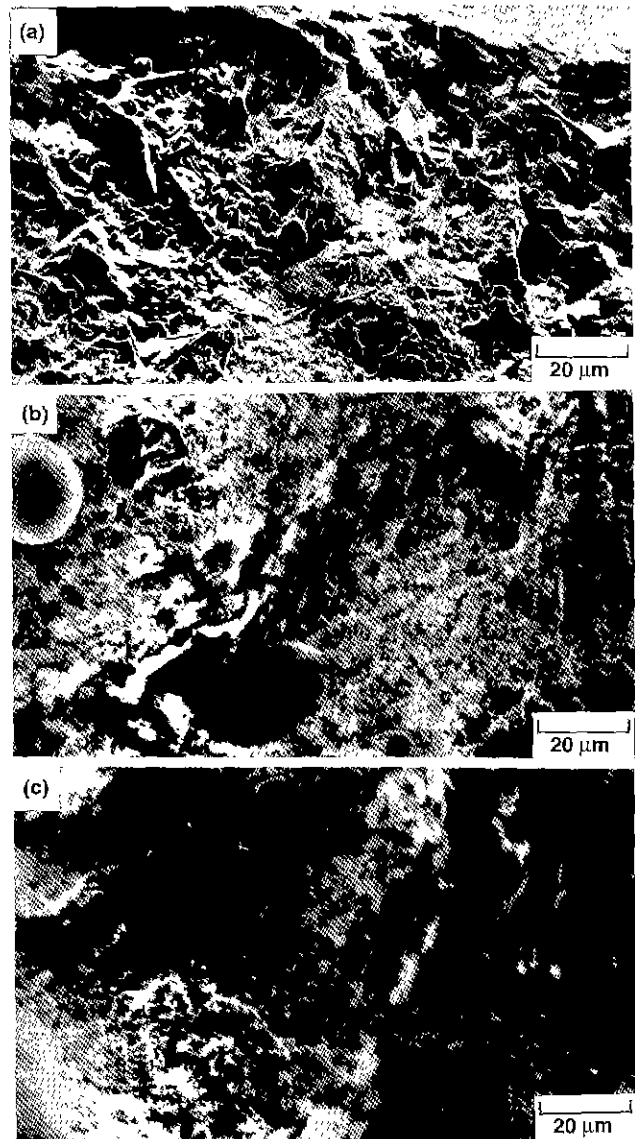

Fig. 4. Surface morphologies of the (a) green specimen, (b) corroded specimen after exposure to Na vapor, and (c) corroded specimen after exposure to K vapor at 1600K for 20h.

temperature. From 1300 K to 1600 K, $Na_2O \cdot Al_2O_3/Na_2O \cdot 11Al_2O_3$ or $K_2O \cdot Al_2O_3/K_2O \cdot 11Al_2O_3$ were observed experimentally as the equilibrium phases; these observations agree with the theoretical calculation. When sodium was present as an alkali impurity, sodium chromate $(NaCrO_2)$ was found to be a metastable phase. When the refractory sample and either Na_2CO_3 or K_2CO_3 were introduced into the furnace, their weight were

equal. Howere, the actual ratio of $Al_2O_3 : Na_2O/K_2O$ was in between $1:1{\sim}1:9$ because of the volatilities of sodium carbonate and potassium carbonate. In the sodium case, it appeared that $Na_2O \cdot Al_2O_3$ more prevalent than $Na_2O \cdot 11Al_2O_3$. On the other hand, $K_2O \cdot 11Al_2O_3$ is the dominant alkali compound in the potassium case. This results are confirmed later in the study of sodium and potassium distributions in the refractory.

After reacting with alkali, the refractory samples suffered serious deformation, especially in sodium reaction case. Macro-and microstructure of the deformed samplses after exposute to alkali at 1600 K are shown in Fig. 3 and Fig. 4, respectively. This phenomenon results from chemical spalling due to the different thermal expansion behaviors and lower densities of the alkali compounds formed when compared to the matrix phase.

Table 3. Alumina-Chromia Refractory-Sodium-Sulfur Phases

Temp.(K)	Calculated	Experimentally Observed
1200K	$(Al,Cr)_2O_3(ss)$, NA_{11}, NA	$(Al,Cr)_2O_3(ss)$
1300K	$(Al,Cr)_2O_3(ss)$, NA_{11}, NA	$(Al,Cr)_2O_3(ss)$, NA_{11}, NA, NA_5,[*] NA_7[*]
1400K	$(Al,Cr)_2O_3(ss)$, NA_{11}, NA	$(Al,Cr)_2O_3(ss)$, NA_{11}, NA, NA_5, NA_7
1500K	$(Al,Cr)_2O_3(ss)$, NA_{11}, NA	$(Al,Cr)_2O_3(ss)$, NA_{11}, NA, NA_5, NA_7
1600K	$(Al,Cr)_2O_3(ss)$, NA_{11}	$(Al,Cr)_2O_3(ss)$, NA_{11}, NA, NA_5, NA_7

Table 4. Alumina-Chromia Refractory-Potassium-Sulfur Phases

Temp.(K)	Calculated	Experimentally Observed
1200K	$(Al,Cr)_2O_3(ss)$, KA_{11}, KA	$(Al,Cr)_2O_3(ss)$
1300K	$(Al,Cr)_2O_3(ss)$, KA_{11}, KA	$(Al,Cr)_2O_3(ss)$, KA_{11}, KA, KA_5[*]
1400K	$(Al,Cr)_2O_3(ss)$, KA_{11}, KA	$(Al,Cr)_2O_3(ss)$, KA_{11}, KA_5
1500K	$(Al,Cr)_2O_3(ss)$, KA_{11}, KA	$(Al,Cr)_2O_3(ss)$, KA_{11}, KA_5
1600K	$(Al,Cr)_2O_3(ss)$, KA_{11}, KA	$(Al,Cr)_2O_3(ss)$, KA_{11}, KA_5

2. Alkali-sulfur-refractory reaction products

Phase identification results (Table 3 and Table 4), both experimentally determined and theoretically calculated, for the alumina-chromia refractory following reaciton with alkali (Na or K) and sulfur indicate that the presence of sulfur in the vapor does not affect the phases that form. The experimental results show the formation of sodium aluminate and β-alumina and the potassium analogues. However, during the identification of the reaction compounds, small amounts of β″-aluminas ($Na_2O \cdot 5Al_2O_3$, $Na_2O \cdot 7Al_2O_3$, and K_2O $5Al_2O_5$) were detected. These compounds are possibly metastable phases[11-14] which may be related to sample cooling rate, annealing time, and alkali concentration. These compounds did not appear in the alkali-refractory reaction. Other than the β″-alumina phases, the results agree with the calculated reaction products. Based on these results, the 90% alumina-10% chromia refractory appears to be very resistant to corrosion by sulfur.

3. Distributions of Na/k in the refractory

To determined the extent of alkali corrosion depth into the refractory, concentration profiles for alkali through the center of the sample were measured using the EDAX mode of an SEM. Fig. 5(a) and (b) show the Na and K concentrations in the test samples as a function of time and distance from the reaction surface at the given temperature of 1600K. Alkali concentration (i.e., corrosion depth) was observed to decrease nonlinearly with increasing exposure time. It is also evident that sodium has higher corrosion depth than potassium at a given
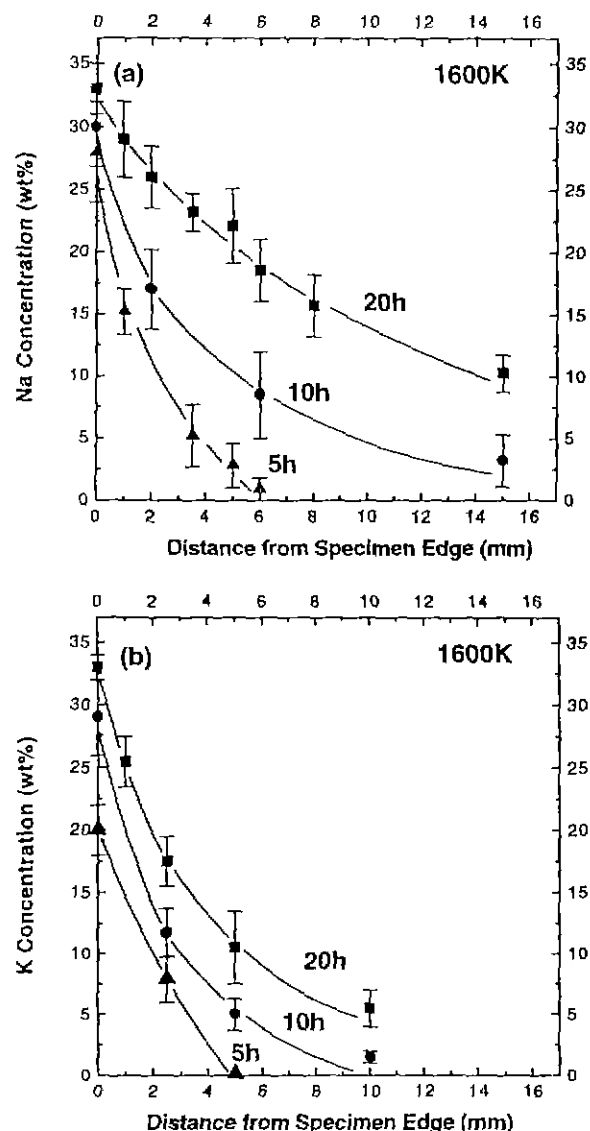
Fig. 5. (a)Na and (b)K concentration profiles of alumina-chromia refractory after test times/temperature indicated.

temperature and time.

It is interesting to consder the physical effects of alkali corrosion of a refractory in view of the lower densities of the reaction products formed. The relationship between sodium concentration, phases present, and volume changes in an alumina-chrome refractory following exposure to alkali vapor is schematically illustrated in Fig. 6(a), (b), and (c), respectively. The refractory sample (Fig. 6(c)) exhibits considerable volume expansion where the alkali concentration (Fig. 6(a)) is high. The Na_2O-Al_2O_3 phase diagram (Fig. 6(b))[14] indicates that high alkali concentrations cause the formation of $Na_2O \cdot Al_2O_3$ which, due to its low density, cause substantial, irreversible volume expansion in the sample. Moderate alkali concentrations cause the formation of β-alumina phases and only moderate expansion occurs since their densities are not as low as that of $Na_2O \cdot Al_2O_3$.
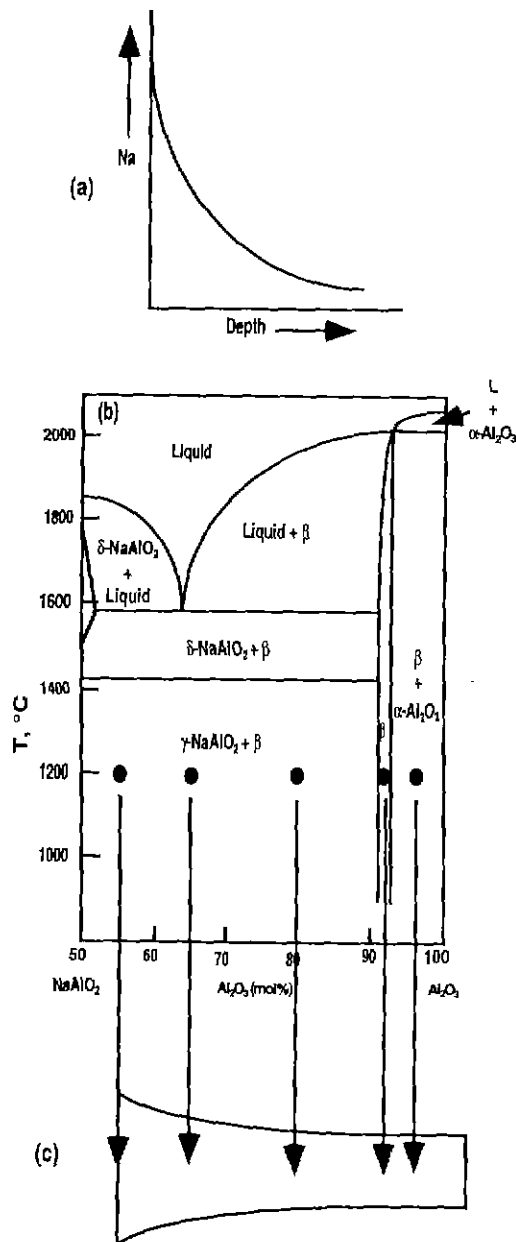
Fig. 6. Illustration showing relationship between (a) Na concentration, (b) phase present, and (c) volume change in an alumina-chromia refractory.

The schematic illustration shown in Fig. 6 is also useful in understanding the chemical-mechanical changes that occur in an alumina-chromia refractory in service in an alkali environment. The hot face of the refractory will have high alkali content and this will cause incipient melting of the hot face due to alkali fluxing. In addition, different thermal expansion of the bulk and the surface alkali compounds will result in surface stresses which will promote mechanical spalling and cause poor thermal shock resistance as the temperature changed. The alkali attack can also result in surface washout of the refractory by dissolution of alkali compounds.

IV. Conclusions

Reaction of sodium and potassium vapors with an alumina-chromia refractory results in the formation of $Na_2O \cdot Al_2O_3$, $Na_2O \cdot 11Al_2O_3$, or $K_2O \cdot Al_2O_3$, $K_2O \cdot 11Al_2O_3$; the metastable compounds $Na_2O \cdot Cr_2O_3$, $Na_2O \cdot 5Al_2O_3$, $Na_2O \cdot 7Al_2O_3$, or K_2O $5Al_2O_3$ may also form.

Alkali reactions with the alumina-chromia refractories cause serious chemical spalling at the hot face of the refractory proving that the alkali concentration is significant. potassium may cause more distructive attack than sodium near the hot face because potassium aluminate has a higher thermal expansion coefficient than the sodium analogue. However, a layer of hot face washout by dissolution of the alkali compounds may be grater when sodium is present because sodium penetrates the alumina-chromia refractory more deeply than potassium.

References

1. L. Y. Sadler. III, H. Heystek, N. S. Raymon and T. A. Clancy, "Refractores for Dry-Ash Coal Gasifiers," BuMines RI 8913 (1984).
2. C. R. Kennedy, Compatibility of Water-Cooled Refractories with a Basic Coal-Ash Slag at 1500°C,' *J. Mater. Energy Syst.*, **2**, 11-20 (1980)
3. C. R. Kennedy and R. B. Poeppel, "Corrosion Resistance of Refractories Exposed to Molten Acidic Coal-Ash Slag," *Interceram.*, **27**[3], 221-226 (1978).
4. E. R. Begley, "Critical Phenomena in the Use of Refractories in Contact with Glass," *Glass*, **55**, 335-340 (1978).
5. S. Mindess and J. F. Young, "Concrete," Prentice-Hall, New York (1981).
6. R. E. Farris and J. E. Allen, "Aluminous Refractories-Alkali Reactions," *Iron and Steel Engineer*, **50**[2], 67-74 (1973).
7. J. H. Chesters, "Refractories for Iron and Steelmaking," The Metals Society, London (1974).
8. C. R. kennedy, "Alkali Attack on a Mullite Refractory in the Grand Forks Energy Technology Center Slagging Gasifier," *J. Mater. Energy Syst.*, **3**[3], 27-31 (1981).
9. K. H. Lee and J. J. Brown, "Corrosion of Alumina-Chromia Refractories by Alkali Vapors : I Thermodynamic Approach," *Kor. J. of Ceram.*, **1**[1], 29-34 (1995).
10. H. M. Ondik, B. W. Christ and A. Pereoff, "Construction Materials for Coal Corrosion, Performance, and Properties Data," NBS Special Publication, 642 (1982).
11. J. S. Moya, E. Criado and S. DeAza, "The $K_2O \cdot Al_2O_3$ System," *J. Mat. Sci.*, **17**, 2213-2217 (1982).
12. J. D. Hodge, "Kinetic of the β″ Transformation in the System Na_2O-Al_2O_3," *J Am. Ceram. Soc.*, **66**[3], 166-169 (1983).
13 Y. LeCars, J. Thery and R, Collongues, "Range of Existance and Stability of β and β″ Aluminas in the System Al_2O_3-Na_2O," *Rev. Int. Hautes Temp. Refract.*, **9**[1] 153-160 (1972).
14. N. Wever and A. F. Venero, "Revision of the Phase Diagram $NaAlO_2$-Al_2O_3," *Am, Ceram. Soc. Bull.*, **49**[4], 491 (1970).