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THERMOCHEMISTRY OF ALKALI INTERACTIONS WITH REFRACTORY ADSORBENTS

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ABSTRACT

The kinetics and mechanism of interactions between alkali vapors and several refractory adsorbents are studied. A unique thermogravimetric reactor is designed and utilized for this study. Bauxite and kaolin are very good adsorbents for alkali chlorides and are potentially good additives for control of alkali during coal combustion and gasification. The experimental data shows that the alkali capturing process is a combination of physisorption, chemisorption and chemical reaction. An analytical model is developed assuming a multi-layer adsorption of alkali on substrate followed by a rate-controlling reaction on the surface. The experimental results and model predictions are in good agreement.

INTRODUCTION

Adsorption and reaction of alkali vapors on ceramics and refractory compounds are important in a number of applications and situations including the following: (i) control of degradation of ceramics at high temperatures in environments where alkali compounds are present, (ii) minimizing corrosion caused by alkali in coal combustors and gasifiers and power generation turbines, (iii) removal of alkali from products of coal combustion and gasification.

The subject of vaporization and condensation of alkali has received considerable attention in recent years. One objective of this study is to explore the feasibility of using additives for removing alkali vapors released during coal combustion and gasification. The additives are expected to control the fate of alkali compounds through two actions: (i) providing additional surface area for adsorption and capture of alkali vapors, (ii) capturing and fixing alkali vapor through chemical reactions. Most of the available experimental and theoretical studies have concentrated on the first action which is the physical interactions of alkali condensation on additive

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particles The second action (chemical fixation) is more complex, less understood and not exploited to its full potential

In recent years, there have been some studies of the fundamentals of alkali adsorption on various substrates [1–6] However, there is no agreement in the literature on the nature and mechanism of adsorption Lee and Johnson [2] studied the adsorption of NaCl, KCl and K_2SO_4 on a number of substrates including bauxite, silica and diatomaceous earth They proposed chemical fixation on silica and physical adsorption on bauxite They also found activated bauxite to be a very efficient adsorbent In another study, Lee et al [3] reported that the adsorption of alkali on activated bauxite was only partially reversible Luthra and LeBlanc [4] measured the extent of adsorption of KCl and NaCl on bauxite under different temperatures and oxygen concentrations Their results indicated non-preferential physical adsorption of both compounds on alumina and activated bauxite Bachovchin et al [1] compared a number of additives including emathlite which was found to be a very suitable adsorbent at temperatures below 900 °C The getter effect was explained as a reaction with the adsorbent controlled by diffusion of alkali through a layer of reaction product around the emathlite particles In addition to the discrepancies in the proposed mechanisms, the available information is generally on the equilibrium characteristics of adsorption, there has been very little work on the kinetics of adsorption The specific objective of this work is to understand the mechanism and kinetics of thermochemical interactions between alkali vapors and refractory substrates

EXPERIMENTAL APPROACH

The experiments were carried out in a special microgravimetric reactor designed for this study. A flow diagram of the apparatus is shown in Fig 1 Nitrogen was used as the carrier gas for the alkali vapor in all experiments The substrate of interest or the alkali metal source, depending on the experiment, was put in a platinum pan suspended from a microbalance (Cahn Model 2000) A quartz reactor was used to contain the alkali vapor source and the adsorbent Nitrogen was used to purge the balance assembly, act as a carrier for the alkali vapor and provide dilution to obtain a desired alkali concentration The furnace allowed either rapid heating/cooling or temperature programmed studies in the reactor A gas chromatograph was incorporated in the exhaust line to examine product gases and detect oxygen leaks. Details of the reactor configuration for each set of tests are shown in Fig 2

The experimental study was divided into two parts The first set of tests involved screening various model compounds and commercially available substrates for potential use as alkali adsorbents The second set of tests were

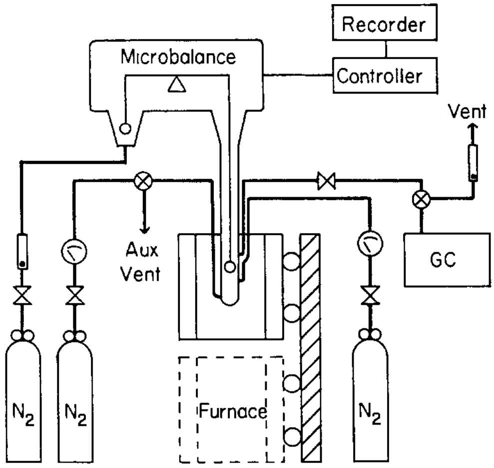

Fig 1 Schematic diagram of the apparatus

designed to probe the adsorption/desorption kinetics of the most promising adsorbent determined in the first set of tests

Screening of adsorbents

For the screening runs, the configuration 2(a) shown in Fig 2 was used The carrier gas was nitrogen supplied from the top of the reactor, and the alkali source was put in a platinum foil pan. The adsorbent was placed in a quartz insert and suspended by a stainless steel 100 mesh screen The purpose of the insert is to allow easy loading and unloading of the adsorbent as well as prevent excessive devitrification of the reactor itself The flow of nitrogen allowed vapor phase transport of the alkali through the adsorbent bed and out the exhaust The amount of alkali vaporized was measured as a weight change by the microbalance

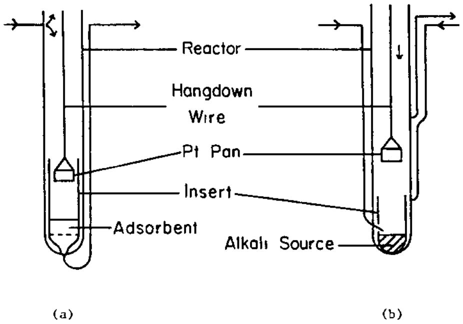

Fig 2 Schematic details of the reactor configuration (a) for screening experiments and configuration (b) for adsorption kinetics measurements

The adsorbents tested were model compounds such as silica, alumina and graphite as well as commercially available substrates such as calcined limestone and bauxite The adsorption capabilities of a Utah bituminous ash collected from the bottom of one of our coal combustion furnaces was also examined, mainly to gain some insight into the chemical interactions of alkali chlorides and ash The speed of gas flow was maintained at 1 4 cm s^{-1} and the volume of the adsorbent bed was held constant at 0.625 cm^3, resulting in a gas residence time of 1/3 s The alkali sources used were NaCl and KCl For each run the amount of alkali delivered to the adsorbent was approximately 22 mg All screening runs were made at 850 °C with 60–80 mesh adsorbent particles

In each experiment, the adsorption was initiated by first starting the nitrogen flow and then raising the furnace The temperature reached steady state in about 5 min The adsorptions was quenched by lowering the furnace The percentage of alkali retained by the adsorbent was determined by taking the difference between the amount of alkali delivered and the alkali content of the adsorbent after the run

Fundamentals of alkali adsorption

The second set of tests were all performed using NaCl as the alkali source In this case, 45 to 50 mesh adsorbent particles were placed on a 80 mesh platinum pan suspended from the microbalance and the alkali source was put in the bottom of a quartz insert (configuration (b) in Fig 2) Nitrogen was passed over the alkali source to vaporize and transport it toward the adsorbent A second nitrogen line near the top of the insert was used to dilute the nitrogen to a desired concentration, after which the diluted vapor passed over the adsorbent A short distance above the pan, the diluted vapor then mixed with nitrogen coming down from the microbalance and went out an exhaust tube The reason for having the exhaust at this point rather than near the top of the reactor was to prevent condensation of alkali chloride on the balance hangdown wire in the cooler portion of the furnace Thermocouples were placed on the outside of the reactor near the alkali source and the adsorbent to monitor the temperature of each throughout the course of the experiment Adsorbent weight was monitored as a function of time with the microbalance

All runs made in this set of tests were at an adsorbent temperature of 800 °C The net flow to the adsorbent bed was maintained at 150 standard cubic centimeters and the alkali concentration was 177 ppm Na by weight unless otherwise specified The sodium concentrations were calculated by assuming equilibrium between the nitrogen and NaCl source Data from JANAF Tables [7] were used to calculate the equilibrium alkali concentrations

A typical run was started by first closing off the normal exhaust and allowing the microbalance purge nitrogen to flow in the reverse direction over the adsorbent and alkali source and then out the auxiliary vent (see Fig 1). The furnace was then raised and time allowed for the temperature and adsorbent weight to stabilize, this usually took about 1 h To initiate adsorption, the normal vent was opened and the auxiliary vent was closed. Adsorption was allowed to continue until a given mass of alkali had condensed on the adsorbent, at which time the flow was again reversed to "turn off" the alkali source and allow desorption for a given period The process was quenched by lowering the furnace.

EXPERIMENTAL RESULTS

The screening test results are shown in Figs 3 and 4 The most obvious feature of these results is the difference in ability of the adsorbents tested to capture the alkali chloride passing through them Alumina and activated bauxite captured the most while silica, graphite and limestone captured only a small percentage of the alkali chlorides It was rather surprising that the Utah bituminous ash was able to capture such a large percentage of KCl This can probably be explained by the fact that Utah bituminous coal contains relatively little potassium to begin with and these tests were performed at a temperature considerably lower than that at which the ash was formed Since the chemistry of ash is rather complicated, the KCl may be bound by physical and/or chemical fixation It is interesting to note that every substrate was able to capture a larger percentage of the KCl than the NaCl The reason for this is not clear at this point Based on these results, it

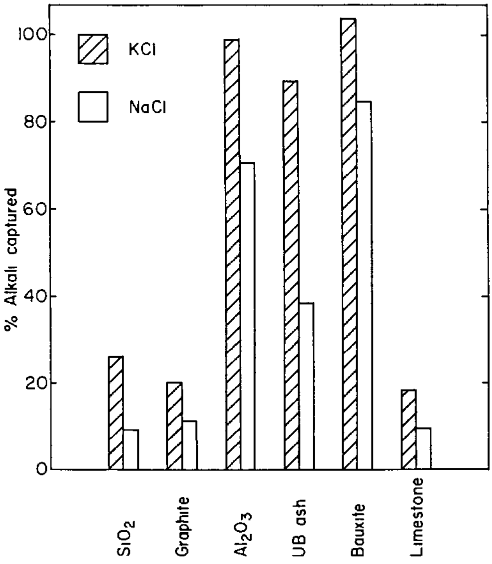

Fig 3 Comparison of alkali removal by various substrates

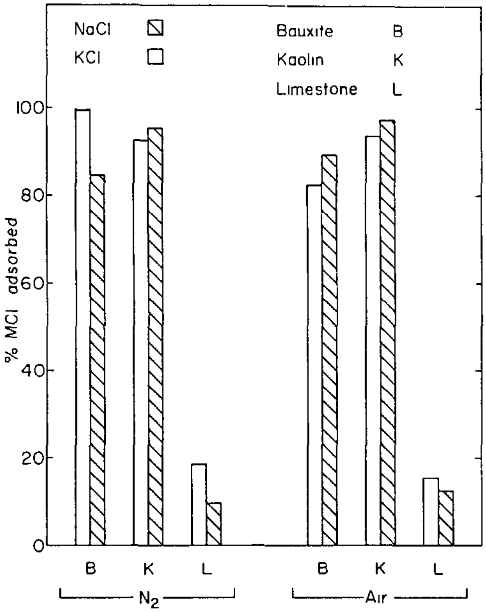

Fig 4 Comparison of bauxite, kaolin and lime as alkali adsorbents

was decided to investigate the adsorption properties of activated bauxite in more detail

A weight gain profile for activated bauxite is shown in Fig. 5. In this experiment about 240 mg of bauxite was used This data shows that the initial weight gain is rather rapid, but after 10 hours it slows considerably.

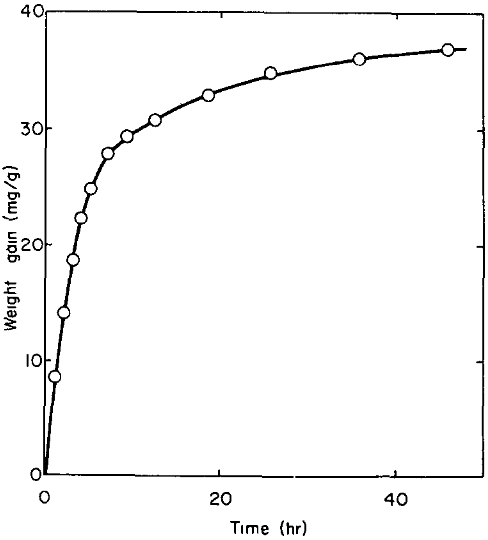

Fig 5 Temporal profile of NaCl adsorption on bauxite

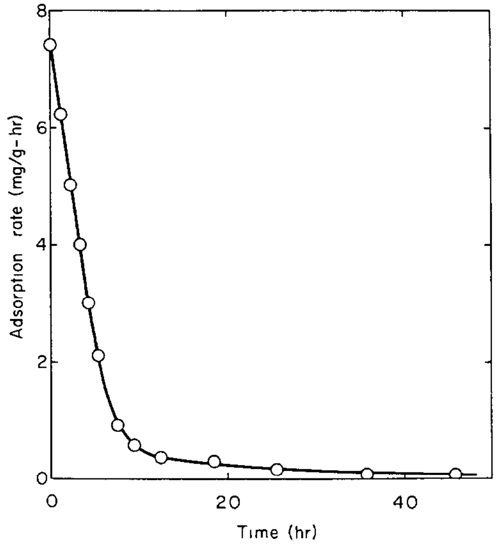

Fig 6 Adsorption rate of NaCl on bauxite

Although the bauxite is able to adsorb a considerable amount of NaCl, the time required is rather long The derivative of this plot, rate of adsorption as a function of time, is given in Fig 6 As expected from the previous Figure, rate begins rather high but decreases rapidly toward zero Although not shown, a similar set of data was collected for alumina In this run the concentration of NaCl was abruptly reduced to zero after 50 hours to observe the desorption profile The initial desorption was rapid, but after 20 hours the weight appeared to be approaching a constant value After 20 more hours (total run time of 90 h) it was quite evident that the weight was approaching an asymptote that was about half the maximum weight observed prior to desorption The data of Luthra and LeBlanc [4] show this behavior as well This suggests that at least some of the NaCl was chemically bound to the surface of the alumina

THEORETICAL MODELING

Based on the results obtained thus far and the results of other investigators [1–4,6] NaCl appears to adsorb on alumina and activated bauxite both chemically and physically. Adsorption of the physically adsorbed NaCl is reversible, while adsorption of the chemically adsorbed NaCl is irreversible. Thus a formulation used to describe the adsorption/desorption kinetics should incorporate both chemical and physical adsorption It should also allow for multilayer adsorption, since this phenomenon was observed as well

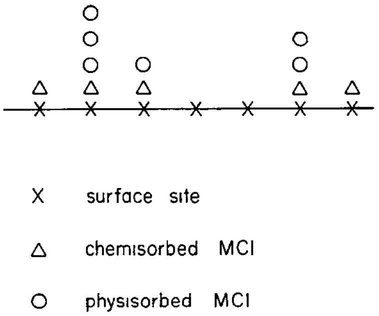

Fig 7 Model for adsorption of alkali chlorides on adsorbent surfaces

In the proposed model, it is assumed that the alkali interaction consists of chemical adsorption in the first layer followed by physical adsorption for all succeeding layers The surface can then be pictured as shown in Fig 7 after some adsorption has taken place Some sites will be unoccupied, some will have chemisorbed alkali (one layer) and others will have physisorbed alkali on top of the chemisorbed alkali (two or more layers) The relevant reactions are

$$\mathrm{M} + \mathrm{X} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{MX} \xrightarrow{k_2} \mathrm{M}_1 \tag{1}$$

$$\mathrm{M}_1 + \mathrm{M} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \mathrm{M}_2 \tag{2}$$

$$\mathrm{M}_2 + \mathrm{M} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \mathrm{M}_3 \tag{3}$$

or in general

$$M_i + \mathrm{M} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} M_{i+1} \tag{4}$$

where M represents the vapor phase alkali, X represents an empty surface site, MX is an activated complex and M_i is the number of sites occupied by i alkali molecules stacked on one another This means that M_1 is the chemisorbed alkali and all succeeding M species are physisorbed.

Other assumptions of this model are that the heat of adsorption for all physisorbed alkali molecules is the same, regardless of how many alkali molecules are below it The chemisorption of M is assumed to be rate-controlling, with all other reactions at equilibrium By making a pseudo steady-state approximation for the concentration of activated complex (concentration of MX is very low and does not change with time) the concentration of empty sites as a function of time is found to follow a first-order expression

$$X = X_0 \exp(-bMt) \tag{5}$$

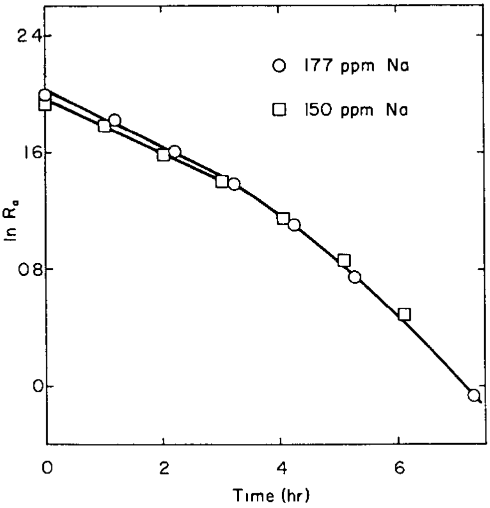

Fig 8 Adsorption rate of NaCl on bauxite

where X_0 is the number of sites at $t = 0$, M is the concentration of alkali in the gas phase and b is a combination of rate constants given by

$$b = \frac{k_1 k_2}{k_{-1} + k_2} \tag{6}$$

Then, by the definition of M_i, the total amount of adsorbed alkali at any time t is given by

$$Z = M_1 + 2M_2 + 3M_3 + \cdot \quad = \sum_{i=1}^{\infty} iM_i \tag{7}$$

From the equilibrium assumption of reaction (4), it follows that

$$M_{i+1} = K_3 M M_i = aM_i \tag{8}$$

where K_3 is the equilibrium constant for reaction (4) and $a = K_3 M$

After some mathematical manipulations of the above equations, the rate of adsorption is obtained

$$R_a = \frac{\mathrm{d}Z}{\mathrm{d}t} = \left(\frac{bMX_0}{1 - K_3 M}\right) \exp(-bMt) \tag{9}$$

This suggests that a plot of the natural log of rate as a function of time should be linear This plot is shown in Fig 8 The linearity is observed for $t < 3$ 5 h, but deviates toward slower rates for $t > 3$ 5 h. Other rate-limiting processes could be occurring after this point such as pore plugging by the alkali chloride

By letting $t = 0$ in eqn (9), an expression for the initial adsorption rate results

$$R_a^0 = \frac{bMX_0}{1 - K_3 M} \tag{10}$$

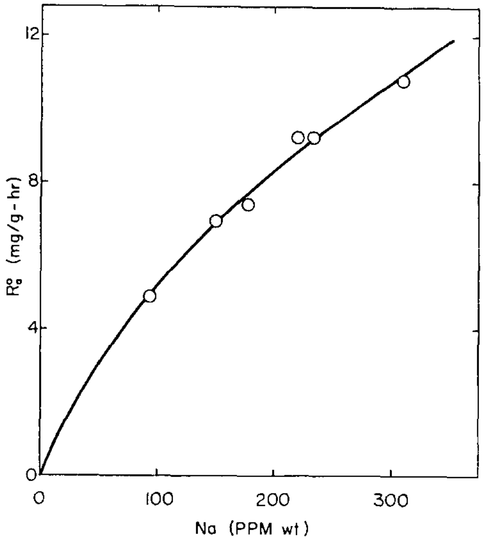

Fig 9 Effect of alkali vapor concentration on the initial adsorption rate

A plot of the initial adsorption rate as a function of vapor phase alkali concentration is shown in Fig 9

A model for the desorption of alkali from a surface predicted by the previous model for adsorption after some time t can be derived In this case, desorption will proceed according to the mechanism

$$M_2 \xrightarrow{k_{-3}} M_1 + M \tag{11}$$

$$M_3 \xrightarrow{k_{-3}} M_2 + M \tag{12}$$

or in general

$$M_{i+1} \xrightarrow{k_{-3}} M_i + M \tag{13}$$

and the rate of desorption can be expressed as

$$R_d = \sum_{i=2}^{\infty} i \frac{\mathrm{d}M_i}{\mathrm{d}t} \tag{14}$$

Using an approach similar to that used for adsorption gives the following expression for the initial rate of desorption

$$R_d^0 = -k_3 a M_1^0 \left(\frac{2-a}{1-a}\right) \tag{15}$$

Since M_1^0 is a function of both a and the total time of adsorption, R_d is

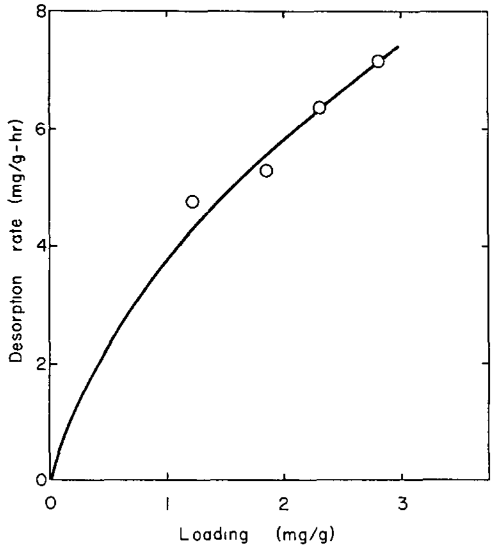

Fig 10 Effect of alkali loading on the desorption rate

dependent on both parameters The initial rate of desorption for several runs is shown in Fig 10

CONCLUSIONS

The experimental results of this study indicate that the interaction between alkali compounds and the refractory adsorbents is a combination of physisorption, chemisorption and reaction The adsorption of the first molecular layer is chemisorption and is irreversible The adsorption on other layers is reversible physisorption Bauxite and kaolin appear to be suitable adsorbents for removing alkali species in combustion environments A model is presented to illustrate the thermochemistry of alkali adsorbent interactions This model incorporates physisorption, chemisorption and chemical reaction, the theoretical predictions agree with experimental results

ACKNOWLEDGMENT

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LIST OF SYMBOLS

a	K_3M
b	parameter defined by eqn 6
k_j	rate coefficient for reaction j
K_3	equilibrium constant for reaction (4)
M_i	total amount of adsorbed alkali in layer i
M_1^0	amount of alkali on the first layer at the beginning of desorption
MX	intermediate compound in reaction (1)
R_a	rate of adsorption of alkali
R_a^0	initial rate of alkali adsorption
R_d	rate of alkali desorption
R_d^0	initial rate of alkali desorption
t	time
X	number of empty adsorption sites
X_0	initial number of adsorption sites
Z	total amount of alkali adsorbed

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