

CONTROL OF ASH DEPOSITION THROUGH THE HIGH TEMPERATURE ADSORPTION OF ALKALI VAPORS ON SOLID SORBENTS

Wayne A. Punjak, Mohit Uberoi and Farhang Shadman
Department of Chemical Engineering
University of Arizona
Tucson, AZ 85715

INTRODUCTION

Coal usually contains sodium and potassium minerals in various chemical and physical forms. During the combustion or gasification of coal, much of this alkali is released into the gas phase. This vapor is usually in the form of alkali chlorides. In the presence of sulfur, alkali sulfates are also formed. This alkali condenses on and reacts with ash to form low melting point phases that enhance fouling¹.

Cleaning of coal removes some of the alkali but is not effective enough to decrease the alkali concentration to acceptable levels. A promising technique for the removal of alkali from hot flue gases is by using materials (sorbents) that will adsorb and/or react with alkali vapors. In general, the sorbents can be used in two ways. One method is by passing the alkali-laden flue gas through a fixed bed of an appropriate sorbent. This process has been considered for alkali removal from flue gases in the combined-cycle power generation from coal^{2,3,4}. The second method is the injection of sorbents with coal for the in-situ capturing of alkali during pulverized coal combustion. This method has received much less attention⁵.

The choice of a suitable sorbent depends on the coal properties and the process operating conditions. In general, however, the important characteristics desired in a potential sorbent are high temperature compatibility, rapid rate of adsorption, high loading capacity, transformation of the alkali into a less corrosive form and irreversible adsorption to prevent the release of adsorbed alkali during process fluctuations.

Previous studies in this laboratory^{6,7} and those of other investigators^{2,3,4,8} have suggested that bauxite, kaolinite and emathlite are promising alkali vapor sorbents. The purpose of this study is to obtain fundamental information on the kinetics and the mechanism of alkali adsorption on these sorbents.

EXPERIMENTAL APPROACH

The composition of the sorbents used in this study are given in Table 1. These sorbents were used in the form of thin flakes with the approximate thickness of 0.5 mm. The flakes were devolatilized and then stored under vacuum until used.

The apparatus used in the sorption experiments consisted of a tubular quartz reactor, an electronic microbalance and a movable electric furnace. A detailed description of this system is given elsewhere^{6,9}. The experiments were performed in two groups. The first set of tests were made at a sorbent temperature of 800°C under a flowing simulated flue gas (SFG) atmosphere. The composition of the SFG was 80% N₂, 15% CO₂, 3% O₂ and 2% H₂O with a flowrate of 150 or 200 scfm, depending on the experiment involved. Crystalline NaCl was used as the alkali source. The alkali vapor concentration was varied between 50 and 230 ppmv, well below saturation to avoid physical condensation.

In these experiments, sorbent flakes were suspended from the microbalance directly above the alkali source which was placed in the bottom of the quartz reactor. The SFG was passed over the alkali source to vaporize and transport it toward the sorbent. A second SFG line, split from the first, entered the reactor a few cm above the first one and was used to dilute the alkali vapor to a desired concentration. A few cm above the sorbent the gases mixed with purging nitrogen coming down from the microbalance and went out an exhaust port. Thermocouples were placed on the outside of the reactor near the alkali source and the sorbent to monitor the temperature of each.

In the second set of tests the alkali source, either NaCl, KCl or K_2SO_4 , was allowed to saturate the simulated flue gas in the vicinity of the sorbent. The temperature in these experiments was varied from 750 to 1135°C. Thermodynamic calculations showed that for all of these experiments, essentially all of the alkali in the vapor phase remains in the form of the salt from which it was vaporized (i.e., NaCl, KCl or K_2SO_4).

EXPERIMENTAL RESULTS

Typical experimental weight gain profiles for the three sorbents tested in the first set of experiments are shown in Figure 1. The results indicate a decrease in adsorption rate with loading and a final alkali saturation limit. Bauxite is observed to have the highest initial rate, while kaolinite has the largest capacity. The effect of varying the alkali vapor concentration on the weight gain profiles for each sorbent was also tested. Typical profiles for kaolinite are shown in Figure 2. It can be seen that an increase in the alkali concentration results in an increase in the adsorption rate.

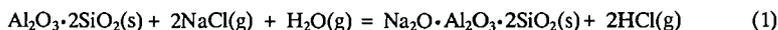
An important difference between the adsorption characteristics of the three sorbents is the reversibility of the adsorption process. After saturation, the reversibility of the alkali uptake was tested for each sorbent by reducing the alkali vapor concentration to zero. No desorption was observed for kaolinite and emathlite, but bauxite lost approximately 10% of its total initial weight gain. This suggests that the mechanism of adsorption is not the same for the three sorbents.

The fresh devolatilized and fully saturated sorbents were analyzed using various chemical analytical techniques to gain further insight into the mechanism of alkali sorption. Scanning Auger microscopy (SAM) was performed on the samples to determine elemental composition and alkali distribution. One important difference between the substrates revealed by these results is in the ratio of sodium to chlorine adsorbed. Chlorine, which has a peak at 176 eV, was not observed in the products of adsorption on emathlite and kaolinite. In contrast, chlorine was partially retained by bauxite.

The cross sections of partially converted samples were mapped for alkali using SAM to study the changes in the substrate during adsorption. The alkali content was observed to be largest near the outer edge of the flake, decreasing rapidly toward the flake center. Similar results were obtained for bauxite and emathlite, indicating that the sorption kinetics for all three sorbents are influenced by intraphase diffusion under the experimental conditions used. Additional details can be found in another publication¹³.

X-ray diffraction (XRD) spectra obtained for the sorbents prior to and after alkali adsorption indicate the formation of several reaction products. Kaolinite saturated with sodium from NaCl

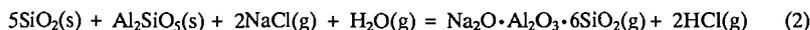
was found to contain primarily nephelite and carnegieite, sodium aluminosilicate polymorphs with the chemical formula $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. In nephelite, which is thermodynamically favored at high temperatures, the sodium cation is octahedrally coordinated and in carnegieite it is tetrahedrally coordinated¹⁰. Based on this information and the absence of chlorine in the adsorption product, the following reaction scheme is proposed:



where metakaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is the dehydration product of kaolinite. The stoichiometry of this reaction suggests a 27.9% increase in sample weight on complete conversion. This is very close to the observed 26.6%. In addition, the alkali uptake determined by atomic emission analysis is very close to that predicted by Reaction 1. Kaliophilite ($\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), the potassium analog of nephelite, was observed as the reaction product of KCl and K_2SO_4 with kaolinite. Other investigators^{10,11} also observed the formation of nephelite and kaliophilite when mixtures of sodium and potassium compounds, respectively, were heated with kaolinite to high temperatures. Due to the relatively high melting points of nephelite and kaliophilite, kaolinite would be a suitable sorbent for the in-situ capture of alkali at high temperatures. It is also an excellent choice for the downstream removal of alkali because of its high capacity.

The XRD spectra for the other sorbents indicate a more complicated process. The spectrum for as-received bauxite shows the presence of alpha-quartz, corundum and hematite. The XRD results for fully saturated bauxite indicate the formation of nephelite and carnegieite produced by a reaction similar to Reaction 1 in which NaCl was used as the alkali source. However, the amount of silica in bauxite is not sufficient for Reaction 1 to account for all the adsorbed alkali. Apparently, the rest of the alkali is present as glassy products or physisorbed chloride not detectable by XRD. Since chlorine is lost from the saturated bauxite during desorption, physisorbed NaCl might be the portion which is removed during the desorption experiments. The non-dissociative adsorption of alkali chlorides on alumina has been reported previously^{7,12}. Hematite, present both before and after adsorption, did not undergo any noticeable transformation.

The XRD results for emathlite show the presence of aluminosilicate (Al_2SiO_5), alpha quartz and cristobalite before adsorption. The sample fully saturated with sodium from NaCl consisted primarily of albite ($\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$) together with smaller amounts of sodium calcium aluminate ($\text{NaCa}_4\text{Al}_3\text{O}_9$). Therefore, much of the sodium capture by emathlite can be described by the following overall reaction:



Since albite has a relatively low melting point (1000°C), it is more suited to downstream alkali removal where the flue gas temperature is lower.

MATHEMATICAL MODEL

A mathematical model was formulated to describe the simultaneous physical and chemical processes that occur during alkali sorption by solid sorbents. A brief description of the model is given here. Additional details are given in another publication¹³. In this formulation the alkali

compound, A, diffuses through the porous sorbent and is then adsorbed upon contact with the sorbent surface. The adsorption process is a combination of physical adsorption and reaction, the details of which depend on the alkali and substrate. Assuming a quasi-steady state for diffusion and reaction in a porous particle, the conservation equation for alkali vapor can be written as follows:

$$\nabla \cdot D_e \nabla C_A = R_A \quad (3)$$

where R_A is the molar rate of adsorption of alkali per unit bulk volume of sorbent. The boundary conditions used to solve Equation 3 are a zero concentration gradient at the flake center and an equation of fluxes at the flake surface. The local alkali loading or alkali concentration in the solid phase, C_s , is given by the following conservation equation:

$$(1 - \epsilon_0) \frac{\partial C_s}{\partial t} = R_A \quad (4)$$

in which ϵ_0 is the initial porosity. The initial condition used to solve Equation 4 is $C_s = 0$ at $t = 0$. It is assumed that the local rate of adsorption is given by the following rate expression:

$$R_A = (1 - \epsilon_0) k C_A \left(1 - \frac{C_s}{C_{sf}}\right) \quad (5)$$

in which k is the overall rate coefficient and C_{sf} is the alkali concentration in the solid phase at sorbent saturation. In this formulation the porosity is allowed to vary with conversion. Equation 3 was solved numerically using a variable-step central-difference technique. Equation 4 was solved simultaneously to obtain the solid conversion. The overall loading at any time is obtained by integrating C_s over the sorbent volume.

The model was first used to extract intrinsic kinetic information from the weight gain profiles. The overall rate constant, k , for each sorbent was obtained by fitting the model to the initial rate data. These rate constants together with the other parameters were then used to predict weight gain profiles for the other three sorbents at different alkali concentrations. The profiles and model predictions for emathlite are given in Figure 5.

The values of the rate coefficients estimated from the model are given in Table 2. The difference in the rate coefficients shows that the adsorption process is not a physical and nonselective process, but rather a chemical process which depends on the chemical nature of the sorbent. Under the experimental conditions used, this model suggests that sorbent particles smaller than $50 \mu\text{m}$ must be used for interphase and intraphase diffusional resistances to have a negligible influence on the observed sorption kinetics.

Evaluation of the experiments performed under saturated vapor conditions was more complicated. The data for these experiments are given in Table 3. Although no desorption of alkali was observed for kaolinite in the previous set of experiments, it was possible to desorb a portion of the alkali in the saturated vapor experiments. This suggests that in addition to chemical reaction, alkali was physically condensing on the sorbent. This can be explained by the Kelvin effect which predicts that the alkali vapor was supersaturated in the sorbent pores under the experimental conditions used. The model described above does not consider the physical condensation of alkali and therefore can not be used to evaluate the data in these runs. This model is currently being modified to allow for the physical condensation and chemical reaction of alkali.

CONCLUSIONS

It was found that kaolinite, bauxite and emathlite are suitable sorbents for the removal of alkali vapors from hot flue gases. However, kaolinite and bauxite are more suitable than emathlite at temperatures above 1000°C. The rate of adsorption was observed to decrease with alkali loading and drop to zero when a final saturation limit is achieved. This saturation limit is the highest for kaolinite. The adsorption of alkali chloride on kaolinite and emathlite is irreversible with the release of chlorine back to the gas phase as HCl vapor. The adsorption on bauxite is partially reversible and a portion of the chlorine is retained. Under the experimental conditions used it was found that interphase and intraphase diffusional resistances influence the kinetics of the adsorption process. The proposed theoretical model agrees with the experimental data and can be used for design and parametric studies if the alkali vapor concentration is well below saturation levels. Near saturation, a model must be used that allows for the physical condensation of alkali and reaction with the sorbent.

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Table 1
Composition of As-received Sorbents

<u>Component</u>	<u>Bauxite¹</u> <u>(wt%)</u>	<u>Kaolinite²</u> <u>(wt%)</u>	<u>Emathlite³</u> <u>(wt%)</u>
SiO ₂	11.0	52.1	73.4
Al ₂ O ₃	84.2	44.9	13.9
Fe ₂ O ₃	4.8	0.8	3.4
TiO ₂	----	2.2	0.4
CaO	----	----	5.0
MgO	----	----	2.6
K ₂ O	----	----	1.2
Na ₂ O	----	----	0.1

1. Alcoa (Paranam)
2. Burgess Pigment Company
3. Mid-Florida Mining Company

Table 2
Overall Rate Coefficients

<u>Rate Constant (units)</u>	<u>Bauxite</u>	<u>Kaolinite</u>	<u>Emathlite</u>
k [cm ³ gas/(cm ³ solid - h)]	6.1 x 10 ⁷	2.1 x 10 ⁷	5.9 x 10 ⁷
k _s [cm ³ gas/(cm ² surface area - h)]	28	9.4	37

Table 3

Initial Rate Data for Saturated Vapor Runs

Alkali	Sorbent	Alkali Vapor T (°C)	Initial Concentration ppmv	Rate (h ⁻¹)
NaCl	kaolinite	750	130	0.0349
NaCl	kaolinite	795	400	0.363
NaCl	kaolinite	875	1690	0.418
K ₂ SO ₄	kaolinite	985	5.5	0.0044
K ₂ SO ₄	kaolinite	1060	25	0.0088
K ₂ SO ₄	kaolinite	1135	270	0.0160
K ₂ SO ₄	bauxite	985	5.5	0.0073
K ₂ SO ₄	bauxite	1060	25	0.0205
K ₂ SO ₄	bauxite	1135	270	0.0403

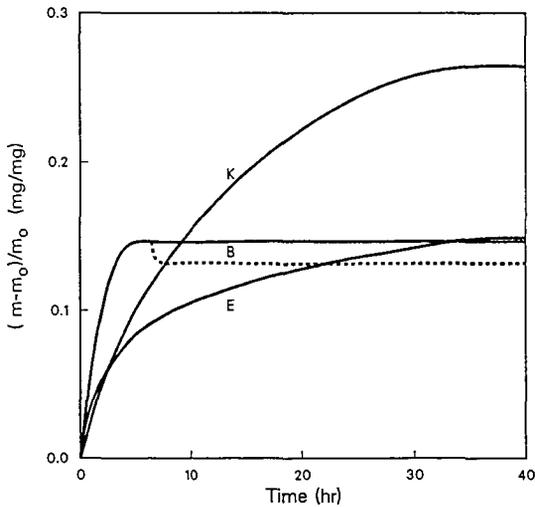


Figure 1. Temporal profile of NaCl adsorption on sorbents.
 K: kaolinite, 230 ppmv Na; B: bauxite, 185 ppmv Na;
 E: emathlite, 150 ppmv Na.

———— adsorption; - - - - - desorption.

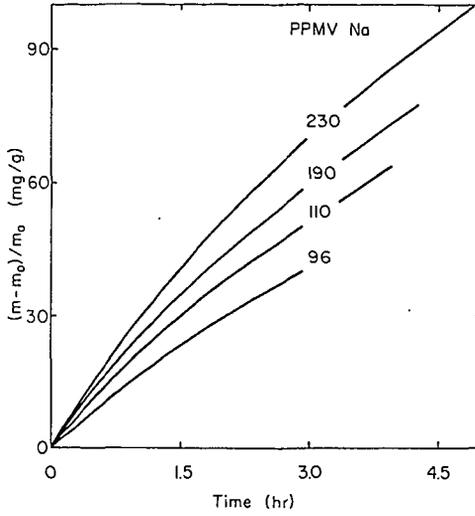


Figure 2. Temporal profile of NaCl adsorption on kaolinite.

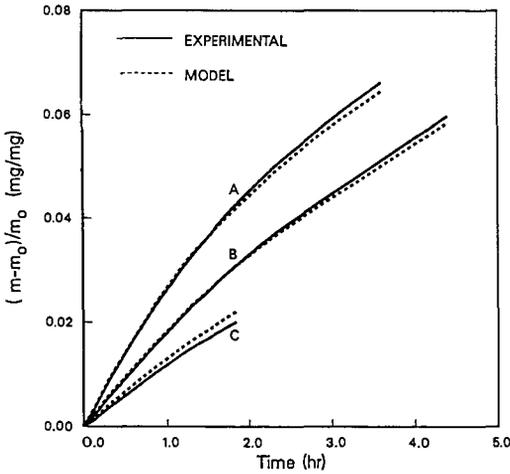


Figure 3. Comparison of model and data for NaCl adsorption on emathlite.

C_{A0} is 125 ppmv for A, 80 ppmv for B and 65 ppmv for C.