

MECHANISM AND KINETICS OF LEAD CAPTURE BY KAOLINITE IN A DOWNFLOW COMBUSTOR

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An 18 kW, 6 m long, gas-fired downflow combustor was used to examine the postflame reaction between lead vapor and kaolinite. Since the focus of this work was to evaluate the reaction with lead vapor, samples were extracted at a temperature above the metal dew point. The sample was rapidly diluted with nitrogen such that lead vapor homogeneously nucleated to form small particles in the presence of a pre-existing particle population. These small lead particles were easily distinguished from lead reacted to large sorbent particles; hence, multicomponent particle size distributions were used to determine the extent of lead capture. A parametric study was conducted in which sorbent/metal molar ratio and sorbent injection temperature were controlled. Temperatures and residence times were varied by changing the sorbent injection point in the combustor, which had the approximate time and temperature profile of practical-scale units. The effect of chlorine was evaluated by doping chlorine gas into the flame.

Results show that lead capture by kaolinite was reduced at higher temperatures and in the presence of chlorine. A two-reaction mechanism is proposed to model the apparent temperature inhibition. In the primary capture reaction, lead oxide reacts with activated kaolinite and forms a lead aluminosilicate product. Subsequently, a reaction between this product and activated kaolinite acts to inhibit further lead capture. First-order rate expressions are proposed for each reaction, and kinetic parameters are estimated from experimental results. The primary capture reaction appears to have an activation energy that is approximately zero. The inhibition reaction has an activation energy of $\sim 10^2$ kJ mol⁻¹. To model the effect of chlorine, the reaction scheme is modified to account for the partitioning of lead between lead oxide and lead chloride. Based on experimental results, the concentration of lead chloride vapor in the system is significantly higher than predicted by equilibrium calculations.

Introduction

The emission of toxic elements from stationary combustion sources, such as incinerators and coal-fired boilers, is a major concern. Of particular concern are semivolatile toxic elements, for example, lead and cadmium, which vaporize and condense within the combustion system. At high temperatures, lead vaporizes and is liberated from ash particles. As the temperature of the combustor decreases, the vapor condenses to form, in part, submicron particles. These submicron particles can penetrate conventional air pollution control systems, like baghouses and electrostatic precipitators, and be emitted to the environment [1,2].

One potential method to control toxic metal emissions is to inject a high-temperature sorbent into the postflame region. The sorbent powder, which is easily collected, reacts with metal vapors and prevents the subsequent vapor-to-particle transformation processes that form submicron particles. Previous researchers have examined the reaction of lead and a clay-based sorbent, kaolinite. In a series of benchtop experiments where large kaolinite flakes were exposed to lead chloride vapor, Uberoi and co-authors

[3] determined by X-ray diffraction that the reaction formed a water-insoluble product, lead aluminosilicate ($\text{PbO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). The authors proposed that a reaction occurred between lead chloride and metakaolinite, the product of the kaolinite calcination process [3]. However, performed at a temperature of 973 K and in the presence of chlorine, the reaction occurred over many hours and was clearly unsuitable for practical application [4]. Scotto and co-authors [4,5] extended this work to higher temperatures in a laboratory combustor. High temperatures allowed the reaction of lead and kaolinite to be studied with and without chlorine. In these experiments, supermicron kaolinite particles were introduced into a downflow combustor at ~ 1590 K, and samples were extracted ~ 2 s later at ~ 1125 K. Under these conditions, the reaction appeared to occur rapidly with 99% reduction of submicron lead particles as measured by a differential mobility particle sizer/condensation particle counter. However when chlorine was introduced at a molar flowrate 17 times that of lead, the reaction between lead and kaolinite was significantly slowed. The reduction of the submicron lead particles by sorbent powder was limited

to 28% in the presence of chlorine. Additionally, the authors noted that the kaolinite particles exhibited significant melting in the presence of lead, although the melting point of pure kaolinite is greater than 1800 K. These observations were verified in a series of experiments by Linak and coworkers [6]. These authors suggested that the reaction between lead and kaolinite occurred through the reaction of lead oxide and metakaolinite. The presence of chlorine was caused by the formation of lead chloride, thus reducing the rate of reaction by removing lead oxide.

The objective of the research presented here is to measure the rate of reaction between lead vapor and kaolinite at high temperatures, with and without chlorine present. As opposed to previous research, a global model for the reaction of lead and kaolinite, which accounts for the effect of melting and the presence of chlorine, is proposed, and kinetic parameters are *quantitatively* determined from experiments. To do this, a parametric study was performed to evaluate the effect of sorbent/metal molar ratio and injection temperature on the capture of lead vapor by kaolinite, with and without 1000 ppmV Cl present in the flame.

Theoretical Background

Based on the previous research, the proposed mechanism of the lead and kaolinite reaction occurs by lead oxide reacting with metakaolinite [3,6]. The product of this reaction is molten at the process temperatures [4]. Furthermore, chlorine reduces the concentration of lead oxide by causing the formation of lead chloride [4,6]. To gain insight into the speciation of lead at high temperature, equilibrium behavior of 100 ppmV lead in a natural gas/20% excess air mixture was calculated by NASA's Chemical Equilibrium Applications (CEA) program [7]. The thermodynamic information database was augmented by the addition of the thermochemical information found in *Thermochemical Data of Pure Substances* [8]. Under these conditions, lead is predominantly found as lead oxide with trace amounts of elemental lead vapor. The lead oxide vapor begins to condense at ~ 1225 K. When 1000 ppmV chlorine is added to the system, lead no longer condenses within the combustor. According to the calculations, lead distributes itself between lead oxide and several chlorinated species (PbCl, PbCl₂, and PbCl₄). At temperatures greater than ~ 1450 K, lead oxide is approximately four times more prevalent than lead chloride. Below ~ 1450 K, the lead vapor is increasingly found as a chlorinated species. At a temperature of ~ 1200 K, all lead in the system is predicted to exist as PbCl₄. Therefore, if the proposed reaction mechanism is valid, the lead/kaolinite reaction in the presence of chlorine should proceed more rapidly at higher temperatures where lead is found as oxide,

and more slowly at lower temperatures where lead is found as chloride. This hypothesis assumes that the lead reaction rates in the downflow combustor are sufficiently fast to approximate the predicted equilibrium. While it is improbable that the rate of PbCl₄ formation is sufficiently rapid, a recent kinetic study seems to support the prevalence of lead oxide at high temperatures and lead chloride at lower temperatures. Cosic and Fontijn [9] examined the reaction of lead with oxygen and chlorine in a high-temperature fast-flow reactor. They determined that the lead/oxygen reactions were exceptionally fast at high temperature and appeared to be catalyzed by the surfaces in the reactor. Furthermore, at temperatures greater than 1200 K, the PbCl dissociation reaction dominated and only a small amount of PbCl was formed. The rate of PbCl formation increased dramatically below 1200 K.

In addition to the speciation of lead, the phase transformations of kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$) in the combustor are important. Since the active form of the sorbent is proposed to be metakaolinite, the formation and destruction of metakaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) at high temperatures is a critical consideration. Typically, kaolinite is calcined by a long and slow process wherein the temperature is gradually increased. Under these conditions, phase transformations of kaolinite begin at temperatures greater than ~ 700 K with the formation of metakaolinite by the dehydroxylation of the kaolinite crystal. At temperatures greater than ~ 1200 K, mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) formation occurs through the formation of an alumina-rich spinel phase [10–12]. This phase transformation acts to remove metakaolinite and thus theoretically prevents reactions with lead vapor. This process is analogous to the benchtop studies of Uberoi and coworkers [3]. By contrast, in high-temperature sorbent injection, particles are rapidly heated to temperatures greater than 1200 K and undergo a rapid calcination process. The dehydroxylation of kaolinite particles ($80\% < 2 \mu\text{m}$ in diameter), which were injected at temperatures of 1300 K, is complete within 0.5 s [13]. The density of the particle decreases and approaches the theoretical density of a dehydroxylated kaolinite particle which has undergone no structural collapse [14]. These experimental observations indicate that particle sintering in the absence of lead is not an important process. Furthermore, the mullite formation has been shown to be negligible under these conditions and for residence, times which are characteristic of a typical combustor [15]. Note that these processes are greatly dependent on the presence of impurities and on the degree of kaolinite crystallinity [16,17]. Since flash calcination conditions are nearly identical to sorbent injection conditions in this work [13], the formation of metakaolinite is not considered to be limiting. Moreover, the formation of mullite is not considered an important inhibition mechanism [13]. Differences in these two processes may

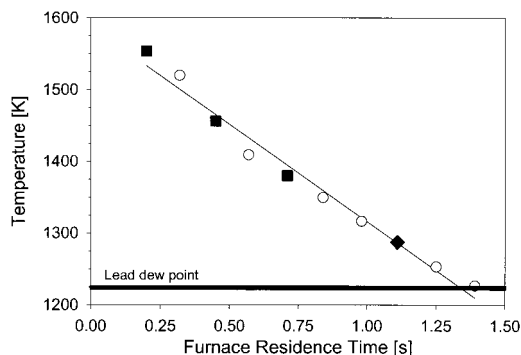


FIG. 1. Measured time/temperature profiles for downflow combustor at 18 kW with experimental sorbent injection points (■), and sampling point (◆) indicated.

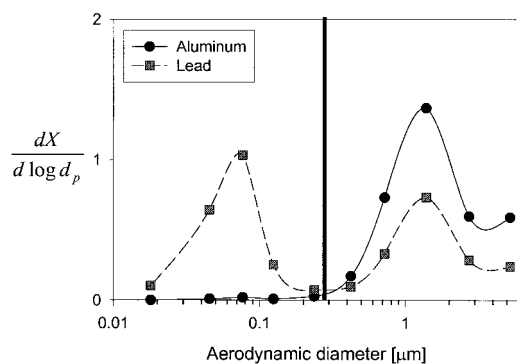


FIG. 2. Multicomponent particle size distribution of the partial capture of lead by kaolinite.

contribute to the observed differences between the benchtop [3] and laboratory combustor studies [4,6].

Experimental Procedures

Experiments were performed in an 18 kW, 6 m tall, 0.15 m inner diameter downflow furnace which has been previously well characterized [5]. This furnace has a time and temperature history typical of full-scale boilers and incinerators; yet it can be modeled as a one-dimensional plug flow reactor. A swirl flame with an internal recirculation zone was maintained at the top of the furnace by introducing axial natural gas and swirling primary air through the centerline of a burner. Natural gas and primary air flows were measured by rotameter and a calibrated laminar flow element-inclined manometer system, respectively. Twenty percent excess air was maintained for all experiments. An aqueous solution of lead acetate was injected into the flame by a plain jet-air blast atomizer.

For all of the experiments, powdered kaolinite (mean diameter = $0.8\ \mu\text{m}$) was introduced along the furnace centerline. Sorbent was pneumatically transported by 12 slpm of air and metered by a twin-screw feeder manufactured by K-Tron, Inc. The sorbent residence time was, calculated from known input gas flow rates and dimensions of the reactor accounting for slight dilution due to leakage. The kaolinite used for these tests was obtained from Burgess Pigment, Inc. The reported purity was approximately 98%, with the remaining fraction composed of titanium oxide and trace quantities of iron oxide. Temperatures were measured at the centerline with an uncorrected bare-wire R-type thermocouple. Fig 1 shows the postflame temperature/time profile of the reactor under experimental conditions.

The aerosol size fractionation system was composed of two primary components, a rapid quench probe and a Berner low-pressure impactor. Samples were extracted from the centerline of the furnace via a water-cooled, rapid N_2 quench probe. The nitrogen dilution was performed immediately at the tip of the probe. The nitrogen dilution, 12:1 for all cases, generated a quench rate in the probe tip of the order of 10,000 K/s. From the probe, samples were sent directly to a Berner low-pressure impactor (BLPI) [18]. The BLPI was prepared with polycarbonate substrates that were sprayed with Apeizon-L vacuum grease in toluene to prevent bounce-off. Each substrate was vacuum desiccated for a minimum of 24 h to remove the solvent. Details of the sampling system design and performance have been previously described [19]. Each sample was digested by a mixture of 3 HF:1 HCL:1 HNO_3 , then analyzed using flame ionization atomic absorption spectroscopy.

For each experiment, samples were extracted above the dew point of lead (predominantly lead oxide) vapor as shown in Fig. 1. Since each sample was withdrawn above the dew point of the semivolatile lead, any lead that had not reacted with the sorbent was found in the vapor phase. Upon extraction from the furnace, lead vapor was exposed to a rapid nitrogen quench where it was forced to nucleate homogeneously in the presence of the pre-existing particle population (kaolinite powder). These small lead particles are easily distinguished from the lead found on the larger sorbent particles. Multicomponent particle size distributions (PSDs) can be used to *quantitatively* determine the extent of lead capture by kaolinite. This process is demonstrated in Fig. 2, which is the multicomponent PSD for a sample in which lead is partially captured by kaolinite. In Fig. 2, the lead PSD has two modes. Since the mode to the right of the vertical line is closely associated with the aluminum mode, which represents the sorbent PSD, this mode represents lead captured by sorbent in the furnace. The area under this mode is equal to the fraction of lead captured by kaolinite as determined by the impactor measurement. The area to the left

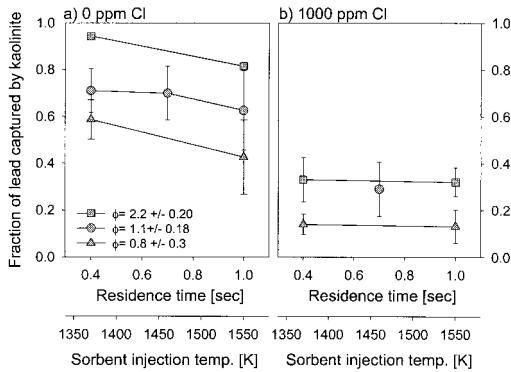


FIG. 3. Summary of the lead/kaolinite parametric tests.

of the horizontal line represents the fraction of lead captured in the impactor that was vapor in the combustor. The dynamics of this process were examined by the authors in previous work where a system of semivolatile cadmium and pre-existing nickel particles was examined [19].

A parametric study was constructed to explore the effect of injection temperature and sorbent/metal ratio. The injection temperatures were chosen to be 1530 K, 1450 K, and 1380 K at 18kW. Note that the sampling point was held fixed, thus, coupling the sorbent residence time and injection temperature. The corresponding sorbent residence times were 1.0s, 0.7s, and 0.4 s, respectively. The sorbent injection and sampling points are indicated on the time-temperature profile shown in Fig. 1. The values of sorbent/metal ratio based on the input flowrates were chosen to be 4, 2, and 1. Lead was maintained at 100 ppmV for all experiments. For experiments with 1000 ppmV Cl, chlorine gas was metered by a rotameter and introduced into the primary air upstream of the flame. Experiments were performed randomly to minimize any systematic bias.

Results and Discussion

Figure 3 shows the results of the experiments. Across the figure, each panel represents the response surface under different chlorine concentrations. The runs with the same average measured stoichiometric ratio, ϕ , are indicated by identical symbols in each panel. Each level is connected with solid lines for clarity. Note that differences between ϕ and designed input stoichiometric ratio are generated by losses in the combustor. The abscissa is the fraction of metal captured by sorbent as measured by the sampling systems, and the ordinate shows the sorbent residence time and corresponding injection temperature. The error bars represent a 95% confidence in the amount of metal captured at each condition. This is based on a minimum of two runs per point.

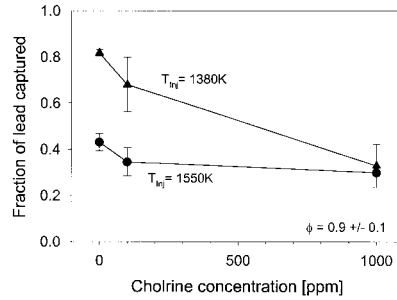


FIG. 4. Lead capture at constant residence time (0.4 s) and injection temperatures of 1530 K and 1380 K.

As expected, increases in the stoichiometric ratio yield increased lead capture. Furthermore, in the presence of 100 ppmV Cl, the amount of lead capture significantly decreases. However, the dependence of the reaction with time and injection temperature is contrary to expectation since little mullite is expected to form. One would expect that at longer times and higher temperatures, that the conversion of lead vapor would be greater. This behavior is noticeable at all three levels of ϕ , although the confidence intervals around each point are relatively large. The negative temperature dependence appears even at high chlorine concentrations. In the presence of 1000 ppmV Cl, lead capture for a 1.0 s sorbent residence time is equivalent to lead capture at 0.4 s residence time without chlorine. This behavior suggests that the global process has an apparent negative activation energy.

Additional samples were extracted for examination by scanning electron microscopy–energy dispersive X-ray analysis (SEM-EDX), X-ray diffraction (XRD), and transmission electron microscopy (TEM). As expected, in the presence of lead, significant melting of kaolinite particles was observed. EDX analysis of particles indicated a mixture of lead and silicon. Chlorine was not detected in the particles for experiments in the presence of chlorine. XRD performed on these samples seemed to indicate that the sample was amorphous. TEM examination indicated that melting occurred throughout the particle. Faint electron diffraction patterns were obtained from TEM; however, these patterns were generated by TiO_2 , a common impurity.

Since the coupling of the time and temperature in these measurements may confound the interpretation of these data, a small set of tests was performed at constant residence time and two injection temperatures. Tests were conducted at the same ϕ ($\phi = 0.9 \pm 0.1$) with chlorine/metal molar ratios of 0, 1, and 10. The injection point was varied between 1530K and 1380 K. Fig. 4 clearly illustrates the apparent negative activation energy. At 0 ppm Cl, the difference in the capture is approximately 50%.

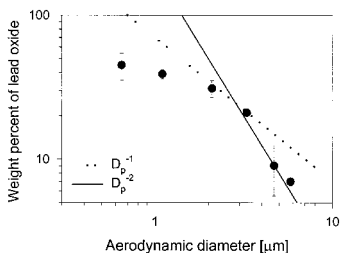


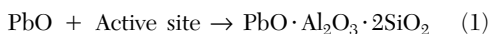
FIG. 5. Plot of the lead concentration as function of diameter.

However, at high concentrations of chlorine, the capture in the same time is approximately equivalent and may indicate that relative rates between the two processes of lead capture and particle melting are important.

To examine the effect of mass transfer, a kaolinite powder with a larger range of particle diameters was injected into the furnace at 1450 K. Fig. 5 shows the effect of particle size on the fraction of lead oxide as determined from impactor measurement. For particles larger than $\sim 4 \mu\text{m}$, the size rotation suggests a $1/D_p^2$ dependence, which indicates a gas-film diffusion controlled mechanism. Particles with diameters between $2 \mu\text{m}$ and $4 \mu\text{m}$ appear to exhibit a $1/D_p$ diameter dependence, indicating that the reaction process is controlled by pore diffusion. Particles smaller than $2 \mu\text{m}$ show little diameter dependence, which suggests reaction control for these particles. Kaolinite powder used in the parametric study had a size distribution in which 90% of the particle mass was found to have diameters less than $2 \mu\text{m}$. Thus, the process is reaction controlled, and reaction kinetics can be determined from these studies.

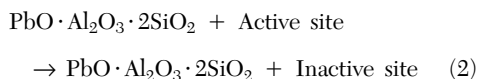
Reaction Model for Lead/Kaolinite Interactions

Based on the results of the parametric study, an elementary reaction mechanism may not provide an accurate description of the system dynamics. The negative temperature dependence would suggest a negative activation energy, which does not exist for an elementary reaction. A more complex reaction mechanism is required to predict the observed temperature behavior. Based on the work of Scotto [20] and Uberoi [3], the capture of lead with a kaolinite sorbent occurs by a simple reaction between lead oxide and activated kaolinite. If we assume that lead aluminosilicate is the reaction product at high temperature, the reaction would be



where the active site may be assumed to be metakaolinite. To introduce the temperature effect, an

inhibition reaction is introduced in which lead aluminosilicate acts to remove available active sites. It is difficult to determine the exact mechanism based on this experimental work, but the phase transformation process may cause inhibition. By direct analogy to the research on mineralizers, phase transformations in the crystal are accelerated by melting which is caused by the presence of a mineralizer. The mineralizer acts to change the coordination of the aluminum atom from tetrahedral to octahedral [21]. This process opposes the process of calcination in which removal of the hydroxyl group transforms aluminum atoms from octahedral to tetrahedral coordination. If metakaolinite is assumed to be the active species, the conversion of tetrahedral aluminum may represent the removal of active kaolinite. This model can be succinctly described by the following scheme:



It is important to note that the study performed was not designed to address the specific molecular mechanisms. The objective was to determine an accurate global model which describes the interactions between lead and kaolinite and can then be applied to the design of practical applications. The reaction represents the overall phase transformation process, which acts to inhibit the lead and kaolinite reaction.

The downflow combustor was modeled as a one-dimensional plug flow reactor. Reactions 1 and 2 are expressed by simple first-order rate equations, thus yielding a model with four adjustable parameters, K_1 , E_1 , K_2 , and E_2 . To determine the kinetic parameters, the numerical solution to the model was coupled to a parameter estimation program. The numerical algorithm used to solve the set of ordinary differential equations was the Livermore solver for ordinary differential equations (LSODE). The nonlinear parameter estimation program, XTRACTR, is based on the Marquardt algorithm and is specifically designed to fit reaction data through the reparameterization of reaction rate constant parameters [22].

Initial conditions were determined from experimental data and input flowrates. Two critical simplifying assumptions were made. First, all kaolinite injected into the reactor is instantly transformed to metakaolinite. Flash calcination studies of similar kaolinite particles and temperatures indicate that calcination is complete within 0.5 s [15]. The second assumption is that all active sites are available for reaction without the influence of intraparticle transport. Thus, the active site concentration is given by the product of ϕ and the lead concentration. The site concentration has units of moles of kaolinite per cubic meter of flue gas. The initial lead concentrations are assumed to be 60 ppm in the reactor. This

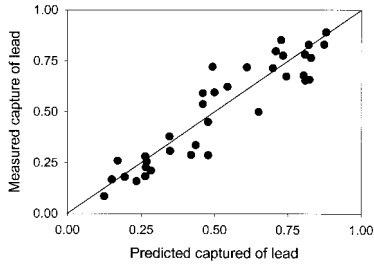


FIG. 6. Correlation between predicted and experimental capture for lead/kaolinite systems.

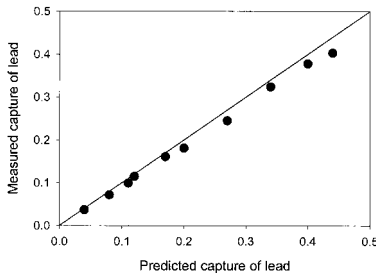


FIG. 7. Correlation between predicted and measured capture for lead/kaolinite in the presence of 1000 ppm Cl.

estimate is based on the average metal recoveries from experiments performed without the kaolinite.

Initial estimates of the parameters were performed and indicated that the activation energy of reaction 1 was ~ 10 J/mol with a correlation coefficient of 0.82. Since the reaction between metal and kaolinite is likely to be exothermic, the activation energy of reaction 1 is expected to be small. To simplify the estimation problem, this activation energy was assumed to be zero, and other parameters were fitted accordingly. Note that this assumption is likely to be valid over the narrow temperature range of the experiments. With E_1 set to zero, other kinetic parameters were estimated to be

$$k_1 = 7.7 \times 10^3 \text{ m}^3 (\text{mol s})^{-1}$$

$$E_1 = 0.0 \text{ J mol}^{-1}$$

$$k_2 = 6.1 \times 10^7 \text{ m}^3 (\text{mol s})^{-1}$$

$$E_2 = 1.1 \times 10^5 \text{ J mol}^{-1}$$

As can be seen in Fig. 6, the predicted capture strongly correlates to the measured lead capture. The correlation coefficient for this model was 0.86 and is better than the 0.82 found for the case where all parameters were estimated.

The effect of chlorine is added to the reaction model by adding a temperature-dependent "partition" factor. This factor is defined as the molar ratio of chlorinated lead to lead oxide vapor. At 1000

ppmV Cl, the partition factor can be estimated from the equilibrium-predicted distribution of lead. With the partition factor defined, the model is solved with the three-parameter model developed previously. A model based on the equilibrium-predicted distribution showed less than 50% correlation and did not describe the measured behavior.

To determine the proper partition function, the coefficients were estimated from the collected data. Based on the individual runs that were performed with 1000 ppmCl, the partition function was estimated to be $K = 0.028T + 4.18$. According to this estimation, a super-equilibrium amount of lead chloride seems to exist in the reactor. Furthermore, the temperature dependence of the partition factor is weak. The correlation coefficient for this estimate is 0.97. Fig. 7 plots the predicted values versus measured values from this model. This is interesting in light of the work by Cosic and Fontijn [9], who reported that at high temperature, PbCl rapidly decomposes.

Conclusions

The interactions between kaolinite and lead were studied in detail. Results from a parametric study indicated that lead capture was lower at high temperature and long residence times in the reactor. To account for this negative temperature effect, a model was proposed wherein the product of the kaolinite reaction was self-inhibiting. Because of the practical nature of the work, a specific molecular mechanism could not be elucidated. A global reaction scheme was able to predict the observed behavior. Kinetic parameters were determined which adequately describe the observed behavior.

In the presence of significant amounts of chlorine, the overall capture was reduced. The reaction model was modified to include a temperature-dependent partition factor. The partition factor was defined as the molar ratio of chlorinated lead vapor to lead oxide vapor. The chlorinated model was solved using the previously estimated parameters. Initial estimates for the partition factor were derived from equilibrium predictions. Equilibrium failed to predict the observed behavior. An estimate of the partition factor was determined to be ~ 4 between temperatures of 1300 K and 1530 K. This parameter suggests that a super-equilibrium amount of chlorinated lead vapor influences the reaction.

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