Carbochlorination of Metal Oxides with Phosgene

Kinetics of the carbochlorination with phosgene of an alumina-silica material are reported for a temperature range of 723 to 1,023 K and a phosgene partial pressure range of 4 to 90 kPa. The oxides react in a constant ratio over most of the conversion range and the grain model accurately predicts conversion as a function of time.

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Introduction

The use of polymetallic ores will become more important as the world's supply of primary ores is depleted. Aluminum, for example, is produced today from bauxite via the Bayer-Hall process but in the future will be derived from lower grade ores containing larger amounts of silica and other metal oxides. Different recovery methods will be required, such as carbochlorination, which produces a mixture of volatile metal chlorides. When using phosgene, $COCl_2$, the following general reaction applies:

$$M_xO_y + yCOCl_2 \rightarrow xMCl_{(2y/x)} + yCO_2$$

The volatile chlorides can be recovered from the effluent gas stream and separated to yield high-purity products. To apply this method, carbochlorination reaction rate and product composition data are needed for reactor and product recovery system design.

The potential use of carbochlorination for the production of $AlCl_3$ as a raw material in the manufacture of aluminum, has generated considerable interest in gas-solid chlorination kinetics. Papers have been published concerning the chlorination of alumina (primarily gamma) (Alder et al., 1977, 1979; Bertóti et al., 1980a,b, 1981a,b, 1982; Landsberg, 1977; Milne, 1976; Milnes and Wibberly, 1978; Seon et al., 1983; Tóth et al., 1982), of bauxite (Kuruvilla and Dadape, 1965; Landsberg, 1977; Milne, 1976; Milne and Wibberly, 1978; Podoinikova and Chernyi, 1963; Raval and Dixit, 1979; Richarz, 1981), of clays (Landsberg, 1975, 1977; Podoinikova and Chernyi, 1963; Smith et al., 1982), and of other aluminum-bearing materials (Bombara and Tanzi, 1984; Mehrotra et al., 1982; Smith et al., 1982). The gamma-alumina studies have provided kinetic information for the production of aluminum chloride from Bayer process aluminum oxide. However, since the efficiency of the Bayer process is greatly reduced by the presence of large amounts of silica in the ore (Adamson et al., 1963), direct chlorination of low-quality ores to produce volatile chlorides has been considered.

The kinetics of the chlorination of a material depend on its chemical composition and physical characteristics and also on the carbon and chlorine source employed. Since ore properties vary greatly, chlorination kinetics of the material under consideration must be determined experimentally. Accurate interpretation of reaction rates measured during such studies requires a knowledge of the rate-limiting mechanism, be it surface reaction, diffusion, or a combination thereof. While this approach seldom has been used in previous studies, it was stressed here to provide a more fundamental understanding of the key carbochlorination parameters.

The metal oxide mixture used in this investigation was derived from a coal fly ash, an abundant material with unique chemical and morphological properties and a significant content of alumina. The finely divided ash contained a large glassy fraction and had low surface area. The investigation was simplified by use of a treated sample that consisted primarily of alumina and silica. Thermogravimetric techniques were employed to obtain reaction rate data and phosgene chemisorption and nitrogen physisorption isotherms. Gaseous diffusion information was derived from steady state–diffusion cell measurements.

Surface reaction control over the conversion range investigated was verified by powder vs. pellet chlorination results and Thiele modulus values. Only one set of Arrhenius parameters was required for the entire conversion range since the metal oxides reacted in constant ratio throughout. Alumina was preferentially chlorinated to leave a silica-rich inert fraction with a constant specific surface area.

An increase in BET specific surface area as a function of conversion was predicted by a semiempirical model. The ratio of the BET surface area to the specific weight of phosgene chemisorbed did not change over nearly the whole conversion range, evidence of a constant surface composition.

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The degree of phosgene dissociation, measured as a function of temperature and reactor residence time, was kinetically limited. The chlorination reaction was first order with respect to the phosgene concentration and phosgene was chemisorbed on the surface of partially chlorinated oxide samples.

Microporosity measurements and SEM observations supported the choice of the grain model to predict fly ash conversions as a function of time for the temperature and phosgene partial pressure range of 723 to 1,023 K and 4 to 90 kPa, respectively. All parameters used in the reaction model were measured experimentally; fitting was not required to obtain agreement between data and model predictions.

While only 40 wt. % of the treated ash reacted, the commercial potential of the method is evident. The portion of ash that did react contained 87% of the alumina present, but only 17% of the silica. In addition to the chlorination kinetics reported in this work, phosgene gas phase and surface dissociation kinetics must be determined before the design of a carbochlorination reactor can be undertaken with confidence.

Experimental

Reactants

The chlorination of aluminum oxide requires an oxygen sink and chlorine source such as solid carbon and chlorine, carbon monoxide and chlorine, or phosgene. The latter was used in this study for several reasons. Most important, available data (Alder et al., 1979; Landsberg, 1975; Tóth, 1982) show that alumina chlorination rates obtained when using phosgene are greater than those measured when carbon monoxide and chlorine or carbon and chlorine are used at much higher temperatures. The kinetic advantage is thought to be related to the requirement that phosgene exist on the alumina surface prior to formation of the metal chlorides (Landsberg, 1975; Milne, 1976; and Raval and Dixit, 1979). Recently, phosgene was detected *in situ* as the predominant adsorbed species on the surface of gamma-alumina chlorinated by carbon tetrachloride (Bertóti et al., 1982). As part of the present study, phosgene was identified among gases that desorbed from the surface of treated ash samples partially chlorinated by phosgene. Thus, the direct use of phosgene could eliminate rate-limiting steps, and it exposes the metal oxides to the oxygen sink (carbon monoxide) and the chlorine source simultaneously.

The use of a solid carbon source (coke or coal) with chlorine has recognized limitations. Bergholm (1961) and Barin and Schuler (1980) have shown that the carbon must be within 30 micron (μm) of the metal oxide surface to obtain reasonable chlorination rates. Barin and Schuler suggest that the close proximity is necessary for successful transfer of active chlorine species, possibly free radicals, from the carbon to the metal oxide.

Further evidence of the need for small separation distances has been provided by Alder et al. (1979) and Milne and Wibberly (1978), who coked alumina samples using hydrocarbons in a reducing atmosphere. When chlorinated, the coked samples reacted initially at high rates, but Alder et al. found recoking was required to obtain final conversions greater than 80 wt. %. One requirement for the success of this approach is a metal oxide with a high initial surface area. Fly ash with an area of 3.5×10^3 m^2/kg is not considered to be a reasonable candidate. With regard to economy in carbon usage, direct use of carbon does not result in a significant savings over phosgene since, at the high temperature (1,073–1,273 K) required to attain reasonable reaction rates with carbon, the CO/CO_2 ratio in the product stream has been measured to be as high as 10 to 1 (Adelman, 1980).

The fly ash used was collected during the combustion of Texas lignite coal. Nearly all of the relatively minor amounts of nonalumina-nonsilica components were removed by leaching the ash at 373 K with 6M aqueous HCl while the physical structure of the ash was retained. The leached ash contained 60.7 and 36.4 wt. % silica and alumina, respectively. No nonalumina-nonsilica component exceeded 1 wt. %, so this material was treated as a binary oxide mixture for carbochlorination. The treated ash was introduced into the reactor either as layers of powder or as thin cylindrical pellets (0.001 × 0.0137 m). The pellets were formed using a punch and die at a pressure of 4.08×10^4 kPa.

CP-grade phosgene was dried over magnesium perchlorate. High-purity helium served as the purge and phosgene diluent gas. The helium was further purified by passing it through a bed of size 5A molecular sieves, over titanium sponge held at 923 K, and finally through a liquid nitrogen trap.

Apparatus

A Cahn 2000 microbalance was incorporated into both a flow and a static system. The former was used to obtain phosgene chemisorption isotherms and treated ash carbochlorination rates at different phosgene concentrations and temperatures. Nitrogen physisorption and desorption isotherms were determined using the static system. A vacuum system was connected to both the flow and static versions and was used to clean samples to constant weight prior to reaction rate or adsorption experiments.

Pellets were pressed directly into a diffusion cell to obtain a good seal. The cell was operated at steady state with inert gases flowing over opposite faces of the pellet and the output stream compositions being analyzed using gas chromatography. The experimental systems are described in greater detail elsewhere (Adelman, 1984).

Reaction Model

A model was derived to predict mixed oxide conversion and aluminum chloride production rates as a function of reaction temperature and phosgene concentration. For simplicity, the reaction of cylindrical pellets with a large ratio of diameter to thickness was assumed. Physical data determined included the initial pellet macroporosity (0.42) and grain microporosity (0.005), grain geometry and surface morphology as a function of conversion, and the unreacted micropore ($10–300 \times 10^{-10}$ m) surface area. The very low initial microporosity indicates that the grains comprising the pellets are nearly solid objects. Furthermore, the pore surface area was only 1.09×10^3 m^2/kg, a value less than one-third the measured BET surface area. A large fraction of the available area was attributed to the rough grain surfaces observed using SEM.

Partially reacted samples were also examined using SEM. Grains reacted to a conversion of only 5 wt. % showed extensive surface roughness and degradation. As the conversion increased to the maximum of about 40 wt. %, the surface morphology did not change. The grains retained their approximate spherical shape as an inert phase began to appear at the surface.

One of the basic assumptions of the grain model is that the grains react as shrinking solid objects. This appears to be the case for the ash particles as the reaction zone moves toward the particle centers, leaving behind an inert matrix. Rate limitation due to diffusion through a product layer is not a consideration since $AlCl_3$, $SiCl_4$, and CO_2 are volatile at the conditions employed.

Intergrain diffusion rates were compared to surface reaction rates using the following form of the Thiele modulus:

$$\sigma = L[(1 - \epsilon_p)k/(2D_{eA}r_o)]^{1/2} \tag{1}$$

To use this form of the modulus it was necessary to assume isothermal reaction and reaction irreversibility. Also, as will be shown later, the reaction is first order with respect to phosgene concentration. Rate constants were calculated from experimental data using a first-order rate expression and phosgene effective diffusion coefficients derived from inert gas steady–state diffusion relationships given by Szekely and Sohn (1973). A modulus value of 0.12 was calculated at 700°C, the highest temperature considered for reaction with phosgene. The value of 0.12 is within the range of 0 to 0.3 estimated for surface reaction control (Szekely and Sohn).

Without diffusion limitations and for the first-order reaction of spherical grains, the grain model reduces to the following form:

$$dX_A/dt = 3M_AbkP_A(1 - X_A)^{2/3}/(r_o\rho_sRT) \tag{2}$$

The variable X_A is the treated ash conversion divided by the final conversion of 0.4. If the variables on the righthand side of Eq. 2 are assumed to be independent of X_A, integration yields:

$$1 - (1 - X_A)^{1/3} = M_AbkP_At/(r_o\rho_sRT) \tag{3}$$

Rate constant values calculated using the differential and integral forms of this equation can be compared to demonstrate the conversion independence of the variables and the applicability of the model.

Results and Discussion

Reaction order

Powder layers of two thicknesses were chlorinated while suspended in the microbalance in a porous quartz boat. Figure 1 is a plot of the resulting specific reaction rates as a function of phosgene partial pressure. The linearity at the three temperatures suggests that the reaction is first order and that no mechanism change occurs over the temperature range investigated. To verify the first-order status, the logarithmic values of the active conversion rate and phosgene partial pressures were analyzed using a least-squares technique. An order of 0.97 ± 0.08 was obtained. Even though the powder intergrain diffusion distance increased with sample size, the specific reaction rates were indistinguishable, suggesting the absence of diffusion rate limitations.

Stoichiometric coefficient

Data were taken to determine whether the composition of the product stream changed as a function of conversion. Samples were reacted to several conversions and then analyzed for individual metal oxide losses (Boar and Ingram, 1970). The results are shown in Figure 2. Iron oxide is included since it represents the largest nonalumina-nonsilica component at 0.9 wt. %. Its reaction could limit the usefulness of the initial reaction rate data in determining the alumina-silica chlorination kinetics. However, it was estimated from the data in Figure 2 that at any ash conversion a maximum of only 2 wt. % of the weight reacted could be attributed to the chlorination of iron oxide, a value within the overall experimental error.

The linear relationships in Figure 2 for alumina and silica conversions at ash conversions greater than 0.05 indicate a constant ratio of alumina to silica in the product stream. The ash conversion extends to only 0.40 since this was the maximum that could be obtained upon extended exposure of samples to phosgene. This is thought to be due to the existence of an unreacted matrix of quartz and alumina-containing mullite in the treated ash. The existence of such a matrix was confirmed using X-ray diffraction and SEM.

Extrapolation of the conversion lines in Figure 2 to an ash conversion of 0.40 yields alumina and silica conversions of 0.86 to 0.17, respectively. This corresponds to 1.86 mol of alumina reacted per mole of silica and corroborates previous work (Adel-

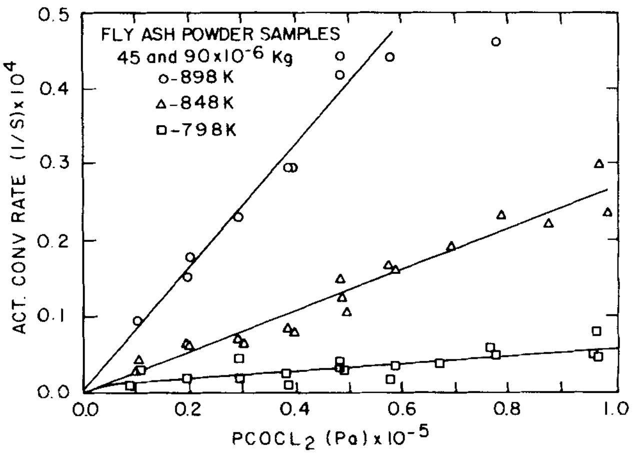

Figure 1. Conversion rates for treated ash reactive fraction as a function of phosgene partial pressure.

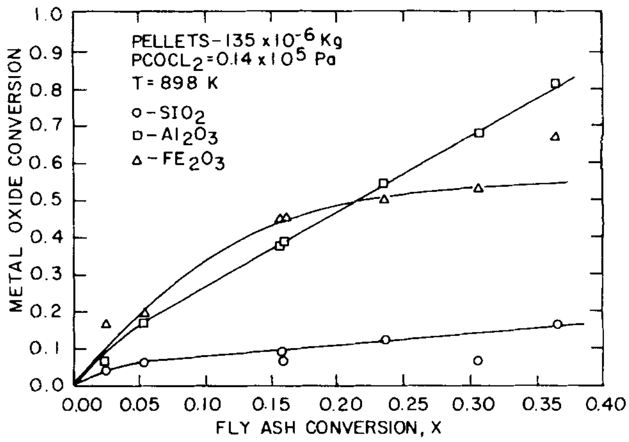

Figure 2. Individual metal oxide conversions as a function of treated ash conversion.

man, 1980) involving the initial chlorination of a bituminous fly ash with carbon and chlorine.

Grain and pellet characteristics

An initial average grain diameter of 3.9×10^{-5} m was calculated from particle size distributions measured with a Coulter counter. A Le Chatelier flask and an ASTM (1972) standard test procedure were used in determining a grain density of 2.03×10^3 kg/m^3. This procedure was selected in view of the grain microporosity of only 0.005. Powder and pellet porosities of 0.8 and 0.42, respectively, were calculated from sample dimensions and weights, and the treated ash density.

Nitrogen desorption isotherm data were used to compute a micropore size distribution (Barrett et al., 1951). The areas of the pore walls were summed to yield a surface area of 1.09×10^3 m^2/kg. This is about one-third of the total BET surface areas of 3.47×10^3 m^2/kg measured for the grains and 3.10×10^3 m^2/kg measured for the pellets.

Effective diffusion coefficient and tortuosity

Coefficient values for the effective diffusion of phosgene within pellets were needed to calculate reaction moduli. Direct measurement did not seem possible, so an alternate method was used. Diffusion rates of nitrogen and helium across pellets, formed using the same force per area as for the pellets that were reacted, were measured. At 297 K and 97 kPa, a coefficient value of $0.103 \pm 0.003 \times 10^{-4}$ m^2/s for nitrogen was obtained. This value yielded a tortuosity factor of 2.7 when used in calculations with a nitrogen molecular diffusion coefficient determined according to the Chapman-Enskog equation, an effective Knudsen diffusion coefficient estimated from an applicable literature relationship (Szekely and Sohn, 1973), and the pellet porosity. The factor of 2.7 is within the range of 2 to 3 reported in the literature (Henry et al., 1967; Szekely et al., 1976).

With the tortuosity factor available, the procedure was reversed to calculate phosgene effective diffusion coefficients at reaction conditions. Molecular diffusion coefficients for nitrogen were computed (Chapman-Enskog equation) and used with the tortuosity factor and pellet porosity to estimate effective molecular diffusion coefficients. These values along with effective Knudsen diffusion coefficients (Szekely and Sohn, 1973) were substituted in the Bosanquet equation to obtain phosgene effective diffusion coefficients. Since pellet porosity and the tortuosity factor are functions of pellet structure, the values determined could be used only in calculations involving initial rate measurements.

Rate constants

To calculate rate constants from conversion vs. time data, plots of the lefthand side of Eq. 3 vs. time were constructed. Several representative sets of data are shown in Figure 3. Each set defines a straight line as required by the model. This confirms that the surface reaction rate is limiting over the entire conversion range, that the grains react as shrinking solids, and that the parameters on the righthand side of Eq. 3 do not change as a function of conversion.

Further support for the above conclusions was obtained when rate constants calculated according to Eqs. 2 and 3 were compared using an Arrhenius plot, Figure 4. The values at a given temperature were indistinguishable, confirming the rate-limiting role of surface reaction. Figure 4 also offers a comparison of rate constants calculated from pellet and powder initial rate data. Considering the large difference in sample porosity, the agreement of rate constants indicates that intergrain diffusion was not limiting and that intrinsic surface reaction rates were measured.

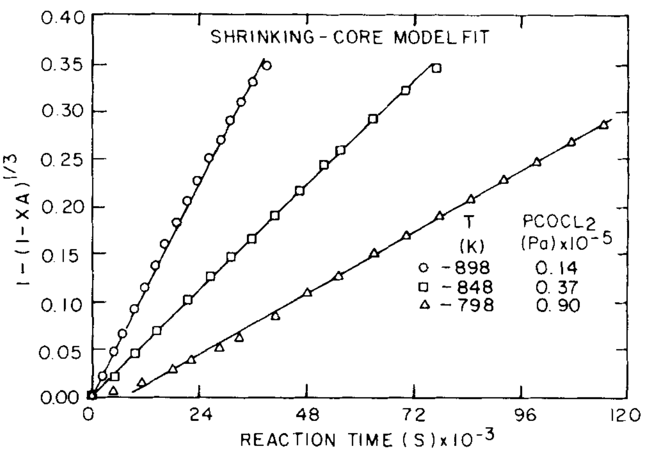

Figure 3. Conversion of the treated ash reactive fraction as a function of time (○ □ △) compared to shrinking-core model (—).

A rearranged form of Eq. 3 and the Arrhenius parameters from Figure 4 were used to predict ash conversion as a function of time. Comparisons of predicted and actual conversions are shown in Figure 5. The close agreement is typical of that obtained at temperatures of 725 to 925 K and phosgene partial pressures of 4 to 97 kPa. Aluminum chloride production rates can be calculated by combining the data of Figures 1 and 5.

Phosgene dissociation

In previous carbochlorination studies involving phosgene (Bertóti et al., 1981b; Landsberg, 1975; Richarz, 1981), deviations of Arrhenius plots from linearity at temperatures as low as 700 K were attributed to phosgene dissociation but without verification. Nonequilibrium dissociation was investigated as part of the present study after the onset of deviation at a given tem-

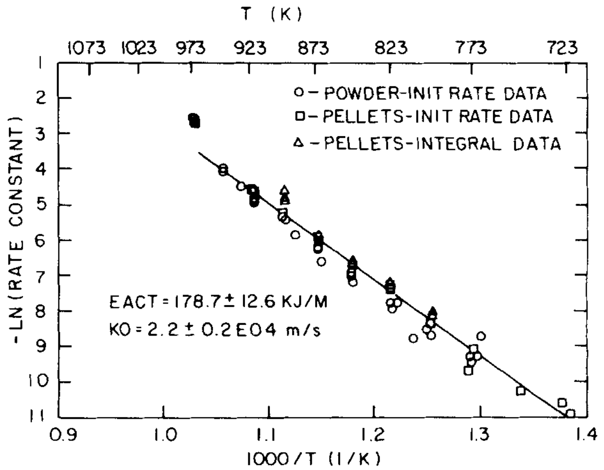

Figure 4. Arrhenius plot for reaction of treated ash powder and pellet samples with phosgene.

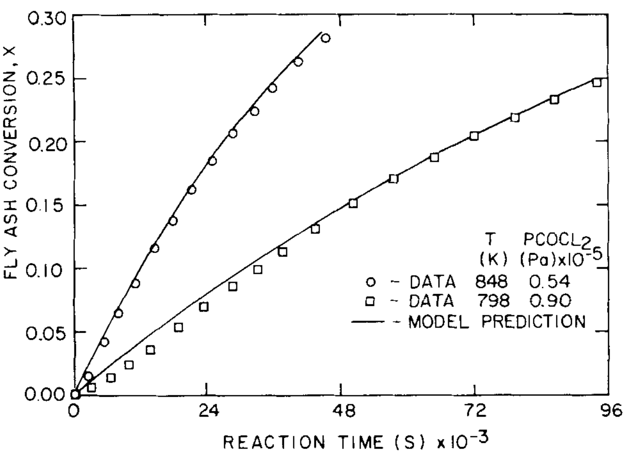

Figure 5. Treated ash conversion vs. time.

perature was found to be a function of the phosgene flow rate and after external mass transfer was eliminated as a possible cause for the deviation.

It had been observed that a bed of quartz chips in the preheating section of the reactor became coated with soot during experiments, possibly due to phosgene dissociation. As a first approximation, it was assumed dissociation occurred only on the chips and that phosgene concentrations measured at the reactor exit were the same as those in contact with the samples. The Arrhenius plot deviation at 973 K shown in Figure 4 could then be attributed to enhancement of the chlorination rate due to reaction with the large amount of carbon monoxide and chlorine present from dissociation of phosgene.

On the other hand, gas phase dissociation of phosgene in the reactor section lying between the chips and the exit could have yielded the same positive deviation. If phosgene partial pressures measured at the exit were smaller than those to which the samples were exposed, the use of the exit values in the calculation of rate constants, Eqs. 2 and 3, would have given inflated values.

To support this explanation, phosgene reactor residence times and a two-parameter model for the gas phase dissociation of phosgene (Kowalczyk, 1968) were used to estimate the phosgene concentrations to which the samples would have been exposed. Rate constants calculated using these data at 973 K fell on the straight line of the Arrhenius plot. Thus, while some phosgene dissociation probably occurred on the quartz chips, the deviation at 973 K can be accounted for by gas phase dissociation alone. It is also clear that phosgene gas phase and surface dissociation kinetics must be known if carbochlorination carried out at about 700 K or higher is to be predictable.

BET surface areas

While the BET surface area and phosgene chemisorption data obtained were not used directly in the reaction model, they gave valuable information about the reactions taking place. The specific surface area of the ash increased dramatically with conversion, as shown in Figure 6. A highly satisfactory semiempirical model was used to predict the line drawn through the data points. To develop this model, it was assumed that the inert fraction had a constant specific surface area, that the fraction of inert material uncovered equaled the fraction of the reactive material removed, and that the exposed reactive surface area was insignificant relative to the inert area. These assumptions can be interpreted as consistent with the shrinking-core mode of reaction required by the grain model. The continuous increase in BET surface area with conversion and the fact that 87 wt. % of the alumina was removed provide additional evidence that the ash grains develop an extensive pore structure and that the maximum conversion of about 0.40 does not result from pore closure.

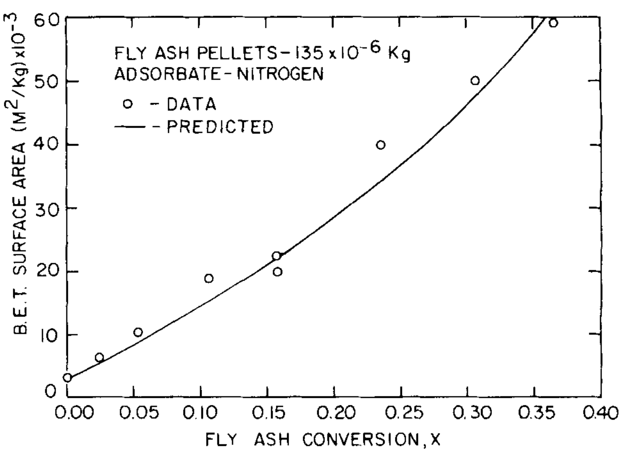

Figure 6. Treated ash specific surface areas as a function of conversion (○) compared to semiempirical model prediction.

Phosgene chemisorption

Phosgene chemisorption isotherms of the same samples used in the BET work were measured. The samples were allowed to equilibrate in the presence of pure phosgene at 523 K. The results are plotted in Figure 7 as the specific weight of phosgene chemisorbed vs. conversion. The line is intended as a visual aid; however, the data point on the ordinate is accurate as it was measured four times with as many samples. The departure from linearity here and in Figure 2 occurs over the same conversion range, indicating a surface composition change up to a conversion of about 0.05.

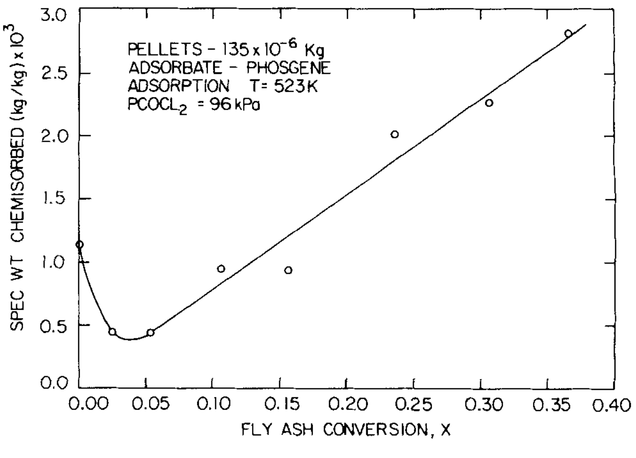

Figure 7. Specific weight of phosgene chemisorbed to treated ash as a function of conversion (○).

For conversions greater than 0.05, the ratio of the BET surface area to specific weight of phosgene chemisorbed was constant at $21.02 \pm 0.1 \times 10^6\ m^2/kg$ phosgene, evidence of constant surface composition. Using an estimated value of $35 \times 10^{-20}\ m^2$ required per phosgene molecule, only about 10% of the surface was covered by phosgene. Of greater significance is the large amount of phosgene chemisorbed as the ash conversion approaches 0.40, where the rate of conversion drops dramatically. A large fraction of the surface on which the phosgene is chemisorbed at this point must be nonreactive, an observation in support of the conversion mechanism proposed.

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Notation

b = stoichiometric coefficient, $kg_{flyash}\ (kg_{COCl_2})^{-1}$
D_{eA} = phosgene effective diffusion coefficient, $m^2 \cdot s^{-1}$
k = rate constant, $m \cdot s^{-1}$
L = pellet thickness, m
M_A = phosgene molecular weight, $kg \cdot kg \cdot M^{-1}$
P_A = phosgene partial pressure, kPa
r_o = average grain radius, m
R = gas constant, $kPa \cdot m^3 \cdot K^{-1} \cdot kgM^{-1}$
t = time, s
T = temperature, K
X_A = conversion of fly ash reactive fraction
ϵ_p = pellet porosity
ρ_s = fly ash density, $kg \cdot m^{-3}$
σ = Thiele modulus, Eq. 1

Literatured cited

Adamson, A. N., E. J. Bloore, and A. R. Carr, "Principles of Bayer Process Design," *Extractive Metallurgy of Aluminum*, **1**, *Alumina*, Metall. Soc. AIME, Wiley, New York, 23 (1963).

Adelman, D. J., "High-Temperature Chlorination of Coal Fly Ash," M.S. Thesis, Iowa State Univ. Ames (1980).

———, "Kinetics of Coal Fly Ash Chlorination by Phosgene," Ph.D. Thesis, Iowa State Univ. Ames (1984).

Alder, H. P., H. Geisser, A. Baiker, and W. Richarz, "The Chlorination of Alumina. A Comparison of the Kinetics with Different Reduction Agents," *Light Metals*, **3**, 337 (1979).

Alder, H. P., H. P. Muller, and W. Richarz, "Kinetic Study of the Alumina Chlorination with Carbon Monoxide and Chlorine," *Light Metals*, **1**, 219 (1977).

ASTM, "Standard Test Method for Specific Gravity of Hydraulic Cement," ASTM ANSI, C188-72 (1972).

Barin, I. and W. Schuler, "On the Kinetics of the Chlorination of Titanium Dioxide in the Presence of Solid Carbon," *Metall. Trans. B.*, **11B**, 199 (1980).

Barrett, E. P., L. G. Joyner, and P. P. Halenda, "The Determination of Pore Volume and Area Distributions in Porous Substances. I: Computations from Nitrogen Isotherms," *J. Am. Chem. Soc.*, **73**, 373 (1951).

Bergholm, A. "Chlorination of Rutile," *Trans. Metall. Soc. AIME*, **221**, 1121 (1961).

Bertóti, I., I. S. Pap, T. Szekely, and A. Tóth, "Kinetics of gamma-Alumina Chlorination by Carbon Tetrachloride," *Thermochim. Acta*, **41**, 27 (1980a).

———, "TG Studies on Chlorination Reactions in gamma-Alumina," *Thermal Analysis*, Birkhaeuser Verlag, Basel (1980b).

———, "Kinetics of gamma-Alumina Chlorination by Tetrachlorethylene," *Thermochim. Acta*, **44**, 333 (1981a).

———, "Kinetics of gamma-Alumina Chlorination by Phosgene," *Thermochim. Acta*, **44**, 325 (1981b).

Bertóti, I., B. Podor, J. Mink, I. S. Pap, A. Szabo, and T. Szekely, "TG, MS, and IR Study on the Chlorination Reaction of gamma-Alumina Oxide with Carbon Tetrachloride," Trav. Com. Int. Etude Bauxites, *Alumine Alum.*, **17**, 185 (1982).

Boar, P. L., and L. K. Ingram, "Comprehensive Analysis of Coal Ash and Silicate Rock by Atomic Absorption Spectrophotometery by a Fusion Technique," *Analyst*, **95**, 124 (1970).

Bombara, G. and R. Tanzi, "Prospects for Carbochlorination in Aluminum Recovery from Italian Leucitites," *J. Metals*, 74 (Jan., 1984).

Henry, J. P., Jr., R. S. Cunningham, and C. J. Geankoplis, "Diffusion of Gases in Porous Solids over a Thousandfold Pressure Range," *Chem. Eng. Sci.*, **22**, 11 (1967).

Kowalczyk, K. J., "Kinetic Study of the Thermal Formation and Dissociation of Phosgene in a Tubular Reactor," M.S. Thesis, Iowa State Univ., Ames (1968).

Kuruvilla, J. and V. V. Dadape, "Studies in the Chlorination of Indian Bauxite Ores," *Indian J. Technol.*, **3**, 244 (1965).

Landsberg, A., "Chlorination Kinetics of Aluminum Bearing Minerals," *Metall. Trans. B.*, **6B**, 207 (1975).

———, "Some Factors Affecting the Chlorination of Kaolinic Clay," *Metall. Trans. B.*, **8B**, 435 (1977).

Mehrotra, A. K., L. A. Behie, P. R. Bishnoi, and W. Y. Svrcek, "High-Temperature Chlorination of Coal Ash in a Fluidized Bed. I: Recovery of Aluminum," *Ind. Eng. Chem. Process Des. Dev.*, **21**, 37 (1982).

Milne, D. J., "The Chlorination of Alumina and Bauxite with Chlorine and Carbon Monoxide," *Proc. Australas. Inst. Min. Metall.*, **260**, 23 (1976).

Milne, D. J., and L. J. Wibberly, "Chlorination of Alumina and Bauxite Using Pyrolytic Carbon as Reductant," *Light Metals*, **2**, 147 (1978).

Podoinikova, K. V., and A. T. Chernyi, "An Investigation of the Kinetics of the Interaction of Hydrargyllite, Boehmite, Diaspore, and Kaolinite with Carbon Tetrachloride," *Zhur. Prikl. Khim.*, **36**, 2625 (1963).

Raval, R. P., and S. G. Dixit, "Some Aspects of the Chlorination of Bauxite," *J. Chem. Tech. Biotechnol.*, **29**, 107 (1979).

Richarz, W., "Alternatives Verfahren zur Herstellurig von Aluminium," *Chimia*, **35**, 279 (1981).

Seon, F., G. Picard, and B. Tremillon, "Industrial Alumina and Hexahydrated Aluminum Chloride Chlorinations by Phosgene in LiCl-KCl Eutectic Melt at 470°C," *Electrochimica Acta*, **28**, 209 (1983).

Smith, K. A., S. C. Riemer, and I. Iwasaki, "Carbochlorination of Aluminum from Non-Bauxite Sources," *J. Metals*, **34**, 59 (1982).

Szekely, J., J. W. Evans, and H. Y. Sohn, *Gas-Solid Reactions*, Academic Press, New York (1976).

Szekely, J. and H. Y. Sohn, "Effect of Structure on the Reaction Between a Porous Solid and a Gas," *Inst. Mining Metall. Trans. C*, **C8**, C92 (1973).

Tóth, A., I. Bertóti, and T. Szekely, "Kinetics of gamma-Alumina Chlorination by Carbon Monoxide and Chlorine," *Thermochim. Acta*, **52**, 211 (1982).

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