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Carbochlorination of metal oxides using a fused salt slurry reactor

Michael Sean Dobbins

Iowa State University

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CARBOCHLORINATION OF METAL OXIDES USING A FUSED SALT SLURRY REACTOR

Iowa State University

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Carbochlorination of metal oxides using a fused salt slurry reactor

by

Michael Sean Dobbins

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of the Requirements for the Degree of DOCTOR OF PHILOSOPHY

Major: Chemical Engineering

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INTRODUCTION

Fly ash is a mixture of metal oxides, the composition of which depends on the coal and method of combustion. The current rate of fly ash generation in the United States is in excess of 52MM Mg/yr (47). Recovery of 80% of the aluminum, titanium and iron present in this material could provide 80% of the United States demand for primary aluminum and 47% and 5% of the same for titanium and iron.

This research project was a study of the carbochlorination of metal oxides of fly ash from the combustion of pulverized coal (and alumina) with carbon and chlorine in a high-temperature slurry reactor using a NaCl-AlCl₃ fused salt as the liquid medium. Carbochlorination has been demonstrated as a method for the recovery of aluminum, titanium and other metals from traditional ores and coal combustion wastes (2,14,22,25,37).

Prior work on the recovery of metals from coal combustion wastes by carbochlorination has focused on gas-solid reaction systems (1,2,41). The reaction rate and conversion levels in gas-solid reaction systems using solid reductants are limited by the contact of the reductant and oxide, and gaseous reductants have been found to be less effective than solid reductants for promoting chlorination. The fused salt system enhances the reaction rate by dissolving the metal oxide which eliminates the need to maintain intimate contact between two solids. The major disadvantage of the fused salt reaction system is the handling of a corrosive salt at high temperatures under moisture-free conditions.

The chlorination of alumina was studied because it is a good simulation of fly ash chlorination. The major constituents in fly ash
will react with $\text{AlCl}_3$ in the melt to produce metal chlorides and alumina as part of the oxide dissolution reaction. Therefore, the carbochlorination reaction occurring in the fly ash chlorination system is the carbochlorination of alumina. Experimentally this was very useful, since the chlorination of a pure oxide is more easily studied than a mixed oxide.

The effect of alumina loading, temperature, carbon loading, stirrer rate and melt composition on the chlorination rate were tested using a stirred tank type reactor. Of these variables, temperature and carbon loading had the most effect on the rate and were studied in detail. Fly ash chlorination was limited to testing the effect of melt composition on the reaction rate.

The processing of fly ash in a fused salt chlorination system with respect to product purification and recovery was also considered. The design of a reactor sized to process $10^4 \text{ Kg hr}^{-1}$ of fly ash was also developed.
LITERATURE REVIEW

Carbochlorination Reactions

The conversion of metal oxides to their respective chlorides is generally carried out in the presence of both a reducing and chlorinating agent. Carbon or carbon monoxide are the most common reductants although sulfur has been used (43). Less stable oxides, such as Fe₂O₃, may chlorinate in the absence of a reductant, but are more easily chlorinated when one is present (34). Alumina, which is of primary interest in this study, is not appreciably chlorinated in the absence of a reductant (36).

Alumina will be used as a general example for the rest of this discussion. Analogous reactions can be written for other oxides. The overall stoichiometry of the chlorination of alumina is described by reactions 1 and 2:

\[
\begin{align*}
\text{Al}_2\text{O}_3 + 3\text{Cl}_2 + 3\text{C} &\rightarrow 2\text{AlCl}_3 + 3\text{CO} \\
\text{Al}_2\text{O}_3 + 3\text{Cl}_2 + 3\text{CO} &\rightarrow 2\text{AlCl}_3 + 3\text{CO}_2
\end{align*}
\] (1) (2)

Both reactions 1 and 2 occur in parallel when carbon is used as the reductant. Reaction 3 (Boudard reaction), will attempt to control the CO:CO₂ ratio. At temperatures above 750°C CO is thermodynamically favored over CO₂, which reduces the effectiveness of CO as a reductant in reaction 2.

\[
\text{C} + \text{CO}_2 \leftrightarrow 2\text{CO}
\] (3)

Although the Boudard reaction theoretically limits the CO₂ content of the product gas, it is very slow at temperatures below 1100°C. This
kinetic limitation explains why levels of CO$_2$ higher than would be predicted from Reaction 3 have been observed in chlorination product gases (44).

Other reaction systems that combine carbon and chlorine into a single compound, such as phosgene or carbon tetrachloride have been investigated. Phosgene has been found to be the most effective agent at low temperatures (<650°C) for gas-solid reaction systems (3). Primary advantages offered by combined reactants are the simultaneous availability of both the reductant and chlorine at a reactive site, and improved mass transfer (3).

**Metal Chloride-Oxide Reactions**

It is also possible for mixtures of different metal oxides and chlorides to undergo an exchange reaction. For example AlCl$_3$ can chlorinate Fe$_2$O$_3$ by the following reaction:

$$\text{Fe}_2\text{O}_3 + 2\text{AlCl}_3 \rightarrow 2\text{FeCl}_3 + \text{Al}_2\text{O}_3$$

(4)

Therefore, in mixed metal systems there are two possible chlorination paths, first through the carbochlorination reactions (reactions 1 and 2) or by the chlorine exchange reaction (reaction 4). Table 1 lists the order of stability for some of the more common metal chlorides.

The order of stability shown in Table 1 is a slight function of temperature. At 750°C AlCl$_3$ is slightly more stable than SiCl$_4$, however, at lower temperatures the two are reversed. These stabilities are based on thermodynamic considerations; poor kinetics may prevent the exchange reaction from occurring to any measurable extent.
Table 1. Relative stability of metal chlorides at 750°C (34)

<table>
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<th>Increasing Oxide Stability</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>Fe</th>
<th>Ti</th>
<th>Al</th>
<th>Si</th>
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In the presence of a large excess of a relatively unstable chloride salt, the chlorination reaction may separate into two distinct paths. For example in systems containing large amounts of AlCl₃, Na₂O through TiO₂ may be chlorinated almost exclusively by AlCl₃, producing Al₂O₃.

Gas-Solid Chlorination Characteristics

The discussion presented here is not intended to be a complete analysis of gas-solid chlorination systems. It is included to provide a background for the comparison of fused salt chlorination to gas-solid systems reported in the literature.

Gaseous reductants

Podor and Bertoti (49) studied the reaction of gamma-alumina with CCl₄ and analyzed the reaction products and intermediates using a quadrupole mass spectrometer. The results of the study indicated that CCl₄ started to chemisorb on the alumina surface at ~200°C and that the production (volatilization) of aluminum chlorides starts at ~330°C. Phosgene concentrations were observed to go through a maximum at ~320°C. It is suggested that the following reactions occur (49).

\[ CCl₄ + O(\text{surface}) \rightarrow COCl₂ + 2Cl(\text{surface}) \]  \hspace{1cm} (5)

\[ COCl₂ + O(\text{surface}) \rightarrow CO₂(g) + 2Cl(\text{surface}) \]  \hspace{1cm} (6)
The method used by Podor and Bertoti (49) did not provide information about chloride products at the alumina surface, but it seems reasonable to assume that as oxygen is removed from the lattice, aluminum oxychloride compounds are formed. As the reaction progresses these compounds must become richer in chlorine until AlCl₃ is formed and removed by vaporization. Chlorination with phosgene would be expected to follow the same reaction path, starting with reaction 6.

The important point of Podor's study is that chlorination did not start until phosgene production started. At temperatures slightly above those at which phosgene production started the reaction rate increased rapidly, yet the observed concentration of phosgene was greatly reduced. This suggests that phosgene is an important intermediate.

Use of CO-Cl₂ mixtures has also been investigated and found to be less effective than phosgene for the chlorination of both aluminas and clays at temperatures below ~700°C (25,36). The reduced efficiency results from the reduced probability of absorbing two molecules at a reaction site as opposed to one. At temperatures above 700°C, CO-Cl₂ mixtures are virtually identical to phosgene owing to the complete dissociation of the latter compound at higher temperatures.

**Solid carbon**

The use of solid carbon as a reductant requires the simultaneous reaction of two solids and a gas. The solid carbon reaction is a complex reaction that is not fully understood. Evidence from titanium dioxide chlorinations indicates that carbon may initiate the reaction by promoting the formation of reactive chlorine species (6). This same study indicated that an oxide-carbon separation of more than 30 microns
stopped reaction, which is further evidence for a reactive species such as a free radical. Although analogous studies have not been done for alumina chlorination, the same effect has been qualitatively observed. Studies using different methods of contacting carbon and alumina have shown that the more intimate the contact the higher the conversion of alumina (3,44). Pyrolytically coating cracked hydrocarbons on gamma-alumina gives the fastest rate and highest conversion, greater than 90%. Less intimate methods of contact resulted in lower conversions and slower reaction times (44).

Landsberg (36) reported that the addition of oxygen to the reactant gas stream resulted in an 800% increase in conversion, presumably by inducing the formation of CO in the packed bed. This result further suggests that the limiting factor in the gas solid-reaction system is contact between the oxide and carbon.

Oxide effects

The form of the metal oxide can have a significant effect on its reactivity. Alpha-alumina (low surface area) is significantly less reactive than gamma-alumina (high surface area). Gamma-alumina is more reactive at low temperatures <800°C (25,36). At higher temperatures, gamma-alumina starts the phase transformation to the alpha form with a subsequent reduction in reactivity.

Chlorination of Aluminum Ores

The above results were obtained from the chlorination of alumina, but the same characteristics hold for bauxite, clay and fly ash chlorination (1,2,3,41,44,46). A complication with low-grade aluminous
ores is that they are typically low surface area materials and exhibit a reduced reactivity compared to gamma-alumina. An additional drawback is that these ores contain one or more oxides that consume chlorine, such as silica.

Much of the work with low grade aluminum ores has concentrated on the chlorination of kaolin, which has a relatively high aluminum content and is readily available (25,36,37,51). An important observation common to all of these studies is that some silica will be chlorinated (25). Silica chlorination appears to result from its incorporation into the mineral structure, since in all of these cases the reactors were constructed of quartz which did not show any signs of attack (25).

Coal fly ash has also been considered as a possible candidate for chlorination in spite of the fact that it exhibits some of the worst possible characteristics. Fly ash has significant silica, calcium and iron contents and very low specific surface areas (1). Silica and calcium chlorides have very little commercial value, and iron chloride presents a significant problem with respect to product purification (25). On the plus side, fly ash is available from a sole source in appreciable quantity, has uniform properties and is a potential disposal problem (1). For these reasons there have been several studies on fly ash carbochlorination (1,2,41).

Mehrotra et al. (41) chlorinated fly ash in a fluidized bed with chlorine using various combinations of CO and carbon. Relatively low conversions, less than 24% alumina over 3 hours, were obtained in this system. It was concluded that the reaction was being hindered by the formation of a molten salt layer composed of alkali chlorides on the
individual ash particles. Much of the support for this argument is that the reaction is very rapid at first but slows dramatically after the first 10 minutes of reaction. A model based on this theory fits the observed data, but ignores published work indicating that alkali metals act as a catalyst for the chlorination of alumina in mixed oxide ores (28,51,57).

An alternate hypothesis that is in better agreement with the literature is that the ash used was not ignited before chlorination and contained carbon. This carbon, being in good contact with the ash, reacted very quickly until it was used up, accounting for the rapid initial reaction. After the in situ carbon was consumed, the only reductant available was CO which was not as effective because of the low surface area of the ash.

Adelman investigated fly ash chlorination using a packed bed reactor and carbon reductant (1), and fly-ash pellets using COCl₂ as a combined chlorinator-reductant (2). Both studies are in general agreement with the alumina/bauxite chlorination studies previously referenced. Some of the more important results are discussed below.

In the packed bed studies (1) a maximum of 80% aluminum recovery was obtained over a two-hour period, by which time the reaction virtually ceased. In addition there was no preferential chlorination of the major ash components since silicon and aluminum were converted at the same rate throughout the entire period of reaction. The completion of reaction at approximately two hours was attributed to loss of contact between the carbon and ash particles.

In the phosgene studies, a pellet or a loose bed of ash was
chlorinated, using a microbalance to monitor the reaction rate. The ash used had been leached in 6M HCl at 100°C to simplify the study by removing all materials except the silicates and aluminates, which were considered to be the primary compounds of interest.

Physical examination of the ash at various conversions showed that the ash is composed of a matrix of reactive material surrounding unreactive particles. Surface reaction was found to control the reaction over the temperature range studied (450-700°C). The chlorination kinetics were also found to be accurately described by the shrinking core model.

A major conclusion of this research was that phosgene dissociation will be a major problem for a commercial system. At the higher reaction temperatures, a significant amount of phosgene dissociated to CO and Cl₂ negating the kinetic advantages of using phosgene. It is also possible that fly ash may catalyze the dissociation at lower temperatures. Phosgene dissociation increases the reactor size and amount of phosgene required to process a given quantity of ash.

Catalysis of Gas-Solid Chlorination

The relatively slow chlorination of low-grade aluminous materials has led to the examination of possible catalysts. Much of this work has been done with the chlorination of kaolin, an aluminous clay (25,28,37), but some work has been done with alumina (51) and plagioclase (57). The most commonly suggested catalyst is NaCl although the other alkali chlorides and B₂O₃ have also been investigated (37).

Hille and Durrwachter (28) tested the catalytic effect of NaCl by chlorinating gamma and alpha-alumina in a three-phase fluidized bed with
phosgene. The yield of AlCl₃ was increased by 300% at 550°C when a ratio of NaCl:Al₂O₃ of 3:5 was used. A maximum increase of 360% was obtained when a ratio of ~1:1 was used. At ratios above 1:1 the AlCl₃ yield declined. The lower yields were attributed to the collapse of the fluidized bed rather than to failure of the catalyst.

Hille and Durrwachter (28) does not specifically report the effect of NaCl on alpha-alumina chlorination other than to report that it is similarly enhanced, although not to the same extent as gamma-alumina. Chlorination of alpha-alumina was not pursued in depth because of technical difficulties with fluidized bed operation and with particulate removal from the product gas stream.

Landsberg and Wilson (37) studied the effect of LiCl, NaCl, KCl, RbCl and CsCl on the chlorination of kaolin pellets in a packed bed reactor. The effectiveness of alkali chlorides appears to be a function of both temperature and molecular weight. In general the higher the molecular weight, the less effective the catalyst. Temperature dependence of catalyst effectiveness is more complicated, but examination of the data suggests that catalyst activity goes through a maximum at a temperature somewhere between the melting and boiling points of the MAICl₄ complex (M=alkali metal). Comparative studies indicated that NaCl is the best overall catalyst for selective chlorination of kaolin (37). A study of the chlorination of plagioclase, a refractory aluminosilicate, gave very similar results (57).

Landsberg and Wilson (37) postulated that the catalytic effect of the NaCl resulted from the formation of NaAlCl₄ which improved reaction rates by solubilizing alumina. This dissolved alumina could be
transported to reaction sites at the carbon by the NaAlCl₄ melt.

**Fused Salt Chlorination**

The majority of the work reported on the use of NaCl as a catalyst used it in gas-solid systems. Recently processes have been patented for chlorinating alumina in carbon-alumina slurries made from NaCl-AlCl₃ melts. The concepts behind the fused salt slurry reactor are an extension of those for using NaCl as a catalyst in the gas-solid reaction system.

One fused salt process reported in the literature is a patent by Slatin (55). In this process, Al₂O₃ is dissolved from low-grade ores by a mixture of molten alkali chlorides and fluorides. The purpose of adding fluorides is to enhance the solubility of alumina. Undissolved material is then removed and the dissolved oxides chlorinated in the presence of carbon using chlorine in a separate reactor. Potential difficulties with this process are disposal of SiF₄ that would form from silicates in the ore and the manipulation of the fused salt in a two-step process.

Haupin et al. (26) and Wohleber and Cochran (64) have patented various aspects of a fused salt process that uses a NaCl-AlCl₃ melt as the reaction medium. Two important claims made in these patents are that chlorine utilization is independent of the type of alumina being used, and that a minimum of 30% AlCl₃ is required in order to maintain chlorine utilization. It is also specified that the reaction temperature should be between 600 and 750°C. The recommended alumina:salt and carbon:salt ratios were as high as possible, 0.05-0.5 lbs/lb of slurry, while still maintaining good mixing of the slurry. Excessively high
levels of either material caused the bath to become too viscous, reducing Cl₂ dispersion.

None of the above processes have been commercialized since AlCl₃ is not currently used as an aluminum precursor. At this time the cost of producing AlCl₃ more than offsets the advantages of using the Alcoa AlCl₃ electrolytic cell (17).

Properties of Sodium Aluminochloride Melts

In order to discuss the chemistry and mechanism behind the catalytic effects of NaCl-AlCl₃ melts, it is necessary to understand the properties of the melt.

**Physical properties**

Figure 1 is a phase diagram for the NaCl-AlCl₃ system. The shaded portion in the single-phase liquid region in the vicinity of 45% AlCl₃ is the operating region for this study. In this region, the vapor pressure of the melt is less than 1 atmosphere and the system is a single phase liquid. Any attempt to operate at AlCl₃ contents to the right of the shaded region will result in boiling of the liquid at 1 atm. system pressure.

The density and viscosity of a 40% AlCl₃-60% NaCl melt at various temperatures is shown in Table 2. In general physical property data for these and other fused salts are limited because of the difficulty of obtaining good measurements. Examination of Table 2 shows that the hydrodynamic properties of the melt are very similar to more common liquids.
Figure 1. NaCl-AlCl₃ phase diagram. Shaded section represents the operating region for fused salt chlorination at 1 atmosphere (19,39,40,61)
Table 2. Density and viscosity of 60% NaCl-40% AlCl₃ melts (10,11)

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>Density g cm⁻¹</th>
<th>Viscosity cP</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>1.44</td>
<td>1.496</td>
</tr>
<tr>
<td>700</td>
<td>1.38</td>
<td>0.853</td>
</tr>
<tr>
<td>800</td>
<td>1.33</td>
<td>0.539</td>
</tr>
</tbody>
</table>

Chemical properties

In contrast to the physical properties, there are significant chemical interactions that occur in the melt as its composition is changed (12). Equations 7-9 describe the equilibrium reactions occurring in the melt:

\[ 2\text{AlCl}_3 \leftrightarrow \text{Al}_2\text{Cl}_6 \] (7)

\[ \text{Na}^+ + \text{AlCl}_4^- + \text{AlCl}_3 \leftrightarrow \text{Na}^+ + \text{Al}_2\text{Cl}_7^- \] (8)

\[ 2\text{Na}^+ + \text{AlCl}_4^- \leftrightarrow 2\text{Na}^+ + \text{Al}_2\text{Cl}_7^- + \text{Cl}^- \] (9)

A basic melt (NaCl-rich) consists primarily of \(\text{Cl}^-\) and \(\text{AlCl}_4^-\) anions with a very small concentration of \(\text{AlCl}_3\). An acidic melt (AlCl₃ rich) contains predominantly \(\text{AlCl}_4^-\) and \(\text{Al}_2\text{Cl}_7^-\) anions with \(\text{AlCl}_3\) concentrations several orders of magnitude greater that for an acidic melt (12). The properties of NaCl-AlCl₃ melts tend to be unstable near equimolar mixtures because of these equilibrium reactions (4).

Linga et al. (40) and Dewing (19) have investigated the vapor pressure of NaCl-AlCl₃ mixtures as a function of temperature and
composition. An important observation of these studies is that in melts containing less than 65 mole percent NaCl, AlCl₃ is a major component in the vapor as well as NaAlCl₄. Therefore, in a chlorination reactor the melt composition will be a function of temperature and AlCl₃ production rate. If the AlCl₃ production rate is low then the melt composition will shift towards pure NaCl until the melt is saturated in NaCl. If the AlCl₃ production rate is higher than the existing vaporization rate, the melt composition will shift towards the boiling point curve shown on Figure 1. It is therefore possible to control the melt composition within the limits indicated in Figure 1 by controlling the vaporization rate of AlCl₃.

A final property of NaCl-AlCl₃ mixtures is that they are extremely hygroscopic. In the presence of water, AlCl₃ decomposes to HCl and Al₂O₃. Because of this, all handling of the chloride melt must be done under a dry atmosphere which complicates both experimental procedures and potential commercial processing.

Reaction Mechanism

Unlike gas-solid reaction systems, it is possible using electrochemical techniques, to monitor the formation of reaction intermediates in a fused salt. In a study of the chlorination of alumina by phosgene in a KCl-LiCl eutectic, Seon et al. (52) determined that the Al₂O₃ was first dissolved in the melt as AlOCl₂ which then reacted with phosgene in two steps. The overall process is shown in equations 10-12:
Oxide dissociation:

\[
\text{Al}_2\text{O}_3(s) + 4\text{Cl}^- \leftrightarrow 2\text{AlOCl}^- + \text{O}^{2-}
\]  
(10)

Melt reaction:

(slow)

\[
2\text{AlOCl}_2^- + \text{COCl}_2(g) \rightarrow \text{Al}_2\text{OCl}_5^- + \text{CO}_2(g) + \text{Cl}^- 
\]  
(11)

(fast)

\[
\text{Al}_2\text{OCl}_5^- + \text{Cl}^- \rightarrow \text{AlCl}_4^- + \text{AlOCl}_2^- 
\]  
(12)

Reaction 11 is said to occur slowly compared to reaction 12 and the rate of reaction 10 is a function of the alumina. Alpha-alumina with its low reactivity takes longer to dissolve and has a lower solubility in the melt than gamma-alumina (52). It was also reported that as the chlorination progressed, the chlorination rate increased which was attributed to a build-up of AlCl3 in the melt. Aluminum trichloride is believed to enhance the solubility of Al2O3 in chloride melts by reaction 13:

\[
\text{AlCl}_4^- + \text{O}^{2-} \leftrightarrow \text{AlOCl}_2^- + 2\text{Cl}^- 
\]  
(13)

Further support for the catalytic effect of reaction 13 is given by Haupin's claim that a minimum AlCl3 concentration is required to obtain maximum chlorine utilization (26).

**Fused Salt Chlorination of Other Metals**

Fused salt chlorination of metal oxides other than alumina has also been studied. One study involved chlorination of titaniferrous ores using FeCl2 or FeCl3 (22,23,24) and a second was a series of studies on
the rate limiting step in the chlorination of metal oxides by
Inyushkina (30,31,32).

Titaniferrous ores

The Gleaser patents (22,23,24) describe a molten salt alternative to
the gas-solid chlorination system traditionally used to refine titania
ores. The primary significance of these patents is that they propose
the use of a molten salt to stabilize some of the reaction species and
create a system that is closer to thermodynamic equilibrium than
otherwise might be possible.

As a result of the closer approach to equilibrium conditions, this
system is capable of producing a selective chlorination between TiO₂ and
Fe₂O₃. Any iron oxides present in the ore are either completely reduced
to the iron metal or, at most, chlorinated to FeCl₂. The purpose of
using a molten salt is to trap FeCl₂ in the melt, rather than letting it
vaporize out of the reactor and contaminate the TiCl₃-TiCl₄ product.

The melt is formed by adding sodium or potassium chloride to the
reaction mixture. According to Gleaser, up to 90% of the melt may be
alkali chloride if very high operating temperatures are desired. This
particular process is a good example of how the chlorine exchange
reactions previously observed can be used to a process advantage.

Oxide chlorination study

Inyushkina attempted to determine the rate controlling step in the
chlorination of oxides in alkali-alkaline earth chloride melts. Three
separate aspects of the chlorination were examined: desorption of carbon
oxides (30), absorption of chlorine (31), and dissolution of metal
oxides (32).

The experimental method in each study was to examine the rate of absorption or desorption of a particular component with and without reaction. If the rate of mass transfer without chlorine was the same as the chlorination rate, then that step was assumed to be rate limiting. The results of these studies are far from conclusive.

In the carbon oxide dissolution study (30), it was found that carbon only influenced the chlorination rate for oxides whose chlorides were less stable than the chloride salt(s) that comprised the melt. This is experimental verification of the chlorine exchange reactions described previously. Another important point was that elements that could form oxychlorides also reacted faster than would be predicted by carbon desorption rates.

The other two studies investigated the rate of chlorine uptake (31) and oxide dissolution (32). The conclusions of these studies were that chlorine adsorption did not limit the chlorination of MgO, CuO, Al₂O₃ or V₂O₃ in alkali-alkaline earth chloride melts. The third study (32) was not as complete, but concluded that the rate controlling step was the dissolution of the oxide for MgO and TiO₂ chlorination in alkali chloride melts.
SLURRY REACTION CHARACTERISTICS

The basic equations used to analyze the behavior of the fused salt chlorination reaction are developed in this section. A description of the two major limiting cases of pure oxide carbochlorination are developed for the analysis of the alumina chlorinations done in this study. The effect of multicomponent oxides on the reaction characteristics is also discussed.

Carbochlorination of a Pure Oxide

A variety of three phase reactions have been described in the literature (21,53). The most common of these is the simultaneous reaction of a dissolved gas and a liquid or another dissolved gas at a solid catalyst surface. The other major class is the reaction of solids suspended in an inert liquid with a dissolved gas. This second class of reactions may be further characterized by the solubility of the solid in the liquid. In all of these systems, only two of the three phases contribute reactants and only one solid phase is present. The carbochlorination of metal oxides in its general form does not fit into any of these classes because there are three reactants. Two are solids, one soluble and the other not, and the third is a dissolved gas.

Based on the results of this study and those reported in the literature (13,52), it was determined that the dissolved alumina and chlorine react at the carbon surface to form volatile reaction products. For this reason, of the systems described in the literature, carbochlorination is most closely related to the case of an insoluble solid reactant that forms soluble products. This particular type of
reaction is analogous to the shrinking core models used to describe gas-solid reactions where the reaction products are volatile. The primary difference between the equations that describe the slurry reaction and the gas-solid reaction is an additional term to account for the mass transfer resistance at the gas-liquid interface. It can be shown that under certain conditions the carbochlorination system can be described by this same slurry reaction model.

The metal oxychlorides chlorinated in this study contain a single oxygen atom so a 1:1 reaction stoichiometry exists between the dissolved oxychloride and chlorine. If it is assumed that the reaction is first order with respect to each of the dissolved aluminum oxychloride and chlorine species, then the following rate expression may be used:

\[ r = -r_M = -r_{Cl} = k_{1} a_{C} C_{Cl, C} C_{M, C} \]  

where:  
- \( r \) = Moles produced, g-mole min\(^{-1}\);  
- \( r_M \) = Moles metal oxychloride produced, g-mole min\(^{-1}\);  
- \( r_{Cl} \) = Moles Cl\(_2\) produced, g-mole min\(^{-1}\);  
- \( k_{1} \) = Reaction rate constant, cm\(^4\) g-mole\(^{-1}\) min\(^{-1}\)  
- \( C_{Cl, C} \) = Concentration of dissolved Cl\(_2\) at carbon, g-mole cm\(^{-3}\);  
- \( C_{M, C} \) = Concentration of metal oxychloride at carbon, g-mole cm\(^{-3}\);  
- \( a_{C} \) = Total carbon surface area, cm\(^2\).

Figure 2 is a schematic of the chlorine and dissolved metal oxide concentration profiles in the slurry. The model, as shown in Figure 2, assumes that the mass transfer resistance in the gas-phase is
Figure 2. Chlorine and metal oxychloride concentration profiles in the carbochlorination reaction.
insignificant and that there is no concentration gradient in the gas. It is also assumed that the melt is saturated in chlorine at the gas-liquid interface. Both of these assumptions are valid for gases that have a low solubility in the liquid (21), which is valid for the chlorine-NaCl-AlCl₃ system (15,62).

Equations 11-12 and 13-14 are expressions for the mass transfer of chlorine and metal oxychloride respectively to the carbon surface. These equations have been written assuming that the chlorine and oxide fluxes are equal to the consumption of each component by reaction, i.e. stable concentrations at the carbon surface have been established. It is also assumed that the melt is saturated in the dissolved oxychloride at the oxide surface.

Transfer of chlorine to the bulk liquid:

$$-r_{Cl} = K_{Cl,g} a_g [C_{Cl,i} - C_{Cl,b}]$$  \hspace{1cm} (11)

and from the bulk liquid to the carbon surface:

$$-r_{Cl} = K_{Cl,ls} a_C [C_{Cl,b} - C_{Cl,s}]$$  \hspace{1cm} (12)

where $K_{Cl,g}$ = Gas-liquid mass transfer coefficient, g-mole min⁻¹cm⁻²;
$K_{Cl,ls}$ = Liquid-carbon Cl₂ mass transfer coefficient, g-mole min⁻¹cm⁻²;
$a_g$ = Total gas surface area, cm²;
$C_{Cl,i}$ = Cl₂ concentration at gas interface, g-mole cm⁻³;
$C_{Cl,b}$ = Cl₂ concentration in bulk fluid, g-mole cm⁻³.
For the metal oxychloride:

$$-r_H = K_{M,s} \cdot a_M \cdot [C_{M,1} - C_{M,b}]$$  \hspace{1cm} (13)

and from the bulk liquid to the carbon surface:

$$-r_M = K_{M,ls} \cdot a_C \cdot [C_{M,b} - C_{M,C}]$$  \hspace{1cm} (14)

where

- \( K_{M,s} \) = Oxide-liquid mass transfer coefficient, g-mole min\(^{-1}\)cm\(^{-2}\);
- \( K_{M,ls} \) = Liquid-carbon oxychloride mass transfer coefficient, g-mole min\(^{-1}\)cm\(^{-2}\);
- \( a_M \) = Total oxide surface area, cm\(^2\);
- \( C_{M,i} \) = Oxychloride concentration at oxide surface, g-mole cm\(^{-3}\);
- \( C_{M,b} \) = Oxychloride concentration in bulk liquid, g-mole cm\(^{-3}\).

Solving equations 11 and 12 to eliminate \( C_{Cl,b} \) gives:

$$-r_{Cl} = \left[ \frac{1}{K_{Cl,ls}a_C} + \frac{1}{K_{Cl,g}a_g} \right]^{-1} \cdot \left[ C_{Cl,i} - C_{Cl,g} \right]$$  \hspace{1cm} (15)

and similarly for \( C_{M,b} \) in equations 13 and 14:

$$-r_M = \left[ \frac{1}{K_{M,ls}a_C} + \frac{1}{K_{M,g}a_M} \right]^{-1} \cdot \left[ C_{M,i} - C_{M,s} \right]$$  \hspace{1cm} (16)

Equations 10, 15 and 16 form a system of nonlinear differential equations that can be used to determine reaction rates as a function of time. The system can be simplified to a linear one, however, if the concentration of one of the two dissolved reactants at the carbon surface is large compared to the other. Such a condition would be
expected if the solubility of one component was significantly larger than the other. In this case a pseudo first-order reaction can be assumed and equation 11 simplified to the following:

\[ r = K' a_C C_{Cl, C} = K'' a_C C_{H, C} \]  

(17)

where \( K' \) = Pseudo first-order rate constant for \( Cl_2 \),
\[ \text{g-moles cm min}^{-1}; \]
\( K'' \) = Pseudo first-order rate constant for oxychloride,
\[ \text{g-moles cm min}^{-1}. \]

Using Equation 17 along with equations 15 and 16 results in the following limiting cases.

For high oxide solubility,

\[ -\frac{C_{Cl, i}}{r_{Cl}} = \frac{1}{a_{Cl, g} K'} + \frac{1}{a_C} \left[ \frac{1}{K_{Cl, Is}} + \frac{1}{K'} \right] \]  

(18)

and high chlorine solubility:

\[ -\frac{C_{H, i}}{r_{H}} = \frac{1}{a_{H} K''} + \frac{1}{a_C} \left[ \frac{1}{K_{H, Is}} + \frac{1}{K''} \right] \]  

(19)

Data reported by Vaernes and Ostvold (62) for chlorine, and Tremillion et al. (60) for alumina, indicate that \( Al_2O_3 \) is at least an order of magnitude more soluble than chlorine in \( NaCl-AlCl_3 \) melts. For this reason equation 19 was not considered for analysis of the alumina chlorinations, but it could be appropriate for less soluble metal oxides.

An important characteristic of equation 18, which is applicable to the alumina chlorinations is that the reaction rate is independent of oxide loading. A second important characteristic is that, assuming
$K_{Cl,g}$ and $a_g$ are not influenced by solids loading, then only $a_C$ will change as the carbon content of the slurry is changed.

If $-C_{Cl,i}/r_{Cl}$ is plotted versus $1/a_C$, then the slope and intercept of this line indicate the extent to which gas-liquid mass transfer and reaction at (or mass transfer to) the carbon surface influence the reaction rate. Gas-liquid transfer control is characterized by a straight line of slope zero, while surface area control is evidenced by a zero intercept. A line with both a nonzero slope and intercept indicates that both gas-liquid mass transfer and particle surface area are important.

If the particle surface area controls the reaction rate, the system is either reaction or solid-liquid mass transfer controlled. Reaction control is indicated by a strong temperature dependence while solid-liquid mass transfer is virtually independent of temperature.

The assumption of constant $K_{Cl,g}$ and $a_g$ with solids loading is not necessarily valid since several studies that have shown that both of these parameters may be affected by slurry composition (16,21,45,53,56). Therefore, the possibility of the $K_{Cl,g}$ and $a_g$ changing with solids loading must not be overlooked when analyzing the effect of different solid-liquid ratios on the reaction rate.

Mixed Oxides

The development presented above is based on the chlorination of a pure oxide. In the case of NaCl-AlCl$_3$ slurries, virtually all the oxides commonly found in multicomponent ores are less thermodynamically stable, in the presence of AlCl$_3$, than their corresponding chloride.
Therefore, the non-alumina oxides in a mixed ore will tend to be chlorinated by AlCl₃ to produce AlOCl and the corresponding metal chloride.

The rate at which the non-alumina metal chlorides are chlorinated by AlCl₃ compared to the carbochlorination rates is a matter of kinetics and cannot be predicted from thermodynamics. However, it is believed that the exchange reaction would be faster than the carbochlorination for the following reasons. First, the oxide must be converted to the oxychloride to be soluble in the melt. Once the oxychloride is formed it will have a high probability of contacting AlCl₃ in the melt before reaching the carbon surface. Secondly, the reaction between AlCl₃ and the oxychloride is homogeneous and bimolecular, so unlike the carbochlorination reaction there is no solid-liquid diffusion and a minimum number of reactants are required. Therefore, the oxychloride-AlCl₃ reaction is probably kinetically favored over the carbochlorination reaction.

Since aluminum oxychloride is the only oxychloride reacting by carbochlorination, equations 18 and 19 would still describe the chlorination process as long as the total reaction rate at the oxide surface was high enough to maintain AlOCl saturation at the oxide surface like pure alumina would. It also follows that in this case, alumina chlorination would be identical experimentally to the multicomponent case.

Unlike a pure oxide a mixed metal oxide could show a change in reactivity as a function time. Since the oxide is heterogeneous, it would be expected to become enriched in less reactive components at the
surface. This could result in an overall decrease in the production of aluminum oxychloride by alumina dissolution or the melt oxide reaction, depending on the rates of surface reaction.

The oxide surface limited reaction would be difficult if not impossible to quantitatively describe a priori, since it would require a great deal of information about the oxide structure and reactivity. However, the following observations may be made. First, the overall consumption rate of chlorine and carbon for the mixed oxide chlorination would be lower than that for the pure alumina, all other conditions being equal. Second, it would be expected that there would be an enrichment in the unreacted oxide of the less reactive components, which would result in a declining reaction rate over the course of an experiment.
EXPERIMENTAL EQUIPMENT AND PROCEDURES

Aluminum Chloride Purification

Aluminum chloride from two sources was used in the experimental work. Anhydrous, sublimed AlCl₃ from Fisher Scientific was used for the fly ash solubility studies. Aluminum chloride used in the chlorination experiments was purchased from Alpha Products (Cat. #89914). Both materials were resublimed to remove hydrolysis products and contaminants.

Up to 130g of AlCl₃ could be purified in the sublimer shown in Figure 3. The impure chloride was placed in the unit and covered with a layer of aluminum turnings (2.5g) or granules (7.5g) to remove iron chloride from the vapor. The charge was then heated to 170°C using heating tape or a tube furnace, while cooling water was run through the cold finger to condense the AlCl₃ vapor. The contaminants were not vaporized, but remained in the lower portion of the sublimer. The sublimer was operated at atmospheric pressure. A mineral oil trap at the gas outlet allowed excess gas to escape, but prevented atmospheric water from contaminating the sample.

Total sublimation time ranged from 18 to 24 hours, and resulted in average product yields of 80 to 90 percent. At the end of the run the sublimer was sealed, cooled and the cold finger dried with compressed air. Once the sublimer was dried it was transferred to a drybox for product collection. The purified product was stored under a dry atmosphere at all times.
Figure 3. Sublimer used for AlCl$_3$ purification
Fly Ash Solubility Experiments

The effect of NaCl-AlCl₃ melts on fly ash was evaluated by a series of solubility experiments. The system used for these experiments is diagrammed in Figure 4. The fused salt and ash were contacted in a quartz reactor 30 cm by 2.5 cm in diameter that was heated using a clam shell furnace. The slurry was agitated by injecting nitrogen into the melt. Gas exiting the reactor was passed through an air-cooled condenser to remove AlCl₃ and FeCl₃ vapor. The condenser outlet was vented through a mineral oil trap that isolated the system from the atmosphere. The effect of fused salt on the ash was determined from the change in ash composition and weight.

For each test the reactor was charged with 50g of the NaCl-AlCl₃ mixture and 2g of ash under an inert atmosphere, and heated in the furnace, which was outside of the drybox. A slow nitrogen purge was continuously run through the reactor to maintain a dry atmosphere over the salt. Once the salt liquified, at approximately 180°C, nitrogen was injected into the slurry at 50 cm³ min⁻¹ until the system reached the test temperature, either 400 or 600°C. The flow rate was then increased to 250 cm³ min⁻¹, and the reactor was held at temperature for 0.5 hours. The furnace was then turned off and opened to cool the reactor.

Once the reactor temperature had dropped to between 200 to 250°C the contents were poured into an Erlenmeyer flask and allowed to cool to room temperature. The solidified melt was dissolved in water and filtered using glass fiber paper and vacuum filtration. The remaining solids were washed and dried, then analyzed using atomic absorption spectrophotometry.
Figure 4. Equipment system used for studying the solubility of fly ash in NaCl-AlCl₃ melts.
Fused Salt Chlorination Experimental Design

Two considerations dominated the chlorination system design, first to be able to study the chlorination of both single and multiple component oxides, and second to extract as much information from an individual experiment as possible. Therefore the equipment was designed to obtain the following data:

1. Chlorination rates of silica, alumina, iron and titanium in the oxide.
2. Chlorine and carbon conversions.
3. Overall mass balances for the major reactants.

This information was gathered through a variety of measurements. Reaction rates of individual oxide components were monitored by sampling the slurry, while chlorine conversion was measured by analyzing the reactor product gas for chlorine. Carbon conversions could be obtained from either the slurry samples or analysis of the product gas. Chlorination of a pure oxide such as alumina did not require slurry sampling, since all desired rate data were obtainable from the product gas analyses.

In addition to measurements taken during chlorination, the contents of the reactor and the metal chloride condensers were collected at the end of each experiment and analyzed. This information was used to determine the overall mass balances for the oxide(s), carbon and melt components.
Chlorination Equipment

The chlorination equipment consisted of three major sections: the reactor, metal chloride condensers and noncondensable product gas analysis system. A major consideration in the construction of this equipment was that it be as mechanically simple and reliable as possible. Figure 5 is a schematic of the system and Figure 6 shows the assembled equipment and its protective enclosure.

Reactor

The reactor, shown in Figure 7, was approximately 50 cm high and 6.8 cm in diameter (lower section). Because NaCl-AlCl₃ melts are very corrosive, the choice of materials in contact with the melt was limited to graphite and quartz (26). Since carbon was a major chlorination reactant, quartz was used for the reactor body and internals. Pyrex was used for the reactor head, as well as all other equipment items.

There were four ports in the reactor head, shown in Figure 7. The two large ports were for the stirrer and slurry sampler, while the smaller ports were for a thermocouple well and chlorine sparger. Purge gas (helium) was injected through inlets on each of the large ports to protect the sampler and stirrer seal from corrosive gases, and to sweep reaction products out of the reactor.

A paddle stirrer was used to suspend the slurry. Although gas sparging might have been a mechanically simpler method of agitation, it was decided that a stirrer would be more likely to produce the uniform solids distribution that was critical for accurate slurry sampling.

The stirrer, shown in Figure 7, was constructed from 316 stainless steel and quartz. A 9 mm diameter quartz rod was used for the wetted
Figure 5. Fused salt chlorination equipment flow diagram
A: Chlorination reactor, condensers and gas valve bypass inside protective enclosure.

B: Detail view of reactor head showing the stirrer seal-bearing assembly and sampler adapter.

Figure 6. Fused salt chlorination equipment
Figure 7. Fused salt slurry reactor schematic
portion of the stirrer shaft, and a 1/16" quartz plate for the blades, which were 1 cm square and spaced 3 cm apart. That portion of the shaft that ran through the seal and support bearings was made from 3/8" stainless steel rod to assure proper alignment. The metal and quartz sections were joined with a stainless steel chuck. The stirrer was supported by a rack mounted bearing assembly above the reactor (Figure 6b). Metal portions of the stirrer inside the reactor were kept as high in the stirrer port as possible in order to minimize corrosion.

The stirrer seal, depicted in Figure 8, was modeled after mechanical seals found in centrifugal pumps. It consisted of a stationary teflon seat attached to the reactor port with a standard glass taper joint and a floating 316 stainless steel face keyed to the stirrer shaft and spring loaded against the teflon seat. Experimentation showed that a recessed center in the metal face resulted in greater tolerance for misalignment of the stirrer shaft with respect to the teflon seat than would a flat surface.

Advantages of this seal over a packing box were low spinning resistance and a high tolerance for misalignment between the reactor and stirrer support bearings, which also reduced equipment vibration. Seal wear during a single experiment was not a problem even though no lubricant was used. However, in order to reassemble the seal properly it was necessary to reface the teflon surface after each run. This was easily done using emery paper on a flat surface.

Chlorine sparging and reactor heating were not significantly different from more conventional reactor systems. The reaction temperature was monitored by a thermocouple probe in the slurry. The
Figure 8. Cross section view of the mechanical stirrer seal
lower 20 cm of the reactor was heated with an electric resistance furnace to reaction temperatures, while the reactor head was maintained at 180 °C with heating tape to heat the purge gas and prevent the condensation of metal chlorides. Control for both the furnace and heating tape was provided by Omega Series 4000 proportional temperature controllers, the output from which was attenuated with a variac to balance heating power against the thermal load to reduce temperature cycling.

Chlorine was injected into the slurry as close to the reactor bottom and as near the agitator as possible to promote gas distribution. The sparger consisted of a 6 mm diameter closed-end tube, with three 3 mm holes placed at the base of the tube, equidistant about the circumference (inset Figure 7). This design was a compromise between an open tube and a glass frit. The latter would normally be preferred; however, frits are virtually impossible to clean once material has solidified in the pores, which would have occurred at the end of a run.

The other major design element of the reactor design was slurry sampling, which was complicated by the necessity of maintaining a water-free atmosphere. A sampling device, shown in Figure 9, and based on a device reported by Bamberger (5) was built and tested on water-ash slurries, which were similar in rheology to fused salt slurries. Results of these tests (Appendix A) indicated that representative samples could be obtained if the -325 mesh (-45 micron) fraction of the ash was used in the slurry. Larger ash particles tended to settle out of the slurry, creating a sampling bias.

The sampler consisted of two parts, an adapter attached to the
Figure 9. Apparatus used for sampling the contents of the fused salt slurry reactor
reactor throughout the chlorination and a detachable section for transporting samples from the reactor to a drybag where they were unloaded in a controlled atmosphere. Large bore ball valves were used to seal the adapter and movable section. Purge ports allowed the unit to be flushed with helium. Samples were collected in quartz buckets attached to the sampling rod (inset Figure 9) that was lowered into the reactor.

Chlorine and helium flows to the reactor were controlled by Matheson #8249 mass flowmeters, as were all gas flows in the system. A check valve in the chlorine line prevented backpressure in the reactor from forcing the melt out of the reactor through the sparger. Pressure in the reactor was monitored by a U-tube manometer attached to the helium purge line.

Metal chloride condensers

In order to complete component mass balances, vaporized metal chloride products were removed from the product gas stream by condensation. Condensing the metal chlorides also protected the gas chromatograph (G.C.) system. If not removed, the metal chlorides would have quickly plugged the sampling system and contaminated the G.C. column.

Product gases were removed from the reactor via a heated tube maintained at 180°C to prevent premature condensation of the metal chlorides. Heating for the transfer tube was provided by a heating tape-controller system identical to that used for the reactor head.

Because aluminum chloride condenses as a solid and may cause blockages, and the wide range of condensation temperatures for potential
metal chloride products (FeCl₃ boils at 315°C while SiCl₄ boils at 57°C), two condensers were used. The first condenser, shown in Figure 10, was 30 cm high and 8 cm in diameter and removed AlCl₃ and FeCl₃ along with any sodium halide complexes that exited the reactor. Internal clearances in this condenser were large in order to reduce the possibility of solid AlCl₃ product plugging the unit. The space below the cold finger and part of the annulus were packed with 5mm glass beads to filter condensed AlCl₃ particulates out of the product gas stream.

Aluminum chloride condensation was most noticeable at the inlet to the condenser, starting immediately at the end of the heated portion of the transfer tube. During high conversion chlorinations, it was usually necessary to clear the condenser inlet once or twice during a run by heating it with an electric heating gun.

The second condenser was similar in design to the first, and was used to trap SiCl₄ and TiCl₄. Internal clearances in this unit were smaller than the first and it was not packed with beads, since SiCl₄ and TiCl₄ condense as liquids. When multicomponent oxides were chlorinated, this condenser was operated at -30°C with a CCl₄-dry ice cooling bath. For alumina chlorinations, it was run at 0°C primarily to insure cooling of the product gas to well below the sublimation point of AlCl₃.

Noncondensable gas analysis:

The last major equipment section consisted of a Hewlett-Packard 5750 G.C., its gas sampling system and provisions for supplying the G.C. with calibration gas mixtures. Figure 11 is a detailed flow diagram of this system, which was used to analyze the product gas for Cl₂, CO, CO₂ and Freon-22. The first three gases were reaction products while Freon-22
Figure 10. Diagram of the condenser used to remove AlCl\textsubscript{3} and FeCl\textsubscript{3} from the reaction product gases
Figure 11. Flow diagram for the gas chromatograph calibration and the noncondensable product gas analysis systems
was injected into the product gas as a method of determining the total gas flow rate.

The G.C. was equipped with a thermal conductivity detector and a 4.6m x 3mm Teflon column packed with 10% H₃PO₄ coated on 60/80 Carbopack B (Supelco). Helium was used as the carrier gas to prevent the generation of negative response peaks, which the integrator, a Hewlett-Packard 3300A, could not process. The choice of carrier gas also dictated the choice of reactor purge gas, since the analytical column could not separate CO from nitrogen or the noble gases. Therefore, the reactor purge and G.C. carrier gases had to be the same to prevent the former from masking the CO peak.

Samples of product gas were taken using an eight-port, zero-deadspace gas sampling valve (Varian) equipped with two 1 ml sampling loops. The sampling valve could also be isolated from the system when not in use to minimize its exposure to corrosive gases and AlCl₃ particulates. Otherwise, it was possible for enough particulates to bypass the condensers and plug the sampling valve.

In order to determine rate data from the product gas analysis, both the gas composition and flow rate had to be known. Flow rate measurements could not be taken using a conventional method such as a wet test meter, so Freon-22 was injected at a known rate into the product stream and the total gas flow rate backcalculated from its concentration in the gas sample.

Gas exiting from the system was passed through a NaOH-Na₂SO₃ scrubber to remove any unreacted chlorine and then vented to an exhaust hood. The scrubber was a 4 cm diameter glass column, packed to a depth
of 65 cm with 3 cm Beryl saddles. Design conditions were 99.99% removal of Cl₂ from 900 cm⁻³·min⁻¹ of gas containing 44% Cl₂ using a solution of 2M NaOH-1M Na₂SO₃ at a rate of 200 ml·min⁻¹.

Chlorination Experimental Procedure

Preparation for a chlorination experiment started with the purification of enough AlCl₃ to make 385g of the desired salt composition. The purified chloride was then ground in a ball mill for 2-4 hours, and combined with NaCl to make the desired composition. This final material was then mixed for 1 hour in the ball mill, to reduce AlCl₃ sublimation during reactor heat-up by insuring intimate contact between the AlCl₃ and NaCl.

Once the salt mixture had been prepared, 375g were transferred to a powder burette (5). One gram of BaCl₂ was added to the mixture to provide a method of monitoring the mass of salt in the reactor by determining its concentration in the slurry samples. Barium chloride was chosen as the tracer because of its low volatility, does not form aluminohalide complexes and is not a significant component in the oxides studied. It has also been shown to have no catalytic effect on the chlorination of alumina (51).

The experimental equipment was assembled and tested the day preceding a chlorination run. Testing included checking the stirrer and sampler for proper clearances and examining the system for leaks or abnormally high pressure drops, which were indicative of AlCl₃-induced corrosion plugging in the gas handling system. After proper operation of the equipment had been verified, the entire system was dried and residual air removed by purging with helium overnight. The reactor was
also heated to 150°C for one to two hours during this period to assist drying. The G.C. was calibrated with known mixtures of He:CO, He:CO₂, He:Freon-22 and He:Cl₂.

The chlorination experiment was started by charging the salt to the reactor. Carbon and metal oxide were usually added to the salt and all three solids charged to the reactor simultaneously, although reactants could be added at any point in the experiment. A powder burette, as described by Bamberger (5), was used to charge solids to the reactor. The chlorine sparging tube was removed from the reactor during initial salt charging and reactor heat-up to reduce the possibility of it plugging at the start of the experiment.

After the reactor was charged, the furnace and auxiliary heaters were turned on and a helium purge of 400 cm³ min⁻¹ started. When the reactor reached about 200°C the salt mixture liquified so the stirrer could be started and brought to 300 RPM. Heating continued for 2 to 3 hours until the reactor reached the final operating temperature. At that time, the oxide and carbon were added to the reactor if not already present, and the stirring speed increased to 900 RPM. If the slurry was to be sampled, one or more samples were taken at this point as a check of the sampling accuracy.

Once initial slurry samples were taken, the Cl₂ sparger was placed in the reactor. Helium was passed through the sparger during placement to prevent slurry from entering the tube. Once it was in place, the Cl₂ flow was started, and the switch of gas flows was made using a four-port valve so that the gas flow was essentially uninterrupted.

Product gas samples were analyzed every 5 minutes from the start of
the chlorine flow. Because the integrator storage capacity was limited to a maximum of 54 peaks, it was necessary to skip sampling at 55 and 115 minutes so that the accumulated data could be processed.

Reactor slurry samples could be taken as often as every fifteen minutes using the following procedure. First, the movable section of the sampler, with quartz bucket attached, was purged with helium. The sampler was then attached to the reactor adapter and the union between the two sections purged with helium. The ball valves isolating the sampler from the reactor were then opened and the quartz bucket lowered into the slurry. The depth of bucket immersion into the slurry was approximately 1 cm, and was controlled by a stop on the sampling rod. After 2 seconds, the sample was lifted back into the upper half of the sampler and the ball valves were closed. The sampler was then detached from the reactor, moved to a drybag and attached to an adapter like that on the reactor so that the sample could be transferred to its weighing vial. The sample was subsequently stored in a desiccator until it could be analyzed.

Once the run was completed, the chlorine flow and furnace power were shut off and the reactor allowed to cool. A helium purge was maintained throughout the cooling period. When the reactor cooled to about 250°C, it was partially disassembled and the stirrer removed before the melt could solidify. The reactor and condensers were then resealed and allowed to finish cooling to room temperature.

The solidified melt was dissolved in water and the resulting slurry allowed to settle. The solution was filtered and the filtrate volume determined as was the weight and composition of the unreacted material.
Material from the condensers was also dissolved in water with the exception of SiCl₄ which hydrolyzed to form insoluble SiO₂. The solution volume from each condenser was measured after filtering and the solutions themselves analyzed for the product chlorides.

Analytical Procedures

Analysis of slurry samples

Figure 12 outlines the procedure used to analyze slurry samples. Each sample was stored in a weighing vial to protect it from hydrolysis during weighing. The bucket-weighing vial pairs were weighed before and after sample collection to determine sample weight.

After a sample was weighed, chloride salts in the sample were dissolved in 150 ml of water and separated from the unreacted solids by filtering the solution through a 0.2 micron membrane filter. The filtrate was diluted to 200 ml and analyzed for aluminum, iron and barium content. Unreacted carbon and oxides were washed off the filter with methanol into a tared crucible, dried, weighed and then ashed at 800°C to determine the oxide and carbon content of the sample. The remaining oxide was saved for further chemical analysis.

Chemical analysis

Iron, aluminum, silicon and barium analyses were made by atomic absorption spectroscopy with a Perkin-Elmer Model 373 spectrophotometer. Samples were prepared using the method of standard additions with the maximum sample concentration being one-half of the maximum recommended by Perkin-Elmer (48). Liquid samples were simply diluted to the proper concentration level, while solid samples were placed in solution by a
Figure 12. Processing scheme for analyzing slurry samples from the chlorination reactor.
lithium metaborate fusion technique described by Boar and Ingram (9).

Titanium, magnesium and calcium were analyzed using ICP spectroscopy. Samples were submitted for ICP analysis after being fused into solution.

**Particle size analysis**

All particle sizing was done with a Coulter Counter Model TA-II particle sizer. The procedure was to take approximately 4 milligrams of material and disperse it in 200 ml of electrolyte. Several 2ml samples of this slurry were analyzed using the Coulter Counter and the results used to develop a mass density (# particles g$^{-1}$ d$^{-1}$) distribution. The mass density distribution was then fitted to an equation of the form:

\[
g(D) = \sum_{i=1}^{n} \exp[f_i(D)]
\]

where \( g(D) \) = Mass density distribution, 
\( f_i(D) \) = Curve fitting function, 
\( D \) = particle diameter.

In most cases \( f_i(D) \) was a first order polynomial, but occasionally it was necessary to fit the data with a second order polynomial for a portion of the range of interest. Equation 20 could then be used in equations 21 to 23 to determine the following powder properties.

\[
D_p = \frac{\int_0^X Dg(D)dD}{\int_0^X g(D)dD}
\]

\[
A_p = \int_0^X Dg(D)dD
\]
\[ V_p(d) = 1 - \frac{\int_{0}^{d} D^3 g(D) dD}{\int_{0}^{\infty} D^3 g(D) dD} \]  

(23)

where \( D_p \) = Mean particle diameter,
\( A_p \) = Powder surface area (assuming spherical particles),
\( V_p(d) \) = Volume fraction of particles larger than diameter \( d \).

Equations 20 through 23 were used to calculate the powder properties and size distributions for the powders. The primary advantage of this method is that it allows interpolation between the data points provided by the Coulter Counter as well as the ability to extrapolate on the existing data. The data points shown on the cumulative volume distribution curves are data calculated from the distribution functions and not data taken directly from the Coulter Counter. Another characteristic particle diameter, \( D_{50} \), is defined as the particle diameter at which equation 33 equals 0.5, and is an appropriate measure of the average particle diameter based on particle volume, whereas the mean diameter is based on the number of particles.

Reactant Characteristics

Alumina

The alumina used in this study was produced by calcining alumina hydroxide (Fisher Chemical #A-581) at 700°C overnight. The particle size distribution for the powder is shown in Figure 13. The \( D_{50} \) diameter was 32.1 microns, while the mean particle diameter was 0.88 microns. The B.E.T. surface area of this material was 100 m² g⁻¹, which is typical of gamma alumina produced by the low temperature calcination
Figure 13. Particle size distribution of the oxides chlorinated in this study by fused salt chlorination
of aluminum hydroxide (44).

**Fly ash**

Fly ash used in this study was derived from a Pennsylvania #6 coal. The original ash was commercially processed by the Halomet Corporation to remove a magnetic fraction of the ash for use as a substitute magnetite, and the residual material from that process was used in this work. A 2 Kg sample of ash was obtained from a 50 gallon drum of material using a sampling probe to obtain representative samples. This sample was then sieved to separate the -325 mesh fraction required for the chlorination studies. The chemical composition of the material is listed in Table 3.

**Carbon sources**

A pulverized foundry coke, from Quinn Foundry and Machine, Boone Iowa was used as the carbon source in all but one chlorination where a high purity graphite was used. The coke was run through three separate

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight Percent</th>
<th>Component</th>
<th>Weight Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>47.66</td>
<td>CaO</td>
<td>3.66</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>32.26</td>
<td>TiO₂</td>
<td>1.09</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>10.41</td>
<td>Na₂O⁵</td>
<td>1.09</td>
</tr>
<tr>
<td>MgO</td>
<td>0.92</td>
<td>K₂O⁵</td>
<td>1.16</td>
</tr>
<tr>
<td>L.O.I.</td>
<td>1.87</td>
<td></td>
<td>(Loss on ignition)</td>
</tr>
</tbody>
</table>

⁵Unsieved ash composition.
crushers (large jaw, small jaw and a roll mill). A 500g charge of the crushed material was then ground for an additional 6 hours in a 6" diameter ball mill with a mixed charge of .25" and 0.5" diameter steel balls. Three separate grinds were used for different sets of experiments. Material referred to as Coke-1 was used for the statistical study (Plankett-Burmann), Coke-2 was used for all but one other alumina chlorination and Coke-3 was used for the fly ash chlorinations. The coke had a 10% ash content by weight, which assayed 53.4% SiO₂, 26.5% Al₂O₃ and 13.7% Fe₂O₃.

The size distribution and physical properties of the three cokes and the graphite used are shown in Figure 14 and Table 4. As noted previously Coke-1 and Coke-3 are relatively similar, while Coke-2 had a significantly smaller size distribution and higher surface area. The graphite (Alpha Products #641) was a high purity material containing less than 1% impurities.

Table 4. Powder properties of carbon sources used as reductants

<table>
<thead>
<tr>
<th>Property</th>
<th>Coke-1</th>
<th>Coke-2</th>
<th>Coke-3</th>
<th>Graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area (m² g⁻¹)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B.E.T.</td>
<td>3.03</td>
<td>8.75</td>
<td>5.22</td>
<td>7.75</td>
</tr>
<tr>
<td>External¹</td>
<td>0.098</td>
<td>0.207</td>
<td>0.125</td>
<td>0.555</td>
</tr>
<tr>
<td>Diameter (microns)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>1.39</td>
<td>1.29</td>
<td>1.91</td>
<td>1.11</td>
</tr>
<tr>
<td>D₅₀</td>
<td>42.66</td>
<td>18.86</td>
<td>37.79</td>
<td>10.93</td>
</tr>
</tbody>
</table>

¹Surface area based on equation 20.
Figure 14. Particle size distribution of the carbon sources used in this study as reductants for fused salt chlorination
RESULTS AND DISCUSSION

The characteristics of carbochlorination in a fused salt slurry were studied first by chlorinating pure alumina rather than a mixed oxide such as fly ash. As previously discussed, the chlorination of fly ash and other mixed metal oxides is comprised of two separate mechanisms, carbochlorination of alumina and a chlorine exchange reaction with the fused salt which, in the case of NaCl-AlCl₃ melts, produces alumina. Because of this behavior, the carbochlorination reaction was studied primarily with pure alumina. Also, the experimental procedure for chlorinating a pure oxide is experimentally more tractable than that for the mixed oxide chlorination. Pure oxide chlorination can be monitored completely from analysis of the product gas composition and flowrate. Mixed oxide chlorination requires analysis of the slurry, which is less sensitive and more prone to error.

Alumina Chlorination Screening Study

The first series of experiments examined the effect of several operating parameters on the chlorination rate of alumina using a statistical study of the Plankett-Burman design (59). Eight experiments were done to test five parameters: temperature, melt composition, melt:alumina ratio, melt:carbon ratio and chlorine flowrate. The Plankett-Burman design is good for determining the major effect of three or more process parameters in a minimum number of experiments. Its one main disadvantage is that it cannot evaluate higher-order effects (interactions between two or more variables), so some care must be taken in interpreting the results.
Experimental procedure

In these experiments, measured amounts of alumina and carbon were charged to the reactor along with the solid salt. After the mixture was brought to melt temperatures and agitation started, slurry samples were taken to develop and test both analytical and calculation procedures. The results of these tests and their effects on the calculation procedures are discussed in Appendix B. Three slurry samples were taken before the chlorine flow was started, and at 15 minute intervals during the reaction, starting 7.5 minutes after the chlorine was turned on. The stirrer speed was 900 RPM for all experiments.

Table 5 shows the two levels used for each parameter tested. Temperatures were based on results from two preliminary experiments to test the equipment (20), while the melt compositions were determined from the maximum allowable composition difference at 800°C. Values for the melt:alumina ratios were based on alumina charges of 50g and 25g, which corresponded to solid-liquid ratios of approximately 200 g/l and 100 g/l. Carbon loadings were then calculated so that the molar ratio of the high Al₂O₃ and high carbon loadings was three, which corresponds to a 1:1 stoichiometry, assuming the formation of CO only (reaction 1). Chlorine flow rates were based on differences in the reactor gas hold-up determined from studies using nitrogen and water to simulate the gas and melt in the reactor. Specific results of this work are discussed in Appendix C.

The combinations of experimental parameters used in each of the eight experiments are listed in Table 6, along with the steady-state chlorination rate of alumina for each experiment, which was determined
Table 5. Variable levels for the variable screening experiment

<table>
<thead>
<tr>
<th>Parameter</th>
<th>High (+)</th>
<th>Low (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) Temperature</td>
<td>800°C</td>
<td>600°C</td>
</tr>
<tr>
<td>(2) NaCl:AlCl₃ molar ratio</td>
<td>48:52</td>
<td>40:60</td>
</tr>
<tr>
<td>(3) Salt:alumina ratio</td>
<td>7.5:1</td>
<td>15:1</td>
</tr>
<tr>
<td>(4) Salt:carbon ratio</td>
<td>21:1</td>
<td>42:1</td>
</tr>
<tr>
<td>(5) Chlorine flowrate - cm³ min⁻¹</td>
<td>255</td>
<td>90</td>
</tr>
</tbody>
</table>

by extrapolating the reaction rate between 30 and 90 minutes back to time zero. This procedure was adopted in order to eliminate the effect of an initial burst of reaction observed in the 600°C.

In order to be statistically significant, the effect of a parameter must be greater than 0.40. This level was determined by calculating the effects of two dummy variables, not shown in Table 6, which are combinations of experimental parameters that completed the statistical design, but were not associated with a physical parameter. This method of determining significance is based on the premise that the observed effect of a dummy variable is a measure of the variance in the experimental procedure (59).

Figures 15 and 16 are plots of the alumina chlorination rate versus time for chlorine flowrates of 255 cm³ min⁻¹ at 600 and 800°C respectively. The profiles for both carbon loadings tested are shown.

Alumina loading and melt composition effects

Of the five parameters tested, melt:alumina ratio had the lowest effect on the reaction rate. This condition is underscored by the
<table>
<thead>
<tr>
<th>EXPERIMENTAL CONDITIONS</th>
<th>17.86 g C</th>
<th>8.96 g C</th>
</tr>
</thead>
<tbody>
<tr>
<td>MELT CARBON</td>
<td>2:1</td>
<td>42:1</td>
</tr>
<tr>
<td>MELT ALUMINA</td>
<td>7.5:1</td>
<td>15:1</td>
</tr>
<tr>
<td>MELT % AlCl₃ (MOLE)</td>
<td>40%</td>
<td>48%</td>
</tr>
<tr>
<td>Cl₂ cm³ min⁻¹</td>
<td>255</td>
<td>255</td>
</tr>
<tr>
<td>TEMPERATURE °C</td>
<td>600</td>
<td>60</td>
</tr>
</tbody>
</table>

Figure 15. Plot of reaction rate versus time for the chlorination of alumina at 600°C and a chlorine flow rate of 255 cm³ min⁻¹.
Figure 16. Plot of reaction rate versus time for the chlorination of alumina at 800°C and a chlorine flow rate of 255 cm³/min⁻¹.
Table 6. Reaction rates and conditions for the Plankett-Burman analysis

<table>
<thead>
<tr>
<th>Trial No.</th>
<th>Parameter No. &amp; Level</th>
<th>Reaction rate, millimoles of alumina min(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>+ + + - +</td>
<td>1.20</td>
</tr>
<tr>
<td>2</td>
<td>+ + - + -</td>
<td>1.10</td>
</tr>
<tr>
<td>3</td>
<td>+ - + - -</td>
<td>1.06</td>
</tr>
<tr>
<td>4</td>
<td>- + - - +</td>
<td>0.23</td>
</tr>
<tr>
<td>5</td>
<td>+ - - + +</td>
<td>1.67</td>
</tr>
<tr>
<td>6</td>
<td>- - + + +</td>
<td>0.45</td>
</tr>
<tr>
<td>7</td>
<td>- + + + -</td>
<td>0.43</td>
</tr>
<tr>
<td>8</td>
<td>- - - - -</td>
<td>0.20</td>
</tr>
<tr>
<td>Effect(^a)</td>
<td>0.93 0.11 0.02 0.24 0.19</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\)An effect greater than 0.40 is statistically significant at the 95% confidence level.

result of the 21:1 melt:carbon chlorination shown in Figure 16. In this experiment, a total oxide conversion of 95\% was obtained with no significant reduction in the reaction rate during the experiment. These results support the observation of Seon et al. (35) that a dissolved oxide species is chlorinated instead of the solid. If the carbochlorination had taken place at the alumina surface, the rate would have been affected by the available alumina surface area. The lack of rate dependence at high alumina conversions also indicates that the dissolution rate of alumina is much faster than the chlorination rate. If this were not the case, there would have been a reduction in the chlorination rate with respect to time.

Melt composition was also found to be unimportant. What effect it
might have had would have been on the solubility and dissolution rates of the dissolved reactants; alumina solubility is known to be a function of melt composition (28). At the conditions tested, however the dissolution rate of the oxide was fast enough to make any solubility differences insignificant. There was also no measurable effect of melt compositions on the solubility and transport of chlorine.

Because the melt:alumina ratio and the melt composition had no appreciable effect on the reaction rate (in the range studied), these two parameters can be ignored for the remainder of the analysis.

**Carbon loading and chlorine flow rate effects**

Carbon loading and chlorine flow rate were also found to be statistically insignificant, although in both cases the effect was larger than for melt composition and oxide loading. The experimental evidence, however, indicated that melt:carbon ratio had a greater than predicted affect on the chlorination rate. At fixed combinations of temperature and chlorine flow rate (trial pairs 1-5, 2-3, 4-6 and 7-8), high carbon loadings (low melt:carbon ratios) produced higher reaction rates than low carbon loadings.

The exception to this was trial pair 2-3, where both rates were approximately the same. In trial 2, total chlorine conversion was attained, so at these conditions (high temperature and low chlorine flow rate) the maximum possible chlorination rate was chlorine limited. A higher chlorination rate in trial 2 would result in an increased significance of the melt:carbon parameter, so the apparent insignificance of carbon loading was a result of trial 2 being rate limited by the choice of experimental parameters.
A strong correlation like that for melt:carbon ratio and reaction rate was not observed between chlorine flow and reaction rate. Further, if the reaction rate in Trial 2 were increased, i.e., was not chlorine limited, the observed effect of chlorine flow would be reduced. This indicates that the observed effect of chlorine flow rate resulted primarily from the choice of chlorine flow rate, rather than from a physical characteristic of the system.

**Temperature effects**

Of the five parameters tested, temperature was the only one found to be statistically significant. Table 6 and Figures 15 and 16 show that temperature had a strong influence on both the reaction rate and nature of reaction.

Comparison of Figures 15 and 16 shows that both the steady-state reaction rate and shape of the time-reaction rate curve were influenced by temperature. At 600°C (Figure 15), the reaction rate started high and then dropped to a lower, steady-state, value after the first 30 minutes of reaction. In contrast, the 800°C reaction profiles were constant for the duration of the experiment. The low reaction rates observed for both temperatures at 5 minutes were a result of calculating reaction rates from the noncondensable gas analysis, which was not an instantaneous measure of what was occurring in the reactor (Appendix D).

There was also evidence of a second order effect between temperature and carbon loading. At 600°C, the reaction rate was proportional to the carbon loading for all conditions tested. This was not the case at 800°C and high chlorine flowrates where an increase in carbon loading increased the reaction rate by only 55%. The temperature/carbon loading
relationship indicates a shift in the controlling reaction mechanism over the temperature range studied. The most reasonable hypothesis, consistent with the observations reported above, was that the rate at 600°C was controlled at the carbon surface, while gas-liquid mass transfer effects influenced the rate at 800°C.

Summary

In summation, the screening study showed the following characteristics:

- Temperature had the strongest effect on the reaction rate.
- Carbon loading had the next strongest effect on the reaction rate.
  At 600°C the rate was proportional to carbon loading, while at 800°C it was not.
- The chlorine flow rate did not have a significant effect on the reaction rate, except to act as a limiting reactant.
- Alumina loading and melt composition did not have any measurable effect on the chlorination rate.
- The chlorination reaction occurs at the carbon surface.
- Alumina reacts as a dissolved oxychloride and its dissolution rate is much faster than the chlorination reaction at the carbon surface.
- There appears to be a change in the controlling reaction step between 800°C and 600°C.

From the results of these experiments it is apparent that a major concern in a process scale reactor will be maximizing the carbon surface area available for reaction and the transport of reactants to that
surface. With regard to reactant transport, the mass transfer of chlorine into the melt will probably be the major concern, since chlorine is significantly less soluble in NaCl-AlCl₃ melts than aluminum oxychloride (60,62).

**Temperature Dependence**

To better define the temperature effect detected in the screening study, a series of experiments was done at a fixed set of conditions between 530°C and 800°C.

The procedure for these experiments was the same as for the screening study, except that only one slurry sample was taken before the chlorine was turned on and samples were taken at 30 minute intervals during reaction. The other difference between this series of experiments and the screening study was that Coke-2 was used as the carbon source instead of Coke-1. Experimental conditions used were:

- Melt:Alumina ratio 7.5:1 (wt.)
- Melt:Carbon ratio 21:1 (wt.)
- Chlorine flowrate 255 cm³ min⁻¹
- Melt composition at 600°C and above 40% AlCl₃-60% NaCl
- Melt composition at 550°C and below 45% AlCl₃-55% NaCl

The two different melt compositions were used in an attempt to eliminate a problem with the chlorine sparger plugging due to the precipitation of NaCl from the melt, which is discussed later in this section. This should not have affected the measured reaction rates.
Reaction profiles

Figure 17 shows the reaction rate-time profiles for chlorinations at 530, 550 and 600°C. All three experiments show the same basic profile, an initial high reaction rate followed by a decline over the next 30 to 45 minutes to a steady-state reaction rate. The initial decrease in rate with time is not attributable to conversion effects such as loss of carbon surface area since the maximum observed carbon conversion over the first 45 minutes of reaction was only 3 percent. Total carbon conversions at 80 minutes ranged from 6.9 percent at 600°C to 2.3 percent at 530°C.

The lack of data points from 40 to 80 minutes on the 600°C curve is the result of a problem with the sparger plugging. There was a period of erratic chlorine flow to the reactor, which is not believed to have affected the reaction, but it did render G.C. measurements in this time period useless.

Figure 18 shows the reaction rate-time profiles for chlorinations at 700, 750 and 800°C, which also show similar reaction profiles as a group, but are different in shape than the low temperature profiles shown in Figure 17. As was previously observed in the screening study, there is no initial burst of reaction in these chlorinations, instead the reaction starts at what would be considered the steady-state value in a low temperature chlorination. There is approximately a 10 percent drop in the reaction rate over a 150 minute period, which might be related to the conversion of carbon. Total carbon conversions in these experiments were 17.3, 21 and 25 percent at 700, 750 and 800°C, respectively.
Figure 17. Comparison of the reaction rate profiles for the chlorination of alumina at temperatures at 600°C and below.
Figure 18. Comparison of the reaction rate profiles for the chlorination of alumina at temperatures 700°C and above.
The reaction rate-time curve for the 650°C chlorination is shown in Figure 19, and appears to be a combination of the high and low temperature profiles. The delayed reaction peak is believed to be caused by the interaction of the high and low temperature reaction mechanisms. Work with the gas-solid carbochlorination reaction has demonstrated a strong temperature effect at 650°C that is attributed to the stability of phosgene (1,25,49). From this run, it appears that the fused salt reaction is also influenced by phosgene stability.

**Arrhenius analysis**

The temperature dependence of the chlorination of alumina is described by the Arrhenius plot shown in Figure 20. There are two temperature profiles shown, one based on initial reaction rates, and the other on the extrapolation of the steady-state reaction rate to zero time. The determination of initial rates for the chlorinations at 530 to 650°C was based on extrapolation of the rate curves for the first 20 minutes of reaction.

The initial reaction rate curve is much more linear over the temperature range studied than the steady-state curve. The activation energy for both the 700-800°C and 530-600°C regions of the initial rate curve are about the same at 7.0 Kcal and 5.2 Kcal, respectively. The overall activation energy of the initial reaction rate for the entire temperature range (530 to 800°C) was 3.3 kcal. These results indicate that the mechanism controlling the initial reaction rate could be mass transfer related.

In contrast, the steady-state rate curve shows significant temperature dependence in the 530 to 600°C range, while there is no
Figure 19. Reaction rate profile for the chlorination of alumina at 650°C.
Figure 20. Arrhenius plot for the reaction of alumina in the fused salt carbochlorination reaction
difference between the initial and steady-state curves at temperatures in excess of 650°C. In the low temperature region, the activation energy is 29.7 Kcal for the steady-state case, which is consistent with kinetic reaction control. The activation energy for the 700 to 800°C region is typical of mass transfer control. These results are also consistent with the results of the screening study. The lower reaction rates observed in the 600°C screening experiments are the result of the reduced surface area of Coke-1 compared to Coke-2.

The inflection point in the reaction rates in the 650 to 700°C region of the steady-state reaction curve has also been reported by previous investigators for the gas-solid chlorination system (49). In the gas-solid chlorination reaction it is caused by the increase in reaction rate with temperature being offset by a decrease resulting from the instability of phosgene at temperatures above 600°C.

**Mechanism versus temperature**

More direct evidence for the role of phosgene in the fused salt reaction mechanism is presented in Figure 21, a plot of the CO:CO₂ ratio in the product gas as a function of time. At temperatures below 650°C, CO was not detectable at all, while above 650°C both the absolute level of CO and the CO:CO₂ ratio increased with temperature. The lack of CO in the product gas at low temperatures and the maxima in the reaction rate at 650°C strongly indicate that phosgene formation is an integral part of the reaction mechanism.

Figure 21 illustrates two points about the mechanism of fused salt chlorination. The first is that the CO:CO₂ ratios change with time and the second is that the levels of CO observed at temperatures above 700°C
Figure 21. Ratio of CO to CO₂ for the chlorination of alumina at temperatures above 650°C.
are extremely low. Theoretically, at 800°C the CO:CO₂ ratio should be 11.0 and not 0.1.

The low CO content of the product gas indicates that oxygen is captured on the carbon surface during the reaction, possibly as part of a ketone-type structure in the conjugated benzene and aliphatic rings that make up the coke structure. If molecular CO were formed, it would not be expected to remain in the reactor long enough to form phosgene at 100% conversion levels, which is what would be required to explain the lack of CO at low temperatures. This expectation is further reinforced by the ALCOA patents (26,64), which state that a solid reductant should be used in a fused salt chlorination process.

The fact that the CO:CO₂ ratio becomes smaller with time, combined with the idea of oxygenated solid carbon leads to the conclusion that the reactivity of the carbon surface changes with conversion. If the CO content of the product gas resulted strictly from the dissociation of phosgene, then the CO:CO₂ ratio would be constant. Since this is not the case, CO must also be generated by the dissociation of the oxygenated carbon structures due to thermal cracking.

The variation in the CO:CO₂ ratio, therefore, indicates the presence of two or more types of reaction sites in the carbon, which would be expected given the heterogeneous nature of coke. The idea of multiple reaction sites also explains the reaction profiles observed in the low temperature chlorinations. These profiles are roughly identical in shape to the CO:CO₂ ratio curves, further suggesting that the same reaction sites that are responsible for the fast initial reaction at low temperatures become unstable at higher temperatures and break down before they can contribute to the reaction.
Chlorine side reactions

There are two methods for determining the alumina reaction rate from the product gas stream analysis. The first method is to integrate the concentration of CO₂ and CO in product gas over time; the second is to use the ratio of CO+CO₂ (COₓ) to Cl₂ in the product stream to calculate chlorine consumption, using the fact that each mole of chlorine that reacts produces one mole of CO or a half mole of CO₂.

The advantage of the first method is that it is independent of the reaction stoichiometry and chlorine side reactions. Its primary disadvantage is that the concentration of COₓ in the product gas was influenced by dispersion effects in the reactor and condensers, and variations in gas sampling. The rate calculation is also dependent on the total product gas flow rate measurement.

In contrast the COₓ:Cl₂ ratio is less influenced by dispersion and is virtually independent of variations in the gas analysis, which makes it especially useful for determining the low temperature initial reaction rates. Also, this method involves calculation of chlorine conversion so the reaction rate is based on the chlorine input which is more accurately known than the total product gas flow rate. The disadvantage with this method is that it assumes that all the chlorine used is consumed by the carbochlorination of alumina. This assumption appears to be valid for reactions below 800°C, i.e., profiles determined by both methods showed the same shape and magnitude.

Figure 22 is a plot of the reaction profiles for the 800°C chlorination, calculated using each method. There is a distinct peak at
Figure 22. Comparison of the chlorination rates of alumina as calculated from chlorine conversion versus the production of $CO + CO_2$. 

**CONDITIONS**
- **TEMPERATURE**: 800°C
- **MELT % $AICl_3$ (MOLE)**: 40
- **MELT:CARBON**: 2:1
- **MELT:ALUMINA**: 7.5:1
- **$Cl_2$ FLOW**: 255 cm$^3$ min$^{-1}$
15 minutes in the chlorine consumption based reaction profile that is not observed in the CO\textsubscript{X} based curve. The only explanation for this behavior is that there is a loss of chlorine to a side reaction that does not generate CO\textsubscript{2} or CO, which could only be the chlorination of carbon.

**Process considerations**

From a process standpoint, the steady-state reaction rates shown in the Arrhenius plot are more meaningful than the initial reaction rates since in a CSTR reactor the majority of the carbon would be reacted to the point of steady-state reaction. Using the steady-state data, the optimum operating temperature would probably be around 700 to 750\textdegreeC.

**Chlorine sparger plugging**

Between 550\textdegreeC and 650\textdegreeC a problem was observed with the chlorine sparger plugging in both this series of experiments and others done to test the reaction mechanism. The sparger plugging was attributed to the selective vaporization of melt in the vicinity of the sparger and was dependent on the reaction temperature and the carbon particle size distribution.

At 530\textdegreeC there was not a significant amount of material collected in the condensers, indicating a low melt evaporation rate. As the temperature was increased, evaporation became more significant and was probably greatest at the sparger since this was a region of high gas velocity. Removal of AlCl\textsubscript{3}, either as AlCl\textsubscript{3} or NaAlCl\textsubscript{4}, from a NaCl-rich melt near the liquidus composition would cause precipitation of NaCl at the sparger and plugging of the unit.
As the temperature was increased the evaporation problem became more severe and plugging occurred sooner. As the reaction temperature was raised above 650°C the melt composition shifted away from the liquidus composition, which eliminated the plugging problem.

The nature of solids in the slurry also influenced the plugging behavior. The screening experiments were run under nearly identical conditions to the temperature dependence study, except for the coke used, and yet showed no plugging problems. The coke in that series of experiments had a significantly larger average particle size. It is possible that the smaller carbon particles used in the temperature dependence study were more easily cemented together by the solidified NaCl.

Plugging could be a major problem in a process-scale reactor, so some consideration should be given to the sparger design and possible methods for clearing the unit during operation.

Summary

The temperature dependence study showed the following.
- Initial reaction rates are not a strong function of temperature.
- At steady-state there are two different reaction regimes. At 600°C and lower the system has the characteristics of kinetic control. At higher temperatures, the system shows characteristics of mass transfer limitations.
- At 800°C a chlorine carbon side reaction becomes significant.
- The system shows behavior at 650°C that suggests a phosgene influence on the reaction rate.
- Based on the low temperature reaction profiles and the behavior of
the CO:CO₂ ratio with time, it appears that the reactivity of the carbon surface changes with conversion.

Mechanism Experiments

The purposes of the experiments discussed in this section were to determine the cause of the reaction profiles observed at temperatures below 600°C, and how the observed behavior was related to the reaction mechanism. As noted in the previous section, the reaction appears to be kinetically controlled between 530 and 600°C at the carbon surface.

There are three possibilities for the increased initial reaction rates. One is that the initial reaction surge is caused by the chlorination of impurities in the coke. A second is that the increased rate results from a reaction between the melt and carbon or alumina during the heat-up period. The final option is that the carbon surface is not homogeneous, but consists of two or more types of reaction sites, each with its own temperature dependence.

Coke impurities

The impurity hypothesis was tested by duplicating the 600°C temperature dependence experiment using a high purity graphite instead of coke. The results of these two experiments are compared in Figure 23. The characteristic drop in reaction rate is still present in the graphite chlorination, which rules out the ash content of the coke as the cause of the initial reaction behavior.

The overall reaction rate for graphite was 40 percent lower than that of Coke-2 in spite of the fact that the surface area of the former was about the same or greater than the latter. Since it is known that
Figure 23. Comparison of the initial chlorination rates of alumina using Coke-2 and graphite as reductants.
the carbon surface area controls the reaction rate at this temperature, this experiment indicated that different carbon sources have differences in reactivities not necessarily related to their surface areas.

Another difference between the graphite and Coke-2 chlorinations is the faster leveling off of the graphite curve. At 30 minutes into the experiment, the change in reaction rate for Coke-2 was three times greater than that for graphite. This shows that the source of the initial reaction peak was not as strong in graphite as in Coke-2, which is also best explained by differences in chemical reactivities.

**Alumina-carbon prechlorination reaction**

The second theory mentioned above was that an intermediate reaction product was formed during the heat-up period when the carbon and alumina were in contact with each other and the melt. The most likely candidate would be an AlOCl-carbon complex. It was postulated that at low temperatures the chlorination rate of this intermediate exceeded its formation rate, resulting in a reduction in the overall reaction rate with time until the intermediate formation was equal to its consumption.

This hypothesis was tested by changing the order and time of reactant charging to the system. In each of these experiments only one of the solid reactants was added with the salt at room temperature; the other was added after the reactor had reached 600°C and the chlorine had been turned on. If the cause of the reaction peak was an alumina-carbon reaction in the heat-up period, then these experiments would have produced a flat reaction profile similar to that observed at high temperatures.
Experimental procedure  Three experiments were done with different reactant charging sequences. In the first, alumina was charged with the salt at room temperature. Carbon was added to the slurry after the chlorine was turned on and the product gas reached steady-state. In the second experiment, the same procedure was followed except the time of addition of the alumina and carbon were reversed.

The third experiment used a procedure that was a combination of the procedure described above and that used in the temperature dependence study. The carbon was added with the salt and the system heated to 600°C at which time the chlorine was turned on for 15 minutes to remove oxide impurities in the melt. The reactor was then purged for 30 minutes with helium to remove residual chlorine before the alumina was added and the slurry mixed for an additional 30 minutes. Finally the chlorine was turned back on.

All three chlorinations were run at the same conditions as the 600°C temperature dependence experiment, except that the melt:alumina ratio which was 7.5:1 for the first experiment and 15:1 for the second and third. This change did not effect the results of this work. All three chlorinations were terminated after 25 to 35 minutes of alumina chlorination because the chlorine sparger plugged. No slurry samples were taken.

Results  The reaction profile for adding carbon to a alumina-molten salt slurry is shown in Figure 24. The alumina slurry was exposed to chlorine for 30 minutes before the carbon was added without any sign of reaction.

Figure 24 shows a clearly identifiable peak in the reaction rate
Figure 24. The effect of adding carbon to the slurry at 600°C on the initial reaction rate of alumina
10 minutes after the carbon was added. The displacement of the peak from zero is attributed to the fact that it took a total of 6 minutes to add the carbon to the reactor. The presence of a reaction peak eliminated a carbon-alumina or carbon-melt reaction during the heat-up period as being the cause of the initial reaction peak.

The purpose of the second experiment was to test for a melt-alumina interaction. There were two difficulties with this chlorination. First, dissolved oxides from the coke or impurities in the AlCl₃ used to make the melt reacted when the chlorine was turned on. This is apparent from curve A in Figure 25, which shows the production of CO₂ that occurred when the chlorine was first turned on, prior to addition of alumina to the reactor. The second problem occurred when the chlorine sparger plugged during the carbon-chlorine equilibration step. It took approximately 85 minutes to clear the sparger and obtain a constant product gas composition. The melt and carbon were exposed to chlorine for virtually this entire period.

It is not clear if there is a peak in curve B at 10 minutes or not. The reaction rate, curve B, drops with time, but by a factor of 9 less than the 600° temperature dependence experiment as shown by Figure 24, curve A. The lack of a strong peak could be caused by changes in the carbon surface by the reaction of carbon with the contaminant oxides. Otherwise, the initial reaction peak is caused by a alumina-melt interaction.

The concept of the third experiment was as follows. By exposing the carbon to chlorine for 15 minutes the majority of the contaminant oxides would be removed. After the reactor was cleared of chlorine, alumina
Figure 25. Initial reaction rate of alumina added to the slurry at 600°C (85 min. carbon-chlorine exposure)
Curve A: Production of CO₂ during prechlorination
Curve B: Initial alumina reaction rate
would be added to the slurry, and the system allowed to equilibrate for 30 minutes. At this point conditions in the reactor would approximate conditions existing in the temperature dependence studies just before chlorine was added to the reactor. If the reaction peak was caused by an alumina-salt interaction, this experiment would produce a profile of the same shape and amplitude as the temperature dependence experiments.

Figure 26, curve B, is the initial alumina reaction rate profile for this experiment. It is similar in shape to the temperature dependence experiment, but the reaction rate is 20 to 30% lower indicating that the treated carbon was less reactive. If this reaction rate profile is compared to the temperature dependence study and a 15 minute offset is factored in to account for the initial chlorine exposure, the two curves are nearly identical. It was therefore concluded that the initial reaction rate peak is caused by changes in the carbon reactivity.

Carbon prechlorination

A final point of interest in this series of experiments is the effect of prechlorinating the carbon on its reactivity. Figure 27 is a comparison of the reaction rates observed in the second and third experiments. In the second experiment, the carbon was exposed to chlorine for approximately 85 minutes before the alumina was added, while in the third it was only exposed to chlorine for 15 minutes.

Based on the results shown in Figure 26 (15 minutes chlorine exposure) it would be expected that the 85 minute chlorine exposure would cause the carbon to be less reactive. As Figure 27 shows, however, the 85 minute prechlorination improved the initial reactivity of the carbon. There was only a 6% drop in the reaction rate of the
Figure 26. Initial reaction rate of alumina added to the slurry at 600°C and equilibrated for 30 minutes (15 minute chlorine-carbon exposure before alumina equilibration).

**CONDITIONS**
- TEMPERATURE 600°C
- MELT % AlCl₃ (MOLE) 40%
- MELT:CARBON 21:1
- MELT:ALUMINA 15:1
- Cl₂ FLOW 245 cm³ min⁻¹

A - Al₂O₃ + C DURING HEAT UP
B - C ONLY DURING HEAT UP
Figure 27. Comparison of the initial chlorination rates for 15 and 85 minute carbon-chlorine exposure
carbon that had been prechlorinated for 85 minutes as opposed to a 30% drop in the 15 minute prechlorination carbon. This is additional evidence of the chlorine-carbon reaction detected in the 800°C temperature dependence experiment.

Summary
The major points of the mechanism experiments were:

- The initial reaction rate peak at low temperatures is the result of a change in the carbon reactivity with conversion.
- Exposure of the carbon to chlorine for extended periods of time improves its reactivity, while short exposures have a negative effect.
- The reactivity of carbon is a function of its chemical structure as well as its surface area.

Carbon Loading and Surface Area Effects
The screening study indicated that at 800°C the carbon loading affected the reaction rate, although the change in rate was not directly proportional to the changes in carbon loading. The temperature dependence study indicated that the reaction was mass transfer controlled from 650 to 800°C. Since the reaction could be gas-liquid or liquid-solid mass transfer controlled, it was necessary to determine the effect of carbon loading (melt:carbon ratio) on the reaction rate in the this temperature range. Once this dependence was known, equation 18 could then be used to analyze the system behavior.

The experimental procedure was the same as that used for the temperature dependence studies. Experimental conditions were:
Temperature 750°C
Melt:alumina ratio 7.5:1 (wt.)
Cl₂ flow 255 cm³ min⁻¹
Melt composition 40% AlCl₃-60% NaCl

The results of five experiments run at the above conditions at different melt:carbon ratios are plotted in Figure 28 as \( -\frac{C_{Cl,i}}{r_{Cl}} \) versus the inverse of the total carbon weight, \( W_C \), which is proportional to the total surface area, \( a_C \). The initial reaction rate was used for \( -r_{Cl} \). The difference between the two curves shown in Figure 28 is the value assumed for \( C_{Cl,i} \). There are two limiting flow patterns for the gas in a stirred tank reactor, either plug flow or completely backmixed. Normally in a two-phase CSTR complete backmixing is assumed. Both conditions, however, have been reported for stirred tank slurry reactors (21), depending on the system studied and the solids content of the slurry. There was no way of determining from this study under which condition the reactor was operating.

To obtain the totally backmixed limit, \( C_{Cl,i} \) was determined from the ratios of chlorine and \( CO_x \) in the product gas. For the plug flow limit, the choice of \( C_{Cl,i} \) was somewhat more difficult. Since CO and \( CO_2 \) were produced in the reaction it is not reasonable to assume pure chlorine at the gas-liquid interface, so an average value of \( C_{Cl,i} \) was calculated from the average of pure chlorine and the product gas composition. A Henry's Law constant of \( 12.5(10^{-7}) \) g-mole cm⁻³ atm⁻¹ was used to determine \( C_{Cl,i} \) from the product gas composition (15). Table 7 lists the values of \( -r_{Cl} \) and mole fractions of Cl₂ in the reaction gas.
Figure 28. Plot of $-C_{\text{Cl}_1}/r_{\text{Cl}}$ versus $1/w_c$ for the chlorination of alumina at 750°C.
Table 7. Chlorine reaction rates and Cl\textsubscript{2} mole fractions versus carbon loading at 750\textdegree{}C (Figure 28)

<table>
<thead>
<tr>
<th>(W_C ) - grams</th>
<th>(-r_{Cl}(10^3)) - g-moles min(^{-1})</th>
<th>Mole fraction Cl\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.46</td>
<td>5.16</td>
<td>0.665</td>
</tr>
<tr>
<td>7.14</td>
<td>5.04</td>
<td>0.666</td>
</tr>
<tr>
<td>17.86</td>
<td>5.55</td>
<td>0.600</td>
</tr>
<tr>
<td>35.74</td>
<td>8.25</td>
<td>0.317</td>
</tr>
<tr>
<td>45.00</td>
<td>7.65</td>
<td>0.367</td>
</tr>
</tbody>
</table>

Both the curves in Figure 28 show the same behavior, except for the offset caused by the different values of \(C_{Cl,1}\). The shape of the curves is not adequately explained by equation 18. Based on Figure 28, equation 18 indicates the reaction rate was gas-liquid mass transfer controlled at low carbon loadings but became carbon surface area dependent as the carbon content was increased. This result cannot be explained by equation 18 since, once gas-liquid mass transfer becomes limiting, increasing the carbon loading (surface area) can have no influence on the rate. In physical terms this means that once the reaction is limited by the amount of chlorine entering the slurry, an increase in the carbon available to react with it has no additional effect.

The observed behavior cannot be explained as a shift in the gas flow from backmixed to plug flow either. In order to do this, it must be possible to draw a straight line between the highest and lowest carbon loadings without crossing either of the limiting flow curves.

Equation 18 is based on the assumption that \(a_g\) and \(K_{Cl,g}\) are independent of changes in the slurry caused by changing its solids content. This can be a poor assumption, depending on the slurry
characteristics (21). If $K_{Cl,g}$ or $a_g$ were functions of the solids loading, they could be dependent on the total solids loading, carbon loading or both. Alumina loading alone could not be the cause of the change because it was held constant in this study.

In order to determine the effect of total solids loading on the mass transfer in the slurry, a chlorination was performed using a melt:carbon ratio of 84:1 and an melt:alumina ratio of 4.6:1. These conditions produced a total solids loading equivalent to that of the 11.5:1 salt:carbon ratio experiment shown in Figure 28. If increasing the total solids loading increased $K_{Cl,g}$ or $a_g$, then the reaction rate of this chlorination would have been faster than the 84:1 salt:carbon experiment rate.

Figure 29 compares the rates of both experiments. It is apparent that the higher alumina loading reduced the reaction rate, so the increased solids content of the slurry was not the cause of the increased reaction rate at high carbon loadings. Therefore, it can be concluded that the change in carbon loading accounts for the increased reaction rate.

The best explanation for the results of these tests is that $K_{Cl,g}$ or $a_g$ are influenced by the total solids loading and the ratio of carbon to alumina. The interrelationship between these two variables is not clear since no definite trend is apparent from the limited amount of data available.

Based on Coulter counter analysis of the mean particulate diameter and the densities of 2.2g cm$^{-3}$ and 1.8g cm$^{-3}$ for alumina and carbon respectively, it can be shown that the number of carbon particles
Figure 29. Comparison of alumina chorination rate profiles for melt:alumina ratios of 7.5:1 and 4.6:1 at 750°C at constant carbon loading.
exceeds that of alumina at a carbon loading of 8.5g \((V_C = 0.117g^{-1})\). On a volume basis, the amount of carbon exceeds the amount of alumina at a carbon loading of 12.6g \((V_C = 0.079g^{-1})\). Both of these loadings are in the region where the reaction rate increases, so the increased reaction rate observed in Figure 28 may be caused by changes in the rheology of the slurry.

Slurry rheology is a function of the characteristics of the particles in suspension \((16,45)\), so it would be expected that a slurry containing primarily carbon by volume would have substantially different properties that a slurry composed primarily of alumina particles. One of the major problems in slurry reactor research has been trying to determine a method of predicting the effects of solids on gas-liquid mass transfer a priori.

The observed effect of carbon loading in the screening experiment at 800°C may have actually been a result of the combination of parameters used. The high carbon loading was coupled with a low alumina loading and vice versa. This combination would enhance the two effects observed in this series of experiments.

**Carbon particle reaction**

The chlorination experiments using melt:carbon ratios of 84:1 and 52.5:1, also show the effects of high carbon conversions on the reaction rate. As previously mentioned in the slurry reaction discussion, the reaction rate is a strong function of \(a_C\), except when gas-liquid mass transfer controls the reaction rate. If the reaction is controlled at the particle surface, then the rate becomes a function of conversion. There are three limiting cases based on an analysis of equation 18 and
Table 8. Characteristic equations and solutions for rate limiting cases in slurry reactors (First order reaction)

<table>
<thead>
<tr>
<th>Limiting Condition</th>
<th>Equation Form</th>
<th>Time - Conversion Behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas-Liquid Mass Transfer</td>
<td>$\frac{C_{Cl,i}}{r} = \frac{1}{a_gK_{Cl,g}}$</td>
<td>$t \propto X$</td>
</tr>
<tr>
<td>Liquid-Solid Mass Transfer</td>
<td>$\frac{C_{Cl,i}}{r} = \frac{1}{a_c} \cdot \frac{1}{K_{Cl,ls}}$</td>
<td>$t \propto 1-(1-X)^{2/3}$</td>
</tr>
<tr>
<td>Kinetic Control</td>
<td>$\frac{C_{Cl,i}}{r} = \frac{1}{a_g} \cdot \frac{1}{K'}$</td>
<td>$t \propto 1-(1-X)^{1/3}$</td>
</tr>
</tbody>
</table>

where $t$ = Time, minutes;

$X$ = Carbon conversion.

$^a$Calculated assuming that $K_{Cl,ls}$ is proportional to the inverse of the carbon particle radius (38).

These are shown in Table 8.

The time versus conversion solutions shown in Table 8 assume that the carbon reacts as a shrinking sphere without the formation of an ash layer. Porosity of the particle is neglected which, based on the results obtained appears to be a reasonable assumption.

Gas-liquid mass transfer This case is the simplest, since the reaction rate is not a function of the particle diameter. Therefore, the reaction rate is independent of surface and the conversion is linear with time.
**Liquid-solid mass transfer** The solution presented in Table 8 is developed in Levenspiel (38). It is based on the assumption that reacting particle is in the Stoke's Law settling regime, so $k_{Cl,ls}$ is proportional to the inverse of the particle radius. The average particle Reynolds number for Coke-2 is 0.01, which is well within the Stoke's law region.

**Kinetic control** The solution for the kinetic control case was also developed in Levenspiel and is a straightforward derivation based on the change in surface area with volume as the particle reacts.

**Results** Figure 30 shows conversion versus time curves for each of these three limiting cases plotted for the two lowest carbon loadings shown in Figure 28. Unfortunately, neither experiment was completely controlled by one mechanism for the duration of reaction. Both experiments initially showed gas-liquid mass transfer control shifting to kinetic control as the experiment progressed.

Figure 30A shows the results for the 84:1 salt:carbon ratio. All three curves are nonlinear in the first 10 minutes of reaction, which is caused by lag time in the condensers. From 10 to 30 minutes, the $X$ versus $t$ curve is the most linear indicating that gas-liquid mass transfer controlled the reaction. By the 40 minute mark however, the $X$ versus $t$ curve shows appreciable curvature and the $1-(1-X)^{1/3}$ versus $t$ curve is linear indicating kinetic control at the carbon surface. The $1-(1-X)^{2/3}$ versus $t$ curve is non-linear over the entire range of reaction, so solid-liquid mass transfer does not limit the reaction under these conditions.

Figure 30B shows the analysis of the 52.5:1 melt:carbon experiment.
Figure 30. Application of the limiting cases of the slurry reactor model to data from two high carbon conversion experiments.

Graph A: Melt:carbon ratio = 84:1
Graph B: Melt:carbon ratio = 52.5:1
This chlorination is gas-liquid mass transfer controlled until 120 minutes into the reaction, at which point the X versus t curve starts to become significantly nonlinear. The $1-(1-X)^{1/3}$ versus t curve may be linear from 120 to 150 minutes, however, this segment of the curve is too short to draw a definite conclusion.

Summary

The major results of the carbon loading experiments were:

- The reaction rate is gas-liquid mass transfer dominated at 750°C. The region of mass transfer influence can be reasonably assumed to extend from 650 to 800°C, as indicated by the Arrhenius plot (Figure 20).
- The melt:carbon ratio and the total solids loading influence the gas-liquid mass transfer coefficient or the gas-liquid interfacial surface area.
- The results of this work indicate that increasing the relative volume of carbon to alumina has a positive effect on the mass transfer of chlorine into the melt.
- Excessive levels of alumina appear to inhibit chlorine mass transfer.
- The carbon particles react following the shrinking core model.

This work indicates that a process scale unit would likely be gas-liquid mass transfer controlled. Enhancement of gas transport into the melt would be a primary concern. One possible solution would be to operate the reactor under pressure in order to increase $C_{CI,1}$, although this would present a whole series of design problems with respect to
corrosion and handling of the fused salt.

Reaction Rate Versus Stirrer Speed

The effect of stirring speed was also investigated. The experiment was conducted at 750°C so that the reaction was mass transfer controlled. The other experimental conditions and procedures were the same as those used in the temperature dependence experiments except no slurry samples were taken.

The study consisted of a single experiment that included several stirrer speeds. The chlorination was started at a stirring rate of 900 RPM, so that the results could be verified against the initial rates from previous chlorinations. After the product gas composition had stabilized and the reaction rate been determined, the stirrer speed was then changed. This took 30 minutes at each stirring speed. By repeating this procedure it was possible to determine the reaction rate at several different stirring rates.

Figure 31 is a comparison of both the alumina reaction rate and gas hold-up in the reactor as a function of stirrer speed. The gas hold-up curve was determined from a series of measurements discussed in Appendix C.

Because the reaction is gas-liquid mass transfer controlled at these operating conditions, the reaction rate is controlled by $a_g$ and $K_{Cl,g}$. Figure 31 shows that the reaction rate and gas hold-up both follow the same trend and are proportional to each other, which indicates that $K_{Cl,g}$ is not a strong function of stirring speed.

It has been reported previously that the gas-liquid mass transfer coefficient is virtually independent of the stirring speed (18,33). It
Figure 31. The effect of stirrer speed on reactor gas hold-up and the chlorination rate of alumina at 750°C

EXPERIMENTAL CONDITIONS
TEMPERATURE 750 °C
MELT: CARBON 2:1
MELT: ALUMINA 7.5:1
MELT % AlCl₃ (MOLE) 40%
Cl₂ RATE 245 cm³/min
also seems reasonable to conclude that the chlorine bubble size is independent of the stirring speed. It is unlikely that both the number and size of bubbles would change in such a way that the gas hold-up would be linear with respect to stirrer rate.

This experiment verifies that gas-liquid mass transfer was important at 750°C. The effect of stirrer speed on the reaction rate, however, has little application to a process scale reactor since such a unit would probably not be mechanically agitated.

**Proposed Reaction Mechanism**

Based on analysis of the alumina chlorination experiments, a reaction mechanism or path as described in equations 24-28 is proposed. Most of the experimental support for this mechanism comes from the screening, temperature dependence and mechanism experiments. The carbon loading and stirring experiments provide support of an indirect nature; they do not contradict the proposal. The proposed reaction sequence is as follows:

\[
\begin{align*}
\text{Al}_2\text{O}_3(s) + \text{AlCl}_3 & \rightarrow 3\text{AlOCl} \quad (24) \\
\text{C}(s) + \text{Cl}_2 & \rightarrow \text{C}\cdot\text{Cl}_2(s) \quad (25) \\
\text{C}\cdot\text{Cl}_2(s) + \text{AlOCl} & \rightarrow \text{C}\cdot\text{O}(s) + \text{AlCl}_3 \quad (26) \\
\text{C}\cdot\text{O}(s) + \text{Cl}_2 & \rightarrow \text{C}(s) + \text{COCl}_2 \quad (27) \\
\text{COCl}_2 + \text{AlOCl} & \rightarrow \text{CO}_2 + \text{AlCl}_3 \quad (28)
\end{align*}
\]

All the chemical species in equations 24-28 are assumed to be dissolved in the melt unless otherwise indicated. The absorption of \(\text{Cl}_2\)
and the desorption of CO₂ to and from the gas and liquid phases is not shown here.

It has also been reported in the literature that chloride melts have good wetting characteristics on carbon (31), so it is reasonable to assume that the gaseous reactants must pass through the melt to move between the gas and solid phases. Chlorine is also known to be soluble in NaCl-AlCl₃ melts as molecular chlorine (15, 62).

Based on reports in the literature (35, 38) and the null effect of alumina loading in the screening experiment, it is apparent that alumina reacts as a dissolved metal oxychloride, which is formed by the reaction shown in equation 24. The AlCl₃ for this reaction comes from the melt.

It is also shown from the screening experiment that the reaction takes place at the carbon surface. The "*'" symbol represents the bonding of chlorine or oxygen to a carbon atom in the carbon surface. This is believed to be a better representation of the reactions occurring at the carbon surface since the stoichiometry of the carbon intermediates is a matter of conjecture.

Equation 25 is based on the observed effect of prechlorination in the reaction mechanism experiments which indicated that exposing the carbon to chlorine for an extended period of time at 600° enhanced the alumina chlorination rate. Also, chlorinations at 800°C showed that Cl₂ will react with carbon directly without producing AlCl₃. These results are interpreted to mean that the chlorination of carbon is an integral step in the reaction process. Aluminum oxychloride is then converted to AlCl₃ by reacting with the chlorinated carbon (equation 26).

Further support for a carbon-chlorine reaction is the fact that
AlCl₃ is a catalyst for the chlorination of aromatic compounds (58). Aluminum chloride is a Lewis acid and chlorine is a Lewis base. The catalytic mechanism for the chlorination reaction is the formation of a Cl₂-AlCl₃ complex, where the Cl₂ molecule develops a positive dipole moment. This positive dipole on the chlorine molecule allows the Cl₂-AlCl₃ complex to act as an electrophile and react with the pi-bonds in the aromatic ring. It seems reasonable to assume that AlCl₃ could serve the same function in the carbochlorination reaction.

It is also possible that AlOCl could have a similar effect on chlorine since it is also a Lewis acid. Therefore, it is possible that it could also catalyze the chlorination of carbon. If this were the case, it is quite likely that the reactions shown separately in equations 25 and 26 occur virtually simultaneously. Unfortunately, it is not possible, with the available equipment, to directly determine what is occurring at the carbon surface or if AlOCl and Cl₂ react in this manner.

A carbon-chlorine reaction, catalyzed or not, also fits with the idea of differences in the reactivity of the carbon surface. The carbon particles used in these experiments did not consist of homogeneous molecular sheets of graphitic carbon, but groups of conjugated aromatic rings linked by aliphatic rings or chains (7). Carbon atoms contained in aliphatic structures would be more reactive since they lack the stabilizing effect of conjugated pi-bonding found in aromatic rings. Because these linkages involve a small fraction of the total number of carbon atoms (7), they would be consumed fairly quickly, resulting in a net reduction in the reactivity of the carbon surface. This explains
the initial peaks in reaction rate for the chlorinations between 650 to 530°C. At higher temperatures, the overall reactivity of the carbon is increased to the point where the rate is controlled by gas-liquid mass transfer effects.

An alternate reaction to Equation 25 is a carbon-AlOCl reaction shown in Equation 29.

\[ \text{C(s) + AlOCl} \rightarrow \text{C·AlOCl(s)} \quad (29) \]

This route was suggested in the Haupin patent (26), however, there was no evidence given to support this mechanism and it was stated that the investigators did not want to be "bound to a specific reaction mechanism". The only reason given for proposing an interaction between AlOCl and carbon was that a true trimolecular reaction is a very unlikely occurrence, which is true. However, that by itself is not sufficient evidence to validate this reaction. The reaction proposed by equation 29 does not explain the increased reaction rate caused by prechlorinating the carbon (Figure 27) or the consumption of chlorine without carbochlorination (Figure 22).

The next step is the reaction of the dissolved AlOCl with the chlorinated carbon to form AlCl₃ and an oxygenated carbon atom as shown in equation 26. This reaction follows from the Cl₂-carbon reaction shown in equation 25 and, as previously discussed, may occur simultaneously with that reaction. Aluminum chloride formed in this reaction goes into solution while the oxygen-carbon complex remains, either absorbed or bonded to the carbon matrix. The oxygen-carbon complex must remain on the carbon surface in order to explain the lack of CO observed in the product gas stream. If discrete molecules of CO
were formed and released to the liquid in quantity, they would be expected to leave the reactor before reacting further to form CO$_2$. This conclusion is further reinforced by the Haupin patent which claims that gaseous reductants are not very effective in fused salt carbochlorination (26).

For the same reason it seems unlikely that C*Cl$_2$(s) reacts with additional Cl$_2$ to form CCl$_4$. If it did, the CO:CO$_2$ ratio observed at 650$^\circ$C and above would be expected to be constant since CO would be formed as a result of the dissociation of COCl$_2$ in the melt, the COCl$_2$ being produced from the reaction:

$$CCl_4 + AlOCl \rightarrow COCl_2 + AlCl_3$$

(30)

The next portion of the reaction is the conversion of the oxygen-carbon complex to CO$_2$, as shown in equations 27 and 28. It appears that chlorine reacts with the oxygenated carbon to produce phosgene. This would explain the inflection in the Arrhenius plot at 650$^\circ$C, since phosgene becomes thermodynamically unstable at temperatures above 600$^\circ$C. This type of Arrhenius behavior has also been reported in the literature with respect to the gas-solid carbochlorination reaction (49).

**CO formation**

It appears that the formation of CO is related to both the dissociation of phosgene and the structure of the carbon. The CO:CO$_2$ ratios shown in Figure 21 are not constant for the duration of the experiment as they should be if phosgene dissociation were the only source of CO. The other possible source of CO is a cracking reaction:

$$C\cdot O(s) \rightarrow C(s) + CO(g)$$

(31)
Such a reaction would fit in with the previously advanced idea of more reactive aliphatic sites. At higher temperatures, the bonding of partially oxygenated aliphatic carbon atoms into the carbon structure might not be as stable as that of aromatic carbons, so these could break down to form CO. As these structures are eliminated by reaction, the level of CO would be reduced.

**Summary**

The mechanism proposed here is probably more accurately described as a reaction path, since the actual reactions and chemical species occurring in the process are certainly far more complicated and numerous than those described in equations 24-29. Of the various steps in the reaction process, equation 25 is based on what would have to be considered the most circumstantial evidence.

It would be desirable, in some future study, to determine a way of directly observing what is occurring on and to the carbon surface. Such an observation would not be a trivial undertaking since reaction intermediates are only present at reaction conditions and then at very low concentrations.

The remaining steps, such as alumina dissolution, have been observed in other fused salt chlorination systems or are in agreement with aspects of the gas-solid reaction mechanism, i.e., phosgene formation and dissociation.

**Effect of NaCl-AlCl₃ Melts on Fly Ash**

As shown in the alumina chlorination studies, a key step in the chlorination process is the conversion of the solid metal oxide to a
dissolved metal oxychloride species. In the case of a pure oxide, this is a straightforward reaction since the oxide surface is homogeneous. The dissolution of a mixed metal oxide, such as fly ash, is not so straightforward a case. Thermodynamically, all of the commonly found oxides are capable of reacting with AlCl₃, however, the kinetics of reaction may not be favorable.

In order to determine the effect of NaCl-AlCl₃ melts on fly ash, a series of experiments was done using 48% AlCl₃-52% NaCl and 40% AlCl₃-60% NaCl melts at 400 and 600°C. The 48% AlCl₃ composition was tested at both 400°C and 600°C, but the 40% AlCl₃ composition was only tested at 600°C since it could not exist as a liquid at 400°C (Figure 1). The purpose of these experiments was to measure changes in the ash composition and weight in order to determine if the ash could be dissolved.

Table 9 shows the residue composition and the percent change in the iron, silicon, aluminum and titanium oxides for the three operating conditions. The potential oxide melt reactions for this system are:

\[
\text{Fe}_2\text{O}_3 + 2\text{AlCl}_3 \rightarrow 2\text{FeCl}_3 + \text{Al}_2\text{O}_3 \quad (32)
\]

\[
3\text{SiO}_2 + 4\text{AlCl}_3 \rightarrow 3\text{SiCl}_4 + 2\text{Al}_2\text{O}_3 \quad (33)
\]

\[
3\text{TiO}_2 + 4\text{AlCl}_3 \rightarrow 3\text{TiCl}_4 + 2\text{Al}_2\text{O}_3 \quad (34)
\]

The conversion of iron oxide to iron chloride occurred in all the tests. This was verified by the presence of FeCl₃ in the condenser used to remove chlorides from the gas stream exiting the reactor. It was also observed that not as much FeCl₃ vaporized from the 40% AlCl₃ melt and that the color of the melt was markedly different from that of the
Table 9. Results of fused salt-fly ash solubility studies

<table>
<thead>
<tr>
<th>AlCl₃ Conc.</th>
<th>Temp. °C</th>
<th>Percent Change of Component</th>
<th>Percent Wt. Loss</th>
<th>Residue Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>SiO₂</td>
<td>Al₂O₃</td>
<td>Fe₂O₃</td>
</tr>
<tr>
<td>Fly Ash</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>400</td>
<td>-14.8</td>
<td>0.57</td>
<td>-15.22</td>
</tr>
<tr>
<td>48</td>
<td>400</td>
<td>-13.5</td>
<td>-9.11</td>
<td>-11.50</td>
</tr>
<tr>
<td>48</td>
<td>400</td>
<td>-5.9</td>
<td>9.80</td>
<td>-8.43</td>
</tr>
<tr>
<td>48</td>
<td>600</td>
<td>-10.3</td>
<td>0.35</td>
<td>-27.21</td>
</tr>
<tr>
<td>48</td>
<td>600</td>
<td>-15.2</td>
<td>-11.50</td>
<td>-24.12</td>
</tr>
<tr>
<td>48</td>
<td>600</td>
<td>-20.2</td>
<td>1.39</td>
<td>-29.58</td>
</tr>
<tr>
<td>40</td>
<td>600</td>
<td>-6.5</td>
<td>11.92</td>
<td>-10.58</td>
</tr>
<tr>
<td>40</td>
<td>600</td>
<td>-3.1</td>
<td>1.86</td>
<td>-11.30</td>
</tr>
</tbody>
</table>
48% AlCl₃ melt at the same temperature. This was probably caused by the formation of NaFeCl₄, which is the iron analog of NaAlCl₄.

The silica removals are statistically significant for the first two sets of conditions reported in Table 9. Silica removal by the 40% AlCl₃ melt at 600°C is not statistically significant at a 95% confidence limit.

Changes reported in the TiO₂ and Al₂O₃ contents are not reliable because of the variance in the results. The variation in the titanium results was caused by the low concentrations present in the samples and the insensitivity of atomic absorption for the detection of titanium. On the average, however, there appears to be little or no trend towards removal of titanium from the fly ash.

Variance in the alumina conversion is probably the result of difficulty with washing of the melt from the residue. Based on equations 31-33 there should have been a net increase in the alumina content of the ash. The alumina formed by these reactions though, was probably not securely bound to the residue surface and could have been removed in the course of washing the solidified melt from the ash. Also some of the alumina in the ash could have been initially dissolved and then reprecipitated by the chloride exchange reactions. This alumina would also have been susceptible to removal in the wash step.

With respect to fly ash processing, the results in Table 9 indicate that temperature and AlCl₃ content have an interrelated effect. The best combination for iron removal was high temperature and a high AlCl₃ content. Reducing the AlCl₃ content by 8%, or the temperature by 200°C, reduced the iron oxide content by about the same level.
Silica removal shows the same general trend as iron, however, the AlCl$_3$ content of the melt was much more important than temperature. A 20% reduction in the AlCl$_3$ content of the melt at 600°C almost eliminated silica removal from the ash, while reducing the temperature by 200°C and holding the AlCl$_3$ content constant only reduced silica removal by 25%.

This result is explained by the equilibrium species present in NaCl-AlCl$_3$ melts as described by equations 7-9. There is more free AlCl$_3$ present in a 48% AlCl$_3$-52% NaCl than a 40% AlCl$_3$-60% NaCl melt. It is this free AlCl$_3$ which is believed responsible for the enhanced dissolution of silica by the AlCl$_3$ rich melt. At 400°C the Gibbs free energy of the reaction:

$$4\text{AlCl}_3 + 3\text{SiO}_2 \rightarrow 3\text{SiCl}_4 + 2\text{Al}_2\text{O}_3$$

is -14 Kcal compared to +266 Kcal for:

$$4\text{NaAlCl}_4 + 3\text{SiO}_2 \rightarrow 3\text{SiCl}_4 + 2\text{Al}_2\text{O}_3 + 2\text{NaCl}$$

Unfortunately, it was not possible to locate data for the thermodynamic properties of NaAlCl$_4$ at temperatures above 424°C. Based on extrapolation of the low temperature data, it is unlikely that a 400°C increase in temperature would cause a 266 Kcal shift in the value of the Gibbs free energy of equation 36.

Scanning electron microscopy and X-ray diffraction patterns showed no appreciable differences between the treated and untreated ash. This was not surprising in view of the relatively small changes in composition induced by the treatment.
Summary

The importance of these results with respect to carbochlorination is that the melt will dissolve the ash. They also indicate that the temperature and composition of the melt can affect this dissolution. Of particular interest is the very strong dependence of silica removal with respect to the AlCl₃ content of the melt, and its relative insensitivity to melt temperatures.

The results of this study should not be directly compared to the chlorination experiments described in the next section. The chlorination experiments were run at 750°C and the only point available for comparison was the sample taken 5 minutes after the ash had been added to the melt, which is significantly different from a sample exposed for 30 minutes to a 600°C melt.

Another major difference between the chlorination experiments and this study is that in this study the system was allowed to cool slowly, whereas samples taken from the chlorination reactor were quenched. Because of this, species that might have been dissolved, such as AlOCl, could recrystallize on the ash surface. In a sample from the chlorination reactor, they would have been frozen in solution.

Fused Salt Chlorination of Fly Ash

Two fly ash chlorination experiments were done to evaluate the chlorination of a mixed metal oxide. Because of the importance of melt composition on silica removal, as described in the previous discussion, melt compositions of 40% AlCl₃-60% NaCl and 48% AlCl₃-52% NaCl were used. For simplicity these two compositions are designated as 40A and 48A, respectively, for the remainder of this discussion.
The other experimental conditions were held constant at:

- **Temperature**: 750°C
- **Melt:carbon ratio**: 21:1 (wt.)
- **Melt:fly ash ratio**: 42:1 (wt.)
- **Cl₂ Flowrate**: 245 cm³ min⁻¹

Slurry samples were taken at 15 minute intervals in order to monitor conversion rates of the individual oxide compounds as closely as possible. The 40A experiment was run for a total of 62.5 minutes, after which it had to be terminated because of an equipment failure. The 48A experiment was 180 minutes in duration. Fly ash was added to the reactor 10 minutes before the chlorine was turned on.

**Major component chlorination**

Silicon, aluminum and iron oxides are the major oxide components of fly ash, making up 90% of the Halomet nonmagnetic ash in that order of concentration. Figures 32 and 33 show the conversion of these three components versus time for the 40A and 48A experiments, respectively.

Iron oxide conversions are virtually identical for the two experiments, which is expected since iron oxide readily reacts with aluminum chloride to form alumina and iron chloride. The similarity of the iron conversions in the two experiments indicates that differences observed in the silica and alumina conversion rates are not artifacts caused by errors in the slurry sampling.

In contrast to iron, the alumina and silica conversion curves are significantly different between the two experiments. In the 40A experiment there is a rapid increase in the conversion of both oxides...
Figure 32. Conversion rates of iron, aluminum and silicon oxides by the fused salt chlorination of Halomet nonmagnetic ash at 750°C in a 40% AlCl₃ melt.
Figure 33. Conversion rates of iron, aluminum and silicon oxides by the fused salt chlorination of Halomet nonmagnetic ash at 750°C in a 48% AlCl₃ melt
between 7.5 and 22.5 minutes, while in the 48A chlorination the silica and alumina conversion rates are virtually constant throughout the experiment.

After 30 minutes, the alumina reaction rate for the 48A chlorination is 1.3 times that of the 40A experiment and the silica rate is 3.6 times larger. As a result, the total ash conversion rate was much faster in the 48A experiment but with less selectivity between silica and alumina than in the 40A chlorination.

The component conversion profiles are supported by the CO$_2$ production, as monitored in the product gas analysis. Figure 34 is a plot of the measured CO$_2$ production versus time. The 40A experiment shows a larger production of CO$_2$ than the 48A chlorination at the start of the experiment and a lower rate at the end, which agrees with the trends in the oxide conversion rates. Carbon monoxide production is not shown since it accounted for less than 2% of the conversion.

The total amount of CO$_2$ in the product gas at the end of the chlorination was within 3% of the amount of CO$_2$ that should have been produced as determined from the oxide conversions for both chlorinations. The product gas analysis was slightly low in both cases.

Although the total CO$_2$ production is in agreement with the oxide conversions, the rate at which CO$_2$ was produced does not agree with the observed oxide chlorination rate, if it is assumed that the oxide was chlorinated as quickly as it dissolved. This discrepancy is very small in the 48A chlorination but is quite large in the 40A case.

In the first 30 minutes of reaction, the CO$_2$ production rate in the 40A experiment, based on oxide conversion, should have averaged
Figure 34. Carbon dioxide production rates for the carbochlorination of Halomet nonmagnetic ash at 750°C in 40% and 48% AlCl₃ melts
4.2(10^{-3}) \text{ moles min}^{-1} \text{ compared to the actual average rate of } 2.9(10^{-3}).

In the last thirty minutes of reaction, the order was reversed. The average oxide-based CO$_2$ rate was 10^{-3} \text{ moles min}^{-1}, while the actual rate averaged 2.1(10^{-3}).

In the 48A experiment, the oxide conversion based CO$_2$ rate was 2.7(10^{-3}) \text{ moles min}^{-1} \text{ compared to an actual value of } 2.6(10^{-3}) \text{ for the first 30 minutes of reaction. Between 30 and 60 minutes, the average oxide conversion rate was } 1.9(10^{-3}) \text{ moles min}^{-1} \text{ compared to an actual rate of } 2.2(10^{-3}).

The difference between the oxide conversion and CO$_2$ production rates indicates that at the start of the 40A experiment the reaction at the carbon surface is slower than the dissolution rate of the oxide into the melt. The same is true for the 48A experiment, but the difference is significantly smaller.

Tremillion et al. (60) has shown that the solubility of alumina in NaCl-AlCl$_3$ melts goes through a minimum at near equimolar compositions. Such a minimum would explain the difference between the oxide conversion data and the observed carbon reaction rate. Based on the solubility characteristics of alumina in NaCl-AlCl$_3$ melts, it can be concluded that the jump in the 40A oxide conversion between 7.5 and 22.5 minutes is in part due to the dissolution of the ash rather than the carbochlorination reaction. The enhanced solubility does speed up the carbochlorination reaction as shown by the CO$_2$ production curves, but not to the extent that the oxide conversion data indicates.

The CO$_2$ product gas data and oxide conversion data can be combined to provide an estimate of the ash solubility. At 20 minutes into the
reaction, 14.7% of the ash in the 40A experiment had dissolved but had not been chlorinated compared to 4% for the 48A experiment based on CO₂ production from the reactor including the CO₃ present in the condensers and reactor. The ratio of these two percentages is in reasonable agreement with Tremillion et al. (60), who reported a ratio of 7.7 between in minimum and maximum solubilities of Al₂O₃ in NaCl rich melts at 210°C. The absolute values Tremillion reported for alumina solubility were an order of magnitude lower, but this would be expected since the work was done at a much lower temperature.

Based on the alumina work, these chlorinations should have been gas-liquid mass transfer controlled so the maximum expected CO₂ production rate would have been 2.55(10⁻³) g-moles min⁻¹. Both experiments exceeded this value for the first 30 minutes of reaction, the 40A experiment by over 50%. The apparent violation of the chlorine mass-transfer limitation is attributed to the presence of FeCl₃ in the melt, which facilitates the transport of chlorine by the reaction (8):

\[ \text{FeCl}_3 \rightarrow 0.5\text{Cl}_2 + \text{FeCl}_2 \]  

(36)

The use of iron chloride and other multivalence metals as catalysts for fused salt chlorination was patented by Wohleber and Cochran (64).

Both experiments appeared to be rate limited by the dissolution of the ash. The 40A chlorination was certainly limited by the ash dissolution rate after 30 minutes of reaction. This conclusion is based on two facts. First, the oxide dissolution rate is approximately half of what would be expected based on the quantity of CO₂ exiting in the product gas. Second, the CO₂ production rate falls below the rate measured for the 48A experiment after the same amount of time.
The evidence for ash dissolution control in the 48A chlorination is not as dramatic as the 40A chlorination. The CO₂ production rates match those predicted by the oxide conversion curves, indicating that the carbochlorination reaction rate was the same as the dissolution rate of the ash. Since the CO₂ production rate fell off throughout the entire experiment instead of being constant, it follows that the reaction was limited by the dissolution of the ash.

**Minor component conversion**

The conversions of calcium, magnesium, and titanium oxides in the ash were also determined. These three oxides make up 5.7 percent of Halomet nonmagnetic ash, which is typical for fly ash (46). Of these three metals, only titanium has any commercial significance. Calcium and magnesium are only important because they consume chlorine. Conversion rates for these three elements in the 40A and 48A experiments are shown in Figures 35 and 36.

Unlike the major oxides, there is no major difference between the two experiments, except that CaO conversion in the 40A experiment was approximately 15% higher than the 48A experiment for the duration of the reaction. The shape of the conversion profiles for each oxide is similar for both experiments.

The most likely explanation for the enhanced CaO removal in the 40A chlorination is that some of the calcium is associated with alumina, which would account for the increased conversion. The high initial conversion of CaO in both experiments is attributed to the removal of calcium anhydrite in the ash. The MgO and TiO₂ conversion profiles are identical for both experiments which probably results from the fact that...
Figure 35. Conversion rates of calcium, magnesium and titanium oxides by the fused salt chlorination of Halomet nonmagnetic ash at 750°C in a 40% AlCl₃ melt.
Figure 36. Conversion rates of calcium, magnesium and titanium oxides by the fused salt chlorination of Halomet nonmagnetic ash at 750°C in a 48% AlCl₃ melt.
these two elements tend to be concentrated on the glassy phase of the ash (29). Magnesium tends to substitute into the crystalline phases of the ash slightly more than TiO₂ which would explain the better overall conversion observed for MgO. The lower conversions for MgO and TiO₂ would indicate that the glass phase of the ash is not readily attacked by NaCl-AlCl₃ melts.

Reactivity of mineral phases in fly ash

Hewlett et al. (29), in a study of the structure of fly ash, defined three major mineral phases, spinel (iron-rich), mullite-quartz and glass. The mullite-quartz phase may be further divided into mullite and quartz as separate groups. If the chlorination rate of titanium is assumed to be an indication of the chlorination rate of the glass phase, it is then possible to deduce the order of chlorination of these four components of the ash.

Based on the observed component conversion rates, the spinel group is the first to chlorinate, followed by mullite and then the glass phase and quartz. This proposed order of chlorination is supported by the X-ray diffraction patterns for the residue of the 40A chlorination and the untreated ash shown in Figure 37. Because of the small size of the slurry samples, it was not possible to get X-ray patterns of the ash as a function of conversion.

In the untreated ash there are observable peaks for hemitite, mullite and silica as well as a discernible amorphous hump between two-theta angles of 15 and 30 degrees. In contrast, after 60 minutes of fused salt chlorination, the chlorination residue shows no evidence of mullite and only slight traces of hemitite. The latter peaks may be the
Figure 37. X-ray diffraction patterns for the Halomet nonmagnetic ash before and after chlorination in a 40% AlCl₃ melt for 65 minutes
result of residual iron from the coke ash or hemitite enclosed in the glass phase of the Halomet ash. Quartz is still present in large quantities and the amorphous hump is still present.

**SEM micrographs**

To determine how fly ash is attacked in the fused salt chlorination process, a series of SEM micrographs were taken of selected slurry samples. Figure 38 shows micrographs of untreated Halomet nonmagnetic ash and samples taken from the 40A chlorination at -6, 22, and 52 minutes. These images show evidence of attack on a greater percentage of the particles as the chlorination progresses.

An important characteristic of the dissolution is that the fly ash particles did not react as shrinking spheres, but instead were selectively attacked. Many of the particles retained much of their original spherical shape, but are fissured or cratered, while others show evidence of more uniform attack. An example of the latter is shown by a particle in Figure 38B where the surface appears to be etched over its entirety. An extreme example of the fissured type of particle is shown in the upper left hand corner of Figure 38C.

Figure 39 shows micrographs of ash samples taken from the 48A chlorination. These samples were taken at -6, 22, 52.5 and 112.5 minutes. There were no discernible differences between the -6 minute samples from two chlorinations. Again there was evidence of surface etching, but most particles showed minimum signs of attack. At 22.5 minutes there was greater evidence of surface attack but most particles retained their original structure. At 52.5 minutes, Figure 39C, there is significant fragmenting and many of the particles show signs of deep
Figure 38. Scanning electron micrographs of Halomet nonmagnetic ash before and after chlorination in a 40% AlCl₃ melt at 750°C

A. Untreated Halomet nonmagnetic ash (-325 mesh fraction)
B. Chlorinated ash sample taken from the reactor at 7.5 minutes
C. Chlorinated ash sample taken from the reactor at 22.5 minutes
D. Chlorinated ash sample taken from the reactor at 52.5 minutes
Figure 39. Scanning electron micrographs of Halomet nonmagnetic ash after chlorination in a 48% AlCl₃ melt at 750°C

A. Chlorinated ash sample taken from the reactor at 7.5 minutes
B. Chlorinated ash sample taken from the reactor at 22.5 minutes.
C. Chlorinated ash sample taken from the reactor at 52.5 minutes
D. Chlorinated ash sample taken from the reactor at 112.5 minutes
fissuring or cratering. By 112.5 minutes, Figure 39D, virtually all the particles show extensive attack.

In all of the micrographs it was evident that the ash was not attacked uniformly, but that certain portions of the particles were dissolved first. The particle just above dead center in Figure 39D appears to be partially enclosed by an insoluble shell, which was a phenomenon that was observed quite often. Close examination of other particles in the micrographs shows several with a similar structure.

The selective attack observed in the dissolution of fly-ash is most likely a result of the relative reaction rates of the crystalline and glass phases in the ash. These differences in reactivity have been previously observed in acid leach studies to characterize fly ash (29). The insoluble shell observed around many particles probably consists of glass and was formed when the particle solidified. Fissures formed in these particles are probably where crystalline phases were originally exposed at the particle surface. Dissolution would start at those points and follow the crystalline phase into the particle interior.

Comparison to gas-solid chlorination

In order to completely evaluate the effectiveness of the fused salt chlorination process it should be compared to the gas-solid chlorination system. Table 10 compares the conversions obtained in the fused salt work to gas-solid chlorinations of Halomet nonmagnetic ash. The latter chlorinations were done at 850°C and a chlorine flow rate of 44 cm$^3$ min$^{-1}$. The ash:carbon ratio used was 10:3 by weight and a total of 10g of ash was chlorinated as a loose powder.

The conditions used in the gas-solid studies are somewhat different
Table 10. Comparison of gas-solid and fused salt carbochlorination of Halomet nonmagnetic fly ash

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Reaction Time-min</th>
<th>Percent Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Gas-Solid 40A 48A</td>
</tr>
<tr>
<td>SiO₂</td>
<td>50</td>
<td>9.5 13 20</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>19.5 -- 51</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>20 -- 95</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>50</td>
<td>45 71 51</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>59 -- 83</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>60 -- 100</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>50</td>
<td>54 81 78</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>64 -- 91</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>73 -- 100</td>
</tr>
<tr>
<td>TiO₂</td>
<td>50</td>
<td>27 47 45</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>31 -- 77</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>40 -- 98</td>
</tr>
<tr>
<td>Al₂O₃:SiO₂</td>
<td>50</td>
<td>4.74 5.46 2.55</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>3.03 -- 1.63</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>3.00 -- 1.05</td>
</tr>
</tbody>
</table>

than those for the fused salt chlorination study. The gas-solid chlorination temperature was 100°C higher, and the chlorine:ash ratio was only \(1.8 \times 10^{-4}\) g-mole min\(^{-1}\)g\(^{-1}\) compared to 4.17 g-mole min\(^{-1}\)g\(^{-1}\) for the fused salt study. None of the gas-solid conversions, however, were limited by a lack of chlorine.

Table 10 shows that both the fused salt chlorinations were more effective at chlorinating the ash than was gas-solid chlorination for the same duration of reaction. The best chlorination for the selective removal of alumina is the 40A chlorination for a period of 50 minutes. If the primary process goal were to maximize the removal of titanium and alumina, and alumina:silica selectivity was of secondary importance,
then the 48A chlorination for a period of 100 minutes might be more appropriate.

The optimum choice of operating conditions is an economic decision that is beyond the scope of this study. It is apparent from Table 10 that fused salt chlorination does provide a greater degree of conversion at lower temperatures than a gas-solid chlorination of the same duration. In this respect, fused salt chlorination is more attractive than the traditional gas-solid route. There are, however, major differences in the equipment requirements for the two processes, and these are considered in the next section.

An interesting result of the fused salt chlorination procedure is that it is possible to obtain 100% ash conversion, which has not been previously reported for fly ash chlorination. From a processing standpoint total conversion is not desirable since it wastes chlorine on the production of SiCl₄. It shows, however, that fused salt chlorination is much more reactive than gas-solid chlorination.

Even though fused salt chlorination gives improved conversions at a lower temperature than gas-solid chlorination, it may not be the best method. As the Al₂O₃:SiO₂ conversion ratios in Table 10 indicate, the selectivity of fused salt chlorination may be significantly less attractive.
FUSED SALT CHLORINATION PROCESS

While the development of a complete chlorination process, including product purification, was not the primary objective of this study, it is important to evaluate how a fused salt reactor-based process might be configured. At the same time, those portions of the overall process that require further investigation and development, can be identified.

Fused Salt - Gas-Solid Reactor Comparison

There are two major differences between the fused salt and gas-solid processes. The first is the method of AlCl₃ product recovery from the reactor and the second is the large quantity of NaCl present as NaAlCl₄ in the gas stream exiting the slurry reactor.

In the gas-solid reactor, AlCl₃ is removed as a vapor along with FeCl₃, SiCl₄, TiCl₄ and the noncondensable gases. The unreacted residue is discharged from the reactor as a silica-rich powder along with any alkaline earth chlorides produced during chlorination. In the fused salt reactor, the unreacted residue is withdrawn in a stream of fused salt slurry. Because of limitations on the maximum solids content of the slurry, and the difficulty of thickening it, there will be a large quantity of AlCl₃ removed from the reactor as part of the fused salt. This AlCl₃ must either be recycled to the reactor or recovered and purified.

The problem of NaCl carryover in the product gas becomes more acute as the composition of the melt is made more rich in NaCl. The problem is not as severe with an AlCl₃ rich melt. However, as shown in the fly ash experiments, using a high AlCl₃ content melt results in a reduction
in the $\text{Al}_2\text{O}_3:\text{SiO}_2$ chlorination ratio. In order to completely eliminate NaCl carryover it is necessary to use a melt containing more than 50% $\text{AlCl}_3 \text{ (molar)}$, which would require reactor pressures well above atmospheric to reach temperatures of 700 to 800°C.

**Fused Salt Process**

A process schematic incorporating the fused salt reactor concept is shown in Figure 40. The process was developed so that the fused salt slurry would not have to be mechanically pumped. Conceivably all the high temperature slurry flows could be gravity driven, although gas sparging might be used to clear the lines of accumulated particulate.

The product purification scheme is based on an aqueous product separation. An anhydrous product separation scheme has been developed for the HiChlor process, but has never been tested (63). Also, the anhydrous process was not designed to accommodate the quantity of NaCl that would be expected in the product stream from a fused salt reactor. The primary advantage of anhydrous processing is that the $\text{AlCl}_3$ product can be fed directly into an aluminum chloride electrolysis cell (35), rather than being converted to $\text{Al}_2\text{O}_3$.

**Reactant feed**

As shown in Figure 40, the ash is first passed through a magnetic separator to remove an iron rich fraction, which is a marketable product (14). The nonmagnetic fraction is passed to the chlorination reactor, along with powdered coke and make-up NaCl. The latter replaces NaCl removed with the unreacted ash from the reactor and lost by the vaporization of $\text{NaAlCl}_4$. Coke is injected into the top of the reactor,
Figure 40. Process schematic for HiChlor process using fused salt slurry reactor
and Cl₂ is injected into the bottom of the reactor after being preheated.

The reactor is expected to be a bubble column reactor since this type of reactor requires no moving internal parts and is well suited for slurry reactions. The specifics of the reactor design are discussed in detail in the next section.

**Vapor phase products**

Unreacted chlorine, CO, CO₂, and metal chlorides are removed at the top of the reactor and unreacted residue is withdrawn from the bottom. Metal chlorides exiting in the vapor phase would be SiCl₄, TiCl₄, AlCl₃, FeCl₃ and NaAlCl₄. The last three chlorides would be condensed and the remaining mixture of permanent gases and chlorides passed on to an absorber and distillation train for purification and recovery.

This portion of the process has not been experimentally verified, however, based on the physical properties of the materials being separated it should work. The first step consists of a TiCl₄ absorber operating at -20°C to separate the metal chlorides and Cl₂ from CO and CO₂. Silicon tetrachloride, TiCl₄ and Cl₂ are separated in two distillation columns operating at pressures of 10 and 1 atmosphere respectively. Chlorine is recovered in the first column, while SiCl₄ and TiCl₄ are separated in the second. Chlorine and SiCl₄ are subsequently routed back to a chlorine recovery/recycle operation.

The condensed AlCl₃, FeCl₃ and NaAlCl₄ would either be passed on to the product purification system, or refluxed back into the reactor. The reflux ratio would be determined by the amount of AlCl₃ removed with the ash residue, which in turn would be dependent on the composition of the
melt and the solid:liquid ratio of the slurry.

**Slurry processing**

Unreacted solids are removed from the reactor along with a quantity of melt. The amount of AlCl₃ removed with the melt must be less than or equal to that generated by chlorination, otherwise it would be necessary to recycle AlCl₃ back into the reactor from the ash residue stream. In order to avoid recycling AlCl₃ it is necessary to maintain a minimum solid:liquid ratio in the residue stream, which is important in sizing the reactor.

It is probably not practical to concentrate the solids in the residue slurry stream exiting the reactor. The free settling rate of the ash particles in the melt averages 0.062 cm sec⁻¹, and the particle settling rate in the slurry would be even lower because of hindered settling. This tends to rule out gravity concentration of the slurry because of the size of the equipment required to concentrate such slow settling particulate. Mechanical concentration is complicated by the difficulty of handling a molten salt in anything but the simplest of process equipment.

The only mechanically simple method of removing AlCl₃ from the residue stream is by vaporization. This would be an energy intensive process that would require a vacuum column (less than 0.03 atm) or very high temperatures (+1100°C) to obtain the high recovery efficiencies required to justify the expense (40).

The most feasible approach to the problem is to dissolve the metal chlorides associated with the unreacted residue in water and recover the AlCl₃ from the resulting solution. As shown in Figure 40, the slurry
from the reactor is passed through a shot tower, countercurrent to a cold airflow, where it is cooled and solidified. The solidified chloride salt-residue mixture is then dissolved in 1M HCl and filtered to remove the ash-coke residue.

Depending on the coke:ash ratio required to maintain the desired reaction rate, it might be feasible to recover the unused coke for recycling. Otherwise provisions should be made to combust the unreacted coke for its energy value.

The metal chloride solution exiting from the filter is mixed with AlCl₃ and NaCl recovered from the vapor stream. A separate dissolver is used for the vapor phase material to reduce the load on the residue filter, however, if the recovery of vaporized AlCl₃ is small it might be more economical to use a single dissolver.

The metal chloride stream is then passed to a solvent extraction process to remove FeCl₃ using tertiary amines in an organic solvent (54). The original investigation, however, did not include alkali and alkaline earth chlorides in the feed stock because it was developed for the gas-solid reaction process. Examination of the process and associated experimental work indicates that alkali and alkaline earth chlorides would not interfere with iron removal, and that they would exit the extraction process in the aqueous phase along with AlCl₃.

No equipment is shown for the final purification of AlCl₃. In the original process proposed by Sheng et al. (54) AlCl₃ was crystallized using a HCl sparge, which is suitable for relatively pure AlCl₃ solutions. Unfortunately, NaCl is insoluble in HCl so a one-step
crystallization in a HCl sparge would produce a mixed NaCl-AlCl$_3$($6\text{H}_2\text{O}$) product.

There are at least three possible solutions to this problem, which could be used singly or together. Examination of the original solubility work for this system suggests that it might be possible to separate NaCl from AlCl$_3$ by crystallizing NaCl using a 10-11M HCl (42). Aluminum chloride would then be recovered by a second crystallization at a 13M HCl concentration. Even if this were not completely effective in removing NaCl, it would probably be a good method of reducing the size of subsequent NaCl-AlCl$_3$ separation steps.

A second possible approach is another solvent extraction. A preliminary examination of the literature did not reveal any published processes for NaCl-AlCl$_3$ separations, but based on solubility data a chlorinated benzene or nitrobenzene compound would be a likely candidate for such a process. Another option is ion exchange.

The third possibility is to coprecipitate the NaCl and AlCl$_3$($6\text{H}_2\text{O}$) and calcine the mixed product in the absence of oxygen. Alumina chloride hexahydrate will decompose to Al$_2$O$_3$, but NaCl should pass through the process unchanged. Therefore, it might be possible to remove the residual NaCl by washing the Al$_2$O$_3$ product. The success of this approach would be very dependent on the purity of individual crystallites and side reactions occurring in the calcining operation.

Summary

The process schematic as shown, represents one approach to incorporating the fused salt reactor concept into a chlorination process. No attempt has been made to develop a complete or optimized
possible, however, to identify those points requiring further study. Concerns specific to the reactor design are discussed in the next section.

- The effect of NaCl on the FeCl₃ solvent extraction must be evaluated and a NaCl-AlCl₃ purification scheme developed.

- More information is required about the handling of the molten salt slurry and suitable materials of construction. It would be useful to know if the slurry could be mechanically pumped at temperatures between 200 and 250°C.

- The effect of minor component chlorides in the melt should be evaluated since these could form immiscible liquid phases.

Other possible areas to investigate are:

- Use of a fused salt extraction step to selectively remove AlCl₃ from a NaCl-AlCl₃ melt.

- Development and testing of an anhydrous product purification scheme. Such an operation would have to be tolerant of unreacted residue and be capable of breaking the NaAlCl₄ complex.
To better evaluate the fused salt reactor concept it is necessary to determine the reactor size required to treat a given quantity of ash. With this information it is possible to more accurately judge the effectiveness of the fused salt approach.

Design Basis

The ash feed rate for this design is $10^4$ Kg hr$^{-1}$, which is the same feed rate used by Adelman (2). The alumina conversion rates for each process are nearly the same, so it is possible to make a rough comparison of the two designs. A major difference between this study and that of Adelman's is that different ashes were used. Also, both studies are of a very preliminary nature with little attention given to optimizing the reactor size.

The reactor conditions for the design study are those for the 40A fly ash chlorination, since that melt composition took about two-thirds less time than the 48A chlorination to affect the same alumina conversion and produced less SiCl$_4$. The range of feasible ash residence times is estimated to be from 20 to 85 minutes. At residence times less than 20 minutes the rate of alumina conversion with respect to time was very high, 2.5% per minute. After 20 minutes the rate dropped to 0.4% per minute. Based on the 48A chlorination experiment, the reaction rate of aluminum oxide falls off significantly when more than 80% has been chlorinated. This occurred 85 minutes with the 40A chlorination. For purposes of this study an average ash residence time of 60 minutes was selected as the design basis to insure that most of the ash would have a
Table 11. Fly ash chlorination reactor design basis \( (10^4 \text{ Kg hr}^{-1}) \)

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Conversion</th>
<th>Metal Chloride - Kg hr(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>25%</td>
<td>3370</td>
</tr>
<tr>
<td>Al(_2)O(_3)</td>
<td>73%</td>
<td>6160</td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>83%</td>
<td>1750</td>
</tr>
<tr>
<td>CaO</td>
<td>92%</td>
<td>669</td>
</tr>
<tr>
<td>MgO</td>
<td>70%</td>
<td>152</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>60%</td>
<td>153</td>
</tr>
<tr>
<td>Na(_2)O</td>
<td>60%^a</td>
<td>124</td>
</tr>
<tr>
<td>K(_2)O</td>
<td>60%^a</td>
<td>101</td>
</tr>
<tr>
<td>Total ash</td>
<td>52%</td>
<td>5200</td>
</tr>
</tbody>
</table>

*aBased on association with TiO\(_2\) in glass phase (29)*

residence time between 20 and 85 minutes, depending on the extent of solids backmixing in the reactor.

Table 11 shows the metal chloride conversion and total product rates that would be expected from the treatment of \(10^4\) kg of ash for 60 minutes in a 40% AlCl\(_3\)-60% NaCl melt at 750°C.

As previously discussed in the Fused Salt Chlorination Process section the volume of the reactor is determined by the requirement that no AlCl\(_3\) be recycled to the reactor (other than vapor reflux), and the maximum solids loading in the slurry be less than 0.5 Kg solid Kg\(^{-1}\) slurry. Table 12 shows the solids:slurry ratios and slurry volumes required for different levels of AlCl\(_3\) product removal with the unreacted solids.
Table 12. Slurry solid:liquid ratios and volumes for different levels of AlCl₃ product removal with unreacted solids

<table>
<thead>
<tr>
<th>Percentage of product AlCl₃ removed with solid residue</th>
<th>Solid:slurry ratio (wt.)</th>
<th>Slurry volume[^a]</th>
</tr>
</thead>
<tbody>
<tr>
<td>40[^b]</td>
<td>0.513</td>
<td>12.3 m³</td>
</tr>
<tr>
<td>50</td>
<td>0.476</td>
<td>14.1 m³</td>
</tr>
<tr>
<td>60</td>
<td>0.446</td>
<td>15.9 m³</td>
</tr>
<tr>
<td>70</td>
<td>0.422</td>
<td>17.7 m³</td>
</tr>
<tr>
<td>80</td>
<td>0.401</td>
<td>19.5 m³</td>
</tr>
<tr>
<td>90</td>
<td>0.384</td>
<td>21.3 m³</td>
</tr>
<tr>
<td>100</td>
<td>0.369</td>
<td>23.0 m³</td>
</tr>
</tbody>
</table>

[^a]Assuming 7400 Kg of unreacted ash in the reactor, specific gravities of 2.35, 1.7 and 1.35 for the ash, carbon and melt respectively, a NaCl-AlCl₃ molar ratio of 60:40, and a gas hold-up of 13%.

[^b]Minimum removal assuming a maximum of 50% solids in the slurry by weight and a carbon:melt weight ratio of 0.206.

Table 12 shows that using a reaction volume larger than 23.0 m³ would require either AlCl₃ recycling or concentrating the slurry before removing it from the reactor, neither of which is attractive. Also, it is not desirable to increase the reactor volume since that increases capital and operating costs for the process. The volumes shown in Table 12 do, however, compare favorably with the gas-solid reactor volume of 16.7 m³ reported by Adelman (2).

Experimental Reactor Scale-up

The 40A chlorination experiment used a solids:slurry loading of 0.103 which is much too dilute to meet the slurry volume requirements shown in Table 12. The experimental loadings would require a total slurry volume of 132 m³ to process 10⁴ Kg hr⁻¹ using a stirred tank,
batch reactor.

Examination of the 40A chlorination data indicates that an average Cl₂ conversion of 60% was obtained and that 100% utilization could have been obtained if the ash dissolution had not been controlling the reaction rate. Doubling the ash content of the melt would reduce the required reactor volume to 66.8 m³, but the solid:slurry ratio of 0.186 would still be too low. The required solid:liquid ratio could be reached by increasing the carbon and ash loading by factors of 5.5 and 11 respectively over those used in the 40A chlorination. It would also be necessary to increase the Cl₂ utilization by a factor of 6 over the maximum 90% conversion observed in the 40A chlorination either by increasing the residence time of gas in the reactor or increasing the reaction pressure. It is also possible that the effect of FeCl₃ on the mass transfer of Cl₂, as observed in the chlorination, could be used to affect the required improvement in gas-liquid mass transfer.

The experimental reactor, however, was mechanically agitated which would be of limited feasibility in a large scale facility. Assuming that the smallest possible volume was used, the tank would still have to have a volume of approximately 12 m³ not including freeboard. It is unlikely that a tank of this size, operating at 750°C in the corrosive environment of Cl₂ and fused salt, could be mechanically agitated. It might be possible to use a number of smaller reactors, but there would still be a significant number of mechanical difficulties to overcome.

Bubble Column Reactor Design

For the reasons cited above, the potential of using a bubble column reactor has been investigated. A bubble column reactor is suited to the
Fused salt chlorination since there are no moving parts. One disadvantage of the bubble column reactor is that it is typically gas-liquid mass transfer limited if the gas is not soluble in the liquid. In this type of reactor, there is little or no backmixing of the gas which in the case of carbochlorination could be an advantage since CO₂ and CO are produced in the reaction. The liquid phase is usually well backmixed although backmixing can be reduced by installing extra distributor plates in the column.

Liquid phase backmixing may or may not be a disadvantage. The disadvantage of liquid backmixing is that the wide range of solid reactant residence times makes it more difficult to insure complete conversion. The advantage of backmixing is that it assures a uniform reaction rate throughout the column. If the solids were in complete plug flow, the bottom portion of the reactor might be under utilized because of the low oxide dissolution rates of partially chlorinated ash.

The design of a bubble column reactor can be simplified if it is assumed that the reaction rate at the solid surface is much greater than the gas-liquid mass transfer coefficient and that the dissolution rate of the ash is fast enough so that there is always sufficient oxide to react with the absorbed chlorine. Using these assumptions equation 37 (equation 19 written on a unit volume slurry basis) can be used to determine an overall transfer coefficient, $K_o$, which can be considered constant over the entire range of reaction.

$$\frac{C_{Cl, i} V_r}{V_{Cl}} = \frac{1}{K'} = \frac{1}{K_{e_i}} + \frac{1}{a_{cV_c}} \left[ \frac{1}{K'} + \frac{1}{K_{Cl, 1s}} \right]$$ (37)
where: \( V_r \) = Reactor volume, m\(^3\);
\( K_o \) = Overall transfer coefficient, min\(^{-1}\);
\( a_c \) = Specific carbon surface area, m\(^2\) g\(^{-1}\);
\( K_l a_i \) = Overall liquid based gas-liquid mass transfer coefficient, min\(^{-1}\).

Examination of equation 37 shows that if:

\[
\frac{1}{K_l a_i} \gg \frac{1}{a_c \nu_c} \left[ \frac{1}{K_r} + \frac{1}{K_{Cl,ls}} \right]
\]  
(38)

then:

\[
\frac{1}{K_o} = \frac{1}{K_l a_i}
\]  
(37a)

If it is assumed that the conditions expressed in equation 37a are maintained over the entire height of the reactor, that plug flow exists in the gas phase of the reactor and that Henry's law is applicable to the solubility of Cl\(_2\) at these conditions, equation 39 can be used to determine the bubble column reactor size (Appendix E).

\[
\int_0^H dH = \frac{0.5 N_{Cl}^0}{K_o K_H P_T A} \int_0^{X_T} \frac{(1-0.5x)}{(1-x)} dx
\]  
(39)

where  
\( H \) = height of reactor, m;  
\( N_{Cl}^0 \) = initial molar feed of Cl\(_2\), g-moles min\(^{-1}\);  
\( K_H \) = Henry's law constant, g-moles m\(^{-3}\) atm\(^{-1}\);  
\( P_T \) = Total pressure, atm;  
\( A \) = Cross section area of reactor, m\(^2\);  
\( X_T \) = Total Cl\(_2\) conversion.
Integrating equation 39:

$$H = \frac{0.5N_{Cl}^0}{K_{Cl,ls}P_{T}A} [X_T - \log(1 - X_T)]$$

(39a)

Equation 39 is used by determining the total number of moles of Cl₂ required for a given ash conversion and then calculating the column size required for different combinations of $K_0$, $A$, $P_T$, $N_{Cl}$ and $X_T$. All of the conditions except $K_0$, which is determined from equation 37, are externally set. The values of $K_0$, $K_{Cl,ls}$, $K'$ and $K_{la_1}$ must be known and $w_c$ be set to determine $K_0$. Values for $K'$ were developed from the alumina chlorination studies, while $K_{Cl,ls}$ and $K_{la_1}$ were estimated from published correlations for bubble columns (18,50).

The coefficients $K_{la_1}$ and $K_{Cl,ls}$ are functions of the superficial gas velocity in the column, which is a function of $P_T$, $A$ and $N_{Cl}$. Assuming that the ideal gas law is correct, then:

$$u_g = \frac{N_{Cl}^0RT}{P_TA} = \frac{N_{Cl}'RT}{X_TP_TA}$$

(40)

where $u_g$ = Superficial gas velocity, m min⁻¹;

$R$ = Ideal gas constant, atm m³ K⁻¹ G⁻¹ mole⁻¹;

$T$ = Temperature, K;

$N_{Cl}'$ = Moles of Cl₂ required to convert oxide, g-moles min⁻¹.

Values for these three coefficients at a superficial gas velocity of 12 m min⁻¹ are listed in Table 13, and their calculation is detailed in Appendix E.
Table 13. Values of $K_{1a1}$, $K_{Cl,ls}$, $K'$ and $K_o$

<table>
<thead>
<tr>
<th>Transfer step</th>
<th>Coefficient</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas-liquid mass transfer</td>
<td>$K_{1a1}$</td>
<td>46.46 min$^{-1}$</td>
</tr>
<tr>
<td>Liquid-solid mass transfer</td>
<td>$K_{Cl,ls}$</td>
<td>0.137 m min$^{-1}$</td>
</tr>
<tr>
<td>Reaction at carbon surface</td>
<td>$K'$</td>
<td>0.00905 m min$^{-1}$</td>
</tr>
<tr>
<td>Overall transfer coefficient$^b$</td>
<td>$K_o$</td>
<td>41.7 min$^{-1}$</td>
</tr>
</tbody>
</table>

$^a$Based on a superficial gas velocity of 12 m min$^{-1}$.

$^b$Based on $w_c=241$ Kg m$^3$ and $a_c=200$ m$^2$ Kg$^{-1}$.

Effect of superficial gas velocity

Figure 41 shows the effect of changing $u_g$ on the slurry volume.

Curve A shows the effects of maintaining $X_T$ constant at 0.99 and changing the column area. The only effect on the slurry volume is a 13% reduction caused by a corresponding increase in $K_o$ with $u_g$. The major benefit of increasing $u_g$ at a fixed Cl$_2$ conversion is to increase the height:diameter ratio of the column.

Curve B, Figure 41, shows the effect of excess Cl$_2$ on the slurry volume. In this case the column area, $A$, and the product of $N_{Cl}$ and $X_T$ are held constant. Ten percent excess Cl$_2$ reduces the slurry volume by 40%, while 20% excess Cl$_2$ produces a 50% volume reduction. This reduction in volume reflects the difficulty of removing Cl$_2$ from the gas phase as it is diluted by CO$_2$ produced by the carbochlorination reaction.

Also shown in Figure 41 are curves for a FeCl$_3$ enhancement factor, $e$, of 1, 3 and 5. These curves reflect the possible enhancement of $K_{1a1}$.
Figure 41. Effect of superficial gas velocity on the slurry volume required to process $10^4$ Kg fly ash hr$^{-1}$ Curve A: $X_T=0.99$ Curve B: $A=15.11$ m$^2$
by FeCl₃ observed in the fly ash chlorinations and reported in the literature. Bezukladnikov et al. (8) reported that a 3% FeCl₃ concentration in melts of alkali and alkaline earth chlorides increased the rate of mass transfer by a factor of 6. Since the fraction of FeCl₃ in the melt would be between 13.6% and 12.3% by weight, (Appendix E) it seems possible that an enhancement factor of 5 or greater might be attained.

The effect of e on the slurry volume is not linear, which is a result of holding the solids loading constant. At the conditions specified in Table 13 the solid surface component of $K_o$ is 10 times as large as $K_{1a1}$. Therefore if $K_{1a1}$ is increased by a factor of 5 the surface component resistance, primarily $1/K'$, starts to exert its influence on $K_o$. Therefore, without an increase in the carbon content of the slurry, there is an effective upper limit on the enhancement effect of FeCl₃ on $K_o$.

Also shown in Figure 41 is the range of slurry volumes allowed by the mass balance constraints. Aluminum chloride product recoveries from the slurry stream of between 40% to 100% are allowable. Figure 41 shows that with an e-factor of 1 it is not possible to obtain acceptably low slurry volumes. Iron chloride enhancements of 3 and 5 do produce usable conditions at the expense of 27% and 6% excess Cl₂ respectively. Larger e-factors would result in acceptable slurry volumes at all velocities in excess of 12 m min⁻¹.

**Effect of pressure**

The effect of pressure on the reaction rate was not studied in this work because of reactor design limitations. It has been assumed in the
previous derivations that the reaction is first order in Cl₂ concentration in the melt and that Henry's law is valid, which gives a first order pressure dependence in Equation 39.

Bruggeman and Edd (13), however, reported an 0.8 order pressure dependence based on the overall transfer coefficient Kₐ, as defined here. There were several possible sources for the nonlinear dependence, but Bruggeman reported that his data was insufficient to determine its source. Three possibilities mentioned were: non-ideal Cl₂ solubility in the melt, non-first order reaction kinetics and simultaneous diffusion-reaction.

An 0.8 order pressure dependence can be achieved by raising Pₜ in equation 39 to the 0.8 power. For purposes of this study, both first and 0.8 order pressure dependence will be examined since it is not clear if the nonlinearity reported by Bruggeman resulted from the reaction conditions or is intrinsic to the fused salt chlorination.

The effect of pressure on the slurry volume is shown in Figure 42, which is analogous to Figure 41 except that the pressure is increased, rather than uₐ. Unlike increasing uₐ, increasing the pressure by reducing the column area (Curve A) does reduce the slurry volume. The slope of Curve A is 1, which reflects the fact that the reaction rate is assumed first order with respect to Pₜ in this plot. It is possible by increasing the pressure to reduce the slurry volume to a value compatible with the reactor mass balance constraints. This requires an operating pressure above 5 atm, which is probably excessive.

Curve B in Figure 42 depicts the pressure-volume relationship for a constant area reactor using excess Cl₂. Increasing the pressure and
Figure 42. Effect of pressure on the slurry volume required to process $10^6$ Kg fly ash hr$^{-1}$

Curve A: $X_T = 0.99$    Curve B: $A = 15.11$ m$^2$
reducing the conversion has a compound effect. First, the reduced conversion makes it less difficult to transfer the required amount of Cl\textsubscript{2} into the melt and second, the increased pressure improves Cl\textsubscript{2} solubility in the melt. Comparison of Figures 41 and 42 at the same Cl\textsubscript{2} conversions shows the effect on increased pressure, since in both cases the same amount of Cl\textsubscript{2} is injected into the reactor.

Assuming an e-factor of 1, it is necessary to operate at pressures above 2.1 atm and a maximum of 48\% Cl\textsubscript{2} conversion to obtain suitable slurry volumes. It is apparent from Figure 42 that if a pressurized reactor is used, it should be designed to use excess Cl\textsubscript{2} rather than to reduce the cross-sectional area of the reactor if it is desired to minimize the reactor volume.

Iron chloride enhancement of Cl\textsubscript{2} transfer is quite effective when operating at pressure. An e-factor of 5 requires only a 5\% increase in pressure to reduce the slurry volume to 23 \text{m}^3. The effect of pressure on the FeCl\textsubscript{3} transport of Cl\textsubscript{2} is not known, so \( e \) was assumed to be independent of pressure.

The affect of an 0.8 order pressure dependence is shown in Figure 43. An e-factor of 1 is the only case plotted. At higher e-factors, the difference between first and 0.8 order dependence is less than 10\% over the pressure range of interest for the constant area curves. Figure 42 shows that the effect of reducing the pressure dependence of the overall reaction is to increase the slurry volume. The difference is more noticeable for the 99\% conversion curves because of the higher pressures involved. Therefore, it is even more desirable to use excess Cl\textsubscript{2} rather than reduce column area if the overall transfer
Figure 43. Comparison of first and 0.8 order pressure dependence on the slurry volume required to process $10^4$ Kg fly ash hr$^{-1}$
coefficient is less than first order with respect to pressure, and the reactor is to be pressurized.

The minimum required pressure ($e=1$) for the 0.8 order dependence using excess $\text{Cl}_2$ is 2.4 atm with 42% $\text{Cl}_2$ conversion. This is a 15% increase in operating pressure over first order dependence. In contrast, the 99% $\text{Cl}_2$ conversion case using a reduced column area requires a minimum pressure of 7.4 atm, which is a 48% increase.

**Fused salt reactor specifications**

Table 14 is a summary of the fused salt reactor design. The fused salt reactor design is based on an e-factor of 1, since its effect is not totally known, and by using $e=1$ the design can be considered conservative. Ninety percent of the product $\text{AlCl}_3$ is to be recovered from the fused salt removed with the solid residue and an operating pressure of 2.25 atm is assumed.

Also shown in Table 14 is the reactor design proposed by Adelman (2). A direct comparison of these two studies cannot be made since different ashes were used in each, but it is worth noting that the two designs are very similar in terms of reactor size and operating pressures. The similarity of the two designs would tend to indicate that neither of the two reactor concepts offers a significant advantage in terms of reactor size. Therefore, other factors such as materials cost, ash conversion and product recovery will determine the final choice between these two reactor systems.

The fused salt reactor design shown in Table 14 has a height:diameter ratio of 0.32, which is not very realistic. This ratio could be improved by increasing $u_g$, but the maximum attainable reactor
Table 14. Comparison of preliminary designs of the gas-solid and fused salt slurry reactors

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Gas-Solid Reactor</th>
<th>Fused Salt Slurry Reactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed diameter</td>
<td>3 m</td>
<td>4.39 m</td>
</tr>
<tr>
<td>Bed height</td>
<td>2.36 m</td>
<td>1.39 m</td>
</tr>
<tr>
<td>Bed porosity</td>
<td>0.57</td>
<td>N.A.(^b)</td>
</tr>
<tr>
<td>Solids:salt ratio</td>
<td>N.A.(^b)</td>
<td>0.44 (wt.)</td>
</tr>
<tr>
<td>Gas velocity, (u_g)</td>
<td>20.3 m min(^{-1})</td>
<td>12 m min(^{-1})</td>
</tr>
<tr>
<td>Pellet porosity</td>
<td>0.25</td>
<td>N.A.(^b)</td>
</tr>
<tr>
<td>Fly ash conversion</td>
<td>0.30</td>
<td>0.52</td>
</tr>
<tr>
<td>AlCl(_3) production</td>
<td>4916 kg hr(^{-1})</td>
<td>6160 kg hr(^{-1})</td>
</tr>
<tr>
<td>SiCl(_4) production</td>
<td>1934 &quot;</td>
<td>3370 &quot;</td>
</tr>
<tr>
<td>FeCl(_3) production</td>
<td>1832 &quot;</td>
<td>1750 &quot;</td>
</tr>
<tr>
<td>TiCl(_4) production</td>
<td>214 &quot;</td>
<td>153 &quot;</td>
</tr>
<tr>
<td>COCl(_2)/Cl(_2) final conversion</td>
<td>0.95</td>
<td>0.44</td>
</tr>
<tr>
<td>Fraction COCl(_2) dissociation</td>
<td>0.69</td>
<td>N.A.(^b)</td>
</tr>
<tr>
<td>Reactor pressure (avg.)</td>
<td>2 atm</td>
<td>2.25 atm</td>
</tr>
<tr>
<td>Reactor temperature</td>
<td>700(^\circ)C</td>
<td>750(^\circ)C</td>
</tr>
</tbody>
</table>

\(^a\)Adelman, Ph.D. Thesis (2).

\(^b\)Not applicable to this reactor type.

Height would still be only 2 m since taller reactors of the same total volume would require gas velocities in excess of 20 m min\(^{-1}\). A 2 m high reactor would have a height:diameter ratio of 0.55, which is still too low.
In order to increase the height:diameter ratio, the only other option is to use multiple reactors in parallel. Table 15 shows various height:diameter ratios versus the total number of reactors required to obtain a total volume of 21 m³ with a reactor height of 2 m. The optimum reactor size cannot be determined from the data in Table 15, however, a height:diameter ratio near 1.5 is probably best. At this ratio the reactor diameter is appreciably reduced, which is desirable for operating at elevated pressures, but the total number of reactors is still relatively small.

Summary

The reactor design shows that gas-liquid mass transfer will be a major factor in the design of a fused salt slurry reactor. For that reason future work should concentrate on quantifying gas-liquid mass transfer in the reactor at reaction conditions. This work should also

<table>
<thead>
<tr>
<th>Height:Diameter Ratio</th>
<th>Diameter - m</th>
<th>Minimum No. of Reactors</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.55</td>
<td>3.66</td>
<td>1</td>
</tr>
<tr>
<td>0.77</td>
<td>2.59</td>
<td>2</td>
</tr>
<tr>
<td>1.00</td>
<td>2.00</td>
<td>4</td>
</tr>
<tr>
<td>1.50</td>
<td>1.33</td>
<td>8</td>
</tr>
<tr>
<td>2.00</td>
<td>1.00</td>
<td>14</td>
</tr>
<tr>
<td>4.00</td>
<td>0.50</td>
<td>54</td>
</tr>
</tbody>
</table>
be done in a bubble column reactor to allow for more accurate scale-up from experimental data.

Another factor that should be investigated is the effect of FeCl₃ on the transfer of Cl₂ on the reaction rate. This could be a major enhancement to the effectiveness of the fused salt process, since it could eliminate the need to operate at pressure.

Based on the preliminary bubble column design, the fused salt process is comparable in terms of reactor volume, operating pressure and temperature to the gas-solid reactor proposed by Adelman (2). However, more detailed and comparable design data for both processes is needed before an accurate comparison can be made of the two concepts. This future work should be done using the same oxide feed and with a bubble column for the fused salt slurry process.

The reactor design as done here was greatly simplified. The effect of the reduced gas volume in the top of the reactor (caused by the conversion of Cl₂) on K₄ₐ₄ was not considered here, nor was the production of CO on the process stoichiometry. Other factors that should be considered in future studies are the effects of forcing the slurry into a plug flow configuration as opposed to total backmixing as assumed here. Finally, the assumption that the ash dissolution rate can be maintained at high ash loadings should be verified.
CONCLUSIONS

The conclusions drawn from this study are presented below for each of the three major phases of the work, alumina chlorination, fly ash chlorination and the process/reactor design. The points made about alumina chlorination can also be assumed to apply to fly ash, unless otherwise stated.

Alumina Chlorination

1. The rate of chlorination of a high surface area alumina is independent of its loading (surface area) in the slurry. This indicates that the rate of alumina dissolution in high surface area aluminas is faster than the chlorination reaction.

2. Melt composition in the range investigated does not have a significant effect on the chlorination of alumina, neither by changing the dissolution rate of alumina nor the transport of Cl$_2$.

3. At temperatures below 600°C, the reaction rate is proportional to the carbon loading and the reaction has an activation energy of 29 Kcal. At temperatures above 700°C, the reaction is rate limited by gas-liquid mass transfer, evidenced by the lack of rate dependence on carbon loading in the melt and a drop in the activation energy to 7.0 Kcal.

4. There is also a change in the reaction mechanism in the vicinity of 650°C. This is indicated by changes in time-reaction rate profiles with temperature as well as the start of CO production. A local maxima in the reaction rate at 600–650°C indicates that
phosgene formation is probably a key reaction intermediate.

5. The carbon:alumina ratio in the melt has a significant effect on the gas-liquid mass transfer of Cl₂. The results of this work indicate that carbon:alumina volume ratios greater than unity may improve Cl₂ mass transfer. The increased mass transfer is believed to be related to changes in the slurry rheology.

6. The chlorination reaction takes place at the carbon surface, the reactivity of which changes with time and conversion. At temperatures below 650°C, there is an initial decrease in the reaction rate of up to a factor of 5 during the first 30 minutes of reaction. This corresponded to a maximum carbon conversion of 3%. At higher temperatures there is no drop in the rate, however, there is an analogous drop in the CO production with time. The change in the carbon reactivity is believed to be the result of differences in the reactivity of aromatic and aliphatic structures in the coke used as a carbon source. A chlorination with graphite supports this hypothesis, since this material had a higher surface area, but lower reactivity than the coke normally used as the reductant.

7. There is also evidence of a Cl₂–carbon reaction in the system. At 800°C there is Cl₂ consumption without corresponding CO₂ production in the first 30 minutes of reaction. Also, prechlorination of the carbon for 85 minutes improved its reactivity by an average of 20% over that of carbon prechlorinated for 15 minutes. This would indicate that a carbon chlorination step, possibly catalyzed by AlCl₃ or AlOCl, is a
part of the reaction mechanism.

8. The reaction of carbon also follows shrinking core reaction kinetics, which is further proof that the carbochlorination reaction is centered around the carbon surface.

Fly Ash Chlorination

1. The chlorination of fly ash is a strong function of the melt composition. A 48% AlCl₃ content melt is more aggressive towards the chlorination of silica than a 40% AlCl₃ melt. However, the overall solubility of oxides in the 40% AlCl₃ melt is much greater.

2. At the 15:1 melt:ash ratio used in both fly ash chlorinations, the reaction rate is limited by the dissolution rate of the ash. Based on the initial production of CO₂, the 40% AlCl₃ melt had a more severe effect on reducing the reaction rate and the onset of dissolution rate control occurred sooner than in the 48% AlCl₃ melt.

3. The chlorination of iron is not a function of the melt composition. The chlorination of iron is 80% complete in the first 20 minutes of reaction, subsequent iron chlorination appears to be limited by the rate at which it is exposed by chlorination of the ash matrix.

4. Chlorination of the minor compounds is not affected by the melt composition, except for calcium, which is chlorinated more effectively by the 40% AlCl₃ melt. Titania and MgO are not effectively removed. X-ray diffraction patterns of the residue from the 40% AlCl₃ chlorination show that the glass fraction of
the glass is not strongly attacked by the chlorination, which explains the low TiO₂ removal.

5. Scanning electron photomicrographs of the treated ash show that the ash particles do not react by the shrinking core model, but are selectively leached. This is in agreement with the x-ray powder patterns which show total removal of the crystalline portions of the ash, with the exception of quartz.

6. Comparison of the fused salt and gas-solid chlorination of Halomet nonmagnetic ash indicates that, for the same exposure time with a carbon reductant and excess Cl₂, fused salt chlorination chlorinates a larger fraction of the ash. This is especially attractive when a 40% AlCl₃ melt is used since this melt composition preferentially chlorinates alumina over silica. A 48% AlCl₃ melt is too effective at chlorinating silica, however, producing more SiCl₄ per unit of AlCl₃ than the gas-solid reaction system.

Process/Reactor Design

Process considerations

1. The fused salt chlorination process is significantly different from the gas-solid process because of the presence of NaCl in the AlCl₃ product stream, resulting from the formation of NaAlCl₄. This is an unavoidable consequence of using low AlCl₃ content melts in order to obtain high alumina:silica chlorination ratios.

2. The vapor phase purification system for SiCl₄, TiCl₄ and the noncondensable product gases, proposed for the gas-solid system,
can be used in the fused salt system.

3. In addition to having to remove FeCl₃ from the AlCl₃ product, the purification system in the fused salt process will also have to remove alkali and alkaline earth chlorides. This is a direct result of having to remove unreacted solids from the reactor.

4. An aqueous separation is more suitable than an anhydrous scheme for the purification of AlCl₃, given the current level of available technology. In fused salt chlorination, the major problem is removing the unreacted solids from the metal chlorides. Currently there appears to be no feasible way of separating the solid residue from the fused salt using conventional process equipment. The most viable approach is to dissolve the metal chlorides in water and filter out the unreacted solids. The only possible anhydrous separation of the solids from the liquid is the vaporization of the metal chloride, which would be quite complicated and expensive.

**Reactor**

1. A process scale reactor should probably be a bubble column reactor. A stirred tank reactor was used experimentally, but a commercial scale stirred reactor would be overly large and difficult to operate and maintain.

2. Based on the observed reaction rate of carbon, the average dissolution rate of fly ash, and published correlations for gas-liquid mass transfer in bubble columns, the gas-liquid mass transfer would control the reaction rate at reasonable carbon:slurry ratios.
3. The size of the reactor is determined by the amount of AlCl₃ removed with the fused salt portion of the unreacted residue slurry. The basis for the design is $10^4 \text{ Kg hr}^{-1}$ fly ash and 73% alumina conversion. If no AlCl₃ is recovered from the product gas stream and no recycling of AlCl₃ is allowed (100% removal with slurry), then the maximum reaction volume is 23.5 m³. The minimum reactor volume is 12.5 m³ based on a maximum solids loading of 0.5 lbs lb⁻¹ slurry.

4. To obtain slurry volumes compatible with the mass balance requirements it will be necessary to operate the reactor under pressure, both to increase solubility of Cl₂ in the melt and to reduce the gas volume. Based on ideal solubility behavior, the reactor would have to be operated at a pressure of 2 to 9 atm, depending on the extent of Cl₂ conversion and AlCl₃ removal with the residue.

5. The presence of FeCl₃ in the melt improves gas-liquid mass transfer, which reduces the required operating pressures for a given set of reaction conditions. The fly ash chlorination data indicate that the gas-liquid mass transfer coefficient is at least doubled by the presence of less than 1% FeCl₃ in the melt.
RECOMMENDATIONS

The work reported in this study indicates several areas of the fused salt reaction process that require further study, either to obtain a better understanding of the reaction process or to obtain more detailed information with which to develop a process. As with the conclusions the recommendations are presented for each of the major research phases.

Alumina Chlorination

1. A better understanding of the chlorine reaction mechanism would be useful. It is apparent that the carbon structure influences the reaction rate, so a series of chlorinations using different carbon sources that have been characterized with regard to surface area and chemical structures could be very informative. Particular attention should be directed towards determination of the graphitization of each carbon since the results of the graphite chlorination indicate that a carbon containing fewer conjugated benzene rings would be more reactive.

2. It would also be useful to develop a small chlorination cell where the melt could be effectively separated from the carbon under an inert atmosphere. In this way it might be possible to preserve the carbon surface for analysis by some of the more sophisticated surface analysis techniques that are becoming available.

3. If the experimental stirred tank reactor is to be used for further work, both the reactor and the condensers should be redesigned to reduce hold-up in the system. The primary source
of difficulty will be redesigning the AlCl₃ condenser so that it
does not plug.

4. The effect of pressure on the reaction should be investigated, as
well as the use of a bubble column reactor. Related to the
pressure study is a study of the solubility of Cl₂ in high
temperature melts. The value of K_H used in this study was
extrapolated from lower temperature data that ended at
approximately 400°C, which means that it is probably not very
accurate. Such a study would not be a trivial matter because of
complications introduced by the high vapor pressure of the melt
at the reaction temperatures.

5. The effect of carbon and alumina loading on gas-liquid mass
transfer in the agitated reactor should be investigated. Exactly
why the reaction rate increased at high carbon loadings after
gas-liquid mass transfer appeared to be controlling needs to be
determined.

Fly Ash Chlorination

1. The effect of pressure also needs to be determined for this
system, although it should follow the same trends as for alumina.

2. Enhancement of gas-liquid mass transfer by FeCl₃ should be
investigated. This could be a very useful method for improving
K_{L*a} and reducing the reactor size and pressure.

3. The reaction in a bubble column reactor at actual operating
conditions should be studied in order to obtain better scale-up
data. Because sampling in a bubble column reactor may not be
very accurate, it may be necessary to determine the time-
conversion profiles with multiple experiments. Therefore, more tests should be done with the agitated reactor to better define the operating conditions first.

4. The multiple bubble-column tests in recommendation #3 would also provide enough material to study the changes in ash mineralogy and structure with conversion, which should be done. Such a study would provide a better understanding of the effect of ash structure on the chlorination process.

5. Lower AlCl₃ concentrations in the reaction melt should be tried. It would be desirable to limit the chlorination of SiO₂ as much as possible. The effect of lower temperatures, 600 to 700°C, should also be tested to see if there is an effect on the silica:alumina chlorination ratio.

6. High solids loading, both ash and carbon, should be tested to determine upper limits for a workable slurry.

**Process/Reactor Design**

**Process considerations**

1. A method will have to be developed to separate NaCl from AlCl₃. A solvent extraction process or two-stage crystallization are possibilities.

2. Information on the flow characteristics of NaCl-AlCl₃-fly ash-carbon slurries will have to be developed, primarily viscosity measurements as a function of temperature and solid loading. This would also be useful information for scaling up the reactor and determining process flow rates.
3. The possibility of pumping molten salt slurries should be investigated. If these slurries could be mechanically pumped, a much greater degree of flexibility in the process design would result.

**Reactor**

1. Ways of improving gas-liquid mass transfer in a bubble column reactors should be investigated. One possible method is the use of a segmented bubble column, where distributor plates are placed throughout the length of the reactor. These plates also decrease backmixing in the liquid phase which could be advantageous.

2. That good solids mixing can be obtained by sparging Cl₂ through the melt requires verification. Additional gas flow might be required to obtain good mixing. The possibility of using a draft tube to enhance solid-liquid mixing should also be examined.

3. Materials of construction other than quartz, for the reactor should be sought.
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This dissertation is dedicated to Maxine Dobbins, who is gone, but not forgotten.
APPENDIX A - ASH-WATER SLURRY SAMPLING TESTS

A series of tests to determine the accuracy of slurry sampling were done using water-based slurries of Halomet nonmagnetic fly ash. Initial tests used a 250 ml beaker to simulate the reactor vessel and a stirrer made to the same specifications as the one used in the FSC reactor. Samples were taken from a slurry made with an ash loading of 375 g l\(^{-1}\), as this was the most concentrated solids loading that the reactor was designed for. Carbon was not included in these tests, since the presence of two different solids would complicate the system. Also, if the oxide was uniformly dispersed, then the carbon should also be well dispersed. The density of carbon (1.7 g cm\(^{-3}\)) is very nearly the same as the melt (1.4 g cm\(^{-3}\)) and much less than that of the ash (2.35 g cm\(^{-3}\)).

Each experiment consisted of taking 10 slurry samples and comparing the solid-liquid ratio of each to the expected ratio. The expected value was adjusted to account for changes caused by samples previously removed. Table A-1 lists the results of tests using slurries made from the whole Halomet nonmagnetic fly ash and from its -325 mesh size fraction. Samples from the whole ash slurry produced solid-liquid ratios that were an average of 3.7% lower than expected. In contrast, the solid-liquid ratios of the -325 mesh slurry samples were within 1% of the expected value as a result of the slurry's lower average settling velocity. Based on these results it was decided to use the -325 mesh fraction of the ash for the chlorination experiments.

Additional tests, using the chlorination reactor and sampler, were also done with water-based slurries made from the -325 mesh size
Table A-1. Comparison of slurry sampling of whole Halomet fly ash and -325 mesh fraction at a 375 g/l solid-liquid ratio

<table>
<thead>
<tr>
<th>Sample</th>
<th>Expected ratio g/l</th>
<th>Average measured ratio - g/l</th>
<th>Standard deviation</th>
<th>Percent error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whole ash</td>
<td>375</td>
<td>361</td>
<td>1.23</td>
<td>-3.73</td>
</tr>
<tr>
<td>-325 mesh fraction</td>
<td>375</td>
<td>372</td>
<td>2.05</td>
<td>-0.80</td>
</tr>
</tbody>
</table>

fraction of Halomet nonmagnetic fly ash. Table A-2 shows data for several tests at S/L ratios of 100, 200, 300 and 400 g/l, and a liquid volume of 250 ml. Under these conditions, a solid-liquid loading of 400 g/l was roughly equivalent to 100 g of fly ash and 375 g of salt, the maximum system design loading. Each test consisted of a total of 10 samples. The stirrer speed was held constant for all tests at approximately 600 RPM.

The error in these measured solid-liquid ratios ranged from ±3%.

Table A-2. Summary of slurry sampling tests of water-ash mixtures in the chlorination reactor

<table>
<thead>
<tr>
<th>Expected S/L ratio</th>
<th>Experimental results</th>
<th>Percent error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Avg. S/L ratio</td>
<td>Std. dev.</td>
</tr>
<tr>
<td>100</td>
<td>98</td>
<td>2.2</td>
</tr>
<tr>
<td>100</td>
<td>101</td>
<td>3.2</td>
</tr>
<tr>
<td>100</td>
<td>97</td>
<td>2.2</td>
</tr>
<tr>
<td>200</td>
<td>204</td>
<td>3.8</td>
</tr>
<tr>
<td>200</td>
<td>201</td>
<td>3.8</td>
</tr>
<tr>
<td>300</td>
<td>308</td>
<td>3.8</td>
</tr>
<tr>
<td>400</td>
<td>408</td>
<td>1.6</td>
</tr>
</tbody>
</table>
with a slight correlation between sampling error and solid-liquid ratio. The measured solid-liquid ratio seemed to increase with solid-liquid ratio, although the trend was not consistent. At higher particulate loadings, it appeared to be more difficult to maintain a uniform suspension.

The standard deviation for all the tests averaged 2.5 g/l and in all but two cases was larger than the measured error. Therefore no attempt was made to generate a correction factor from these data for use in the chlorination experiments. Based on these studies, the measured solid-liquid ratios were expected to be within 5% of the true value.

The increased variance observed in the reactor tests compared to the preliminary tests is related to sampling equipment. Because of the chlorination reactor sampler design, it was difficult to place the sampling boat at exactly the same location for each sample and to hold the immersion time constant. In addition, it was not possible to set the equipment up for identical submersion depths for different experiments, which would account for the differences observed between tests at the same solid-liquid ratio.
The accuracy of the techniques used for slurry sampling and measurement of the product gas flow rate are discussed here. Much of this discussion is based on the results of the parameter screening study, since that group of experiments was used to evaluate the accuracy of the slurry sampling and the total gas flowrate measurements. From this evaluation, a consistent set of procedures was developed for evaluating the experimental measurements. By using these procedures, internal consistency was maintained throughout the study.

**Slurry Sampling**

Slurry sampling was not required to analyze the alumina chlorinations, since all the necessary information could be developed from the product gas analysis. Therefore, it was possible to compare alumina conversion as determined from the slurry samples with conversions calculated from the product gas analysis. By analyzing any differences between the two conversions, using the Plankett-Burman analysis, it was possible to check for correlations between the observed differences and the experimental parameters.

Measurements obtainable from the slurry samples are oxide conversion, carbon conversion and the mass of salt in the reactor. Of these three, oxide conversion and salt mass are the most important, since both are required in fly ash chlorinations to measure the conversion of the individual component oxides. Carbon conversion is not that important, since it can be more accurately determined from analysis of the product gas.
Salt mass

The change in salt mass was determined by monitoring changes in the concentration of the BaCl₂ tracer in the slurry samples. There was initially some concern that evaporation of the fused salt during the chlorination run could be significant, which would influence the calculation of the oxide conversion.

It was found that the variance in the salt mass measurements was such that the accuracy of a single measurement was approximately ±10%. The scatter in this measurement was probably related to errors in determining the weight of melt in each sample. The melt weight was determined by subtracting the total weight of carbon and ash in the sample from the total sample weight, which in turn was determined from the difference between the full and empty weights of the sampler. Therefore, the accuracy of the salt weight was influenced by the accuracy of four separate measurements. The total mass of a sample was between 1.5 to 1.9 g depending on the sampler size. Because of this variation, a straight line was fit to the data and its slope used to determine changes in the melt weight.

The maximum observed increase in salt mass was 11% in Trial 6, which was done at 600°C (high conversion), 40% AlCl₃ melt and 90 cm³ min⁻¹ chlorine flow rate. These conditions were the most conducive to an increase in salt mass since a low AlCl₃ content melt will absorb AlCl₃ (Figure 1) and the low chlorine flow rate will minimize melt evaporation.

The maximum observed decrease was 8.9% in Trial 1, which was done at 800°C with a 48% AlCl₃ melt and 255 cm³ min⁻¹ chlorine flowrate,
conditions exactly opposite to those of Trial 6. At 800°C the vapor pressure of a 48% AlCl₃ melt is near atmospheric, which coupled with the high Cl₂ flow raises the evaporation rate of the melt.

In most cases, the change in salt mass over the duration of the experiment was negligible; there was an average change of only 1% in the screening study experiments. This result was independently verified by the fact that it was usually unnecessary to readjust the submersion-depth stop on the slurry sampling rod during the experiment. If there had been a change of more than 5-7% in the slurry volume, it would have been necessary to readjust the depth to which the sampling boat was lowered into the reactor. Based on changes in the heights of solidified melt on the sampling bucket it is estimated that the average change in slurry volume was less than 5%.

The initial mass of salt in the reactor was assumed to be equal to the amount charged. Sublimation of AlCl₃ during reactor heat-up and melt evaporation was estimated to be less than 0.5% of the initial salt charge based on the amount of material present in the condensers just before chlorination was started.

**Carbon:melt ratio**

Variation in the slurry-based carbon conversions was very large. Differences of a factor of two were observed between G.C. calculated conversions and the slurry data. The lack of accuracy in the slurry sample data results from carbon being a small fraction (at most 4.3%) of the sample weight and its weight being calculated from the difference in the ashed and unashed solid residue weights. It was also difficult to completely recover carbon from the dissolved sample because of the
carbon's poor wetting characteristics with water. Because of this, the determination of the carbon content of a sample was not very accurate, and carbon conversions were calculated from the G.C. measurements.

**Oxide:melt ratio**

The only way to evaluate the accuracy of the oxide:melt ratio as determined from the slurry samples was by comparing those ratios to the oxide conversions calculated from the G.C. data. The problem with this approach is that it does not account for the dissolution of material in the melt. It is possible for the slurry samples to show an apparent conversion before being chlorinated. Therefore, it could not be completely determined if the difference between the conversions derived from the slurry samples and the G.C. data is an error in the slurry sampling or the result of dissolution in the ash.

Figure B-1 is a plot comparing the slurry and G.C. based oxide conversions for two experiments from the screening study. The change in conversion with time is comparable for both experiments, which is important in terms of determining the reaction rate of the oxide. There is, however, an offset in Figure B-1b that is not present in Figure B-1a. Comparison of this offset to the experimental parameters for all eight experiments in the screening study produced a correlation between the offset and melt composition. Samples taken from the 40%-AlCl$_3$-60%NaCl melts had an average difference of 8.2 between the two conversions, while 48%-AlCl$_3$-52%NaCl melts had an average difference of 2.3. In all but one case, the slurry-based conversion was greater than the product gas based conversion. This result is supported by work reported in the literature (60) showing that at 210°C alumina is less
Figure B-1. Comparison of alumina conversions based on slurry samples and G.C. analysis of experiments from the screening study
A= Trial 7, B= Trial 4
soluble in near equimolar NaCl-AlCl₃ melts than in NaCl-rich melts.

Theoretically it should be possible to determine the solubility of Al₂O₃ in the melt from the y-intercept of the slurry-based conversion curve, but there is too much scatter in the data to make more than a rough estimate of the difference. Based on the average difference, the solubilities of Al₂O₃ in 40% AlCl₃-60% NaCl and 48% AlCl₃-52% NaCl melts (excluding temperature effects) are 0.83% and 0.23% respectively, which are approximately twice those predicted by Tremillion et al. (60). The temperature dependence of alumina solubility is not known, but it would be expected to increase with temperature. The values reported here could also be low because of the reprecipitation of dissolved alumina in the melt as it is cooled. Such a reprecipitation would also explain the difficulty encountered in filtering the residues from the 800°C chlorinations.

Measurement of Product Gas Flow

The last item in the experimental procedure was the calculation of the total product gas flow rate. As previously discussed, a Freon-22 tracer was injected into the gas stream and its concentration in the gas sample used to determine the product gas flowrate. Figure B-2 is a plot of measured flowrates versus time for Trial 5 in the screening study, which corresponds to the 17.86g carbon curve in Figure 15. Since two moles of chlorine are consumed for each mole of CO₂ produced, this particular experiment would show the greatest change in the total gas flow rate between the initial and steady state reaction rates.

Figure B-2 shows there is significant noise in the gas flow rate measurement, most of which did not result from the G.C. analysis. Test
Figure B-2. Comparison of the measured total product gas flow rate to the expected flow rate for Trial 6 of the parameter screening study.
mixtures of Freon-22 and the product gases using the G.C. calibration system gave measurements that varied by less than 2% at the same flow rates, which was the normal experimental variation observed for all G.C. measurements. Examination of Figure B-2 shows differences of up to 10% between the measured and expected values.

After analysis of the experimental system and the results obtained, it was concluded that the increased variance resulted from the experimental equipment itself. The tracer flow was held constant by a mass flow controller but the flow rate out of the reactor was subject to two sources of variation, fluctuations caused by chlorine bubbling into the reactor and by fluid cycling in the chlorine scrubber.

Fluctuations caused by the scrubber were minimized by installing a siphon break on the fluid drain from the bottom of the scrubber. No good solution was found for flow rate fluctuations caused by chlorine bubbling and it is not certain that one exists. In general, the primary difficulty with using tracers is that any errors in the analytical techniques used to identify the tracers are greatly magnified. This does not invalidate their use, but it does reduce the accuracy of the measurements derived from them.

Figure B-2 is a comparison of the predicted and measured flow rates (based on the chlorine conversion data). There is a 3% difference between the average total flow rate as determined by the tracer measurements and the predicted flow in the steady-state reaction region. The largest deviation between the average and predicted flow rates occurs in the first 30 minutes of reaction where the initial difference is 6%.
Fitting the measured flow rate data to a straight line or a second order curve does not, in general, provide a better fit than simply assuming a constant uniform flow. In the case of the high temperature runs (700°C and higher), a uniform flow would be the expected profile. At lower temperatures, there should be a slight increase in the flow rate over the first 30 minutes, however, the change in the measured data is larger than this. Therefore, an average value for the flow rate was used for all the conversion and rate calculations for alumina chlorinations.

A correction factor was also sometimes applied to the total flow rate to account for errors or changes in the Freon-22 calibration flow rate. If a correction factor was used, its value was determined by adjusting the total flow rate to obtain agreement between the oxide conversions as calculated from the CO\textsubscript{x} content of the product gas and chlorine consumption. The total conversions predicted by these two methods were also checked to make sure they agreed with the total oxide conversions as determined from analysis of the unreacted solids.

An average gas flow rate was not used in the fly ash conversions or in the 84:1 melt:carbon ratio chlorination. In these experiments, there was a measurable change in the flow rate over time resulting in the data obtained being divided into two regions. Straight lines were fitted to the data and then used in the product gas calculations.
APPENDIX C - ESTIMATION OF GAS HOLD-UP IN THE SLURRY

Gas hold-up in the reactor was estimated using a water-nitrogen system to simulate the fused salt system. The hydrodynamics of this system are similar to those of the melt so gas hold-up should be similar. Solids were not included in the system because it was not possible to accurately measure the volume change of a slurry. The lack of solids would indirectly influence the gas hold-up by reducing bubble coalescence (21).

Figure C-1 shows the effect of nitrogen flow and stirrer speed on the gas hold-up, using either a three-hole sparger (Figure 7) or a 4mm diameter open tube. Gas hold-up was estimated by measuring changes in total liquid volume, which was calculated by measuring the liquid height at the center of the reactor and at four points equidistant around the periphery of the reactor. The liquid volume was then determined from the volume of each of the four quarter sections. There was virtually no vortex, other than a slight depression in the center of the reactor which vanished as the gas hold-up increased.

Figure C-1 shows that above a critical flow rate there is no increase in the gas hold-up. This critical gas flow rate decreases with increasing stirring speed, however, at a given flow rate the gas hold-up increases with stirring speed. The efficiency of the three-hole sparger over the one-hole sparger is attributed to the small bubble diameter produced by the former, which had a 2mm injection holes compared to the 4mm diameter tube of the one hole sparger.

The observed maximum in the gas hold-up explains why there was no effect of gas flow rate observed in the initial screening study. The
Figure C-1. Reactor gas hold-up versus gas flowrate and stirrer speed in a nitrogen-water system.
flow rates of 90 and 255 cm$^3$ min$^{-1}$, after thermal expansion, were equivalent to flow rates in this experiment of between 287 and 1000 cm$^3$ min$^{-1}$, depending on the flow rate and temperature. Figure C-1 shows that these flow rates are well above the critical flow rate for 900 RPM at which the gas hold-up became constant.
Although analyzing the reaction rate from the product gas composition is experimentally more tractable than analyzing the slurry, there are lag time and dispersion effects caused by the reactor and condensers that must be considered. These effects are most noticeable at the start of reaction when the change in gas composition is the greatest. To obtain a measure of these effects a series of residence time distribution studies were done to determine the following:

1. The level of dispersion in the system and its individual components.
2. Whether system dispersion could be reduced significantly by changing the condenser design.
3. Average lag time for the system.

The first study was done with a reactor purge gas flowrate of 400 cm$^3$ min$^{-1}$ and a chlorine injector flowrate of 100 cm$^3$ min$^{-1}$ (using helium-nitrogen mixtures to simulate chlorine flow) to produce condenser flow conditions similar to those during a chlorination reaction. Reactor flow conditions were not the same as in chlorination since a 500 cm$^3$ min$^{-1}$ flow in the condensers requires a chlorine injection flowrate of ~300 cm$^3$ min$^{-1}$ to account for thermal expansion of the gas in the hot zone of the reactor. Running the test in this manner permitted comparison of all three units on an equal basis.

Figure D-1 is the response time curve for a step change in the chlorine injector gas composition for various configurations of the operating system. The G.C. was used to analyze the gas...
Figure D-1. System response curve to a step change in tracer content
composition every 30 seconds. The system response was normalized and then analyzed using the axial dispersion model described in Hille (27).

Figure D-1 shows that the dispersion coefficient for the reactor is not significantly different from the whole system at these flow rates. The dispersion of the system is measured by $D_T/uL$, which is proportional to the square of the slope of the response curve at the average time. The $D_T/uL$ coefficient of 0.15 for the reactor alone indicates a high degree of dispersion, and the additional dispersion induced by the condensers is not significant. This result was counter to the initial expectation that the condensers would be the major source of dispersion.

Examination of flow patterns in the reactor shows clearly why the system behaves in this manner. The reactor can be broken into two zones. The upper zone, which is ~15 cm high, is dominated by the downflow of He which keeps the reactor head clear of product gases. The lower zone is about 20 cm deep and consists of the bottom section of the reactor and is dominated by the upflow of product gases.

The large dispersion and residence time of gas in the reactor occurs in the lower zone. Gas flow in this region is dominated by the chlorine injection flow into the reactor which is relatively slow (2.75 cm min$^{-1}$ at 100 cm$^3$ min$^{-1}$ at test conditions). Under these and reaction conditions the gas flow is laminar, although convection currents may provide some turbulence. Laminar flow produces a degree of axial dispersion that almost equivalent to a stirred tank reactor (27). Therefore, dispersion in the product gas composition is primarily a result of the reactor design which was controlled by physical constraints. The design of the condensers, while not conducive to
eliminating dispersion, was not the major source of mixing in the system.

The response curve shown in Figure D-2 is from a test to simulate reactor conditions using a lower zone flow rate of 300 cm$^3$ min$^{-1}$, and an upper zone flow of 400 cm$^3$ min$^{-1}$. The average residence time in the reactor was reduced to 1.92 minutes, a factor of three less than the 100 cm$^3$ min$^{-1}$ test, which shows that changes in the residence time can be estimated from changes in the flow rate in the reactor. For purposes of analysis the data from both these experiments were combined to produce estimated lag times of 5 and 3 minutes between the G.C. analysis and events occurring in the reactor for, the 90 and 255 cm$^3$ min$^{-1}$ chlorine flow rates used in this study.

The only attempt made to correct for dispersion effects was to use the Cl$_2$-CO$_x$ ratio to calculate reaction rates. As previously mentioned this ratio is relatively immune to dilution by the pure helium present in the condensers, so it is useful for calculating initial rates. The ratio is however, still subject to axial dispersion of the reaction gases (CO$_x$ and Cl$_2$), so it is not a perfect solution. The best way to counter the dispersion effects observed in the reactor would be to reduce the length of the lower zone.
Figure D-2. Reactor response curve to a step change in tracer flow at reaction flow conditions.
APPENDIX E - REACTOR MASS BALANCE AND DESIGN EQUATIONS

Mass Balance

The basic assumptions used for the mass balance calculations are shown in Table 11, which was determined from the fly ash composition shown in Table 3 and the component conversions of the 40A chlorination at 60 minutes. The allowable range of AlCl₃ recoveries from the melt removed with the unreacted residue is a function of the amount of AlCl₃ produced, the maximum allowable solids content of the slurry and the NaCl:AlCl₃ ratio in the melt. These parameters also define the steady-state composition of the melt.

Calculation

The melt fraction of the unreacted solid stream is assumed to contain all of the KCl, MgCl₂ and CaCl₂ produced. It is also assumed SiCl₄ and TiCl₄ are vaporized from the melt and that FeCl₃ is split between the liquid and vapor phases in the same proportions as AlCl₃. Any NaCl produced by chlorination simply reduces the amount of make-up NaCl required. A 60:40 NaCl:AlCl₃ molar ratio and a constant carbon loading of 0.206 Kg C Kg⁻¹ melt are also assumed. Using these assumptions gives:

Total weight of KCl, MgCl₂, CaCl₂ = 992 Kg hr⁻¹;
Total weight of AlCl₃ and FeCl₃ produced = 7910 Kg hr⁻¹;
Total weight of NaCl required = 4050 Kg hr⁻¹.

The total weight of the melt in residue stream is given by:

\[ 992 + 11960X_r = W_m \]  \hspace{1cm} (E-1)
where  \( X_r = \text{Fraction of AlCl}_3 \text{ removed with residue}; \)
\( W_m = \text{Total weight of melt removed, Kg hr}^{-1}. \)

Assuming an ash residue weight of 4800 Kg hr\(^{-1}\) gives a solid:slurry ratio of:

\[
\text{Solid:slurry ratio} = \frac{4800 + 0.206W_m}{4800 + 1.206W_m}
\]

Equations E-1 and E-2 are used to determine the slurry volumes shown in Figures 41 and 42, assuming a gas-hold up of 13%, which was estimated from the correlation (50):

\[
e_g = \frac{u_g}{2.2u_g + .3(gD_T)^{0.5}}
\]

where  \( D_t = \text{Column diameter, m.} \)

Doubling the gas hold-up will increase the required slurry volumes shown in Figures 41 and 42 by approximately 12%.

Melt compositions in the solid residue stream (and the reactor) are

Table E-1. Melt compositions for different levels of aluminum chloride product recovery with the unreacted residue

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent AlCl(_3) Recovery with Unreacted Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40%</td>
</tr>
<tr>
<td>AlCl(_3)</td>
<td>43.2</td>
</tr>
<tr>
<td>NaCl</td>
<td>28.4</td>
</tr>
<tr>
<td>FeCl(_3)</td>
<td>12.3</td>
</tr>
<tr>
<td>CaCl(_2)</td>
<td>11.7</td>
</tr>
<tr>
<td>MgCl(_2)</td>
<td>2.7</td>
</tr>
<tr>
<td>KCl</td>
<td>1.7</td>
</tr>
</tbody>
</table>
shown in Table E-1 for different AlCl₃ recovery percentages from the residue stream. There are significant levels of CaCl₂ and FeCl₃ in the melt that will have to be removed in the product purification operations. Removing as much AlCl₃ as possible with the solid residue will reduce the concentration of the minor chlorides in the melt.

Intrinsic Carbon Reaction Rate

To determine \( K' \), the intrinsic reaction rate at the carbon surface, \( K' \), must be determined. An estimate of \( K' \) can be determined by equation E-4 using data from the carbon surface limited reaction shown in Figure 30A (38):

\[
t = \tau \left[ 1 - (1 - x)^{1/3} \right]
\]  

and

\[
\tau = \frac{\rho_c R_0}{b K' C_{Cl,b}}
\]

where \( \rho_c \) = Molar density of carbon, g-moles m\(^{-3} \);
\( R_0 \) = Initial carbon particle radius, m;
\( b \) = Carbon:chlorine stoichiometry.

The value of \( \tau \) is the inverse of the slope of the \( t \) vs \( 1-(1-x)^{1/3} \) curve in Figure 30A, while the other parameters are determined from the system properties. Using the values shown in Table E-2 gives a value of \( 9.05(10^{-2}) \) m min\(^{-1} \) for \( K' \). The value of \( C_{Cl,b} \) is estimated using a Henry's law constant of \( 12.5(10^{-7}) \) g-mole cm\(^{-3} \) atm\(^{-1} \) (62) and an average chlorine partial pressure of 0.64 atm, which is based on the average between the inlet and outlet gas compositions of the reactor.
Table E-2. Parameters used to calculate $K'$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_C$</td>
<td>$1.42 \times 10^2$ Kg-mole m$^{-3}$</td>
</tr>
<tr>
<td>$R_o$</td>
<td>$9 \times 10^{-6}$ m</td>
</tr>
<tr>
<td>$b$</td>
<td>0.5</td>
</tr>
<tr>
<td>$C_{Cl,b}$</td>
<td>$8 \times 10^{-4}$ Kg-mole m$^{-3}$</td>
</tr>
<tr>
<td>$\tau$</td>
<td>353 min</td>
</tr>
</tbody>
</table>

Solid-Liquid Mass Transfer

The following correlation was used to estimate the value of $K_{Cl,ls}$ in the melt (50):

$$\frac{K_{Cl,ls} d_p}{D_{Cl}} = 2 + 0.212 \left( \frac{d_p (\rho_C - \rho_1) g}{\mu_1 D_{Cl}} \right)^{1/3} \left( \frac{d_p u_g \rho_1}{\mu_1} \right)^{0.112}$$  \(\text{(E-5)}\)

where
- $d_p = \text{Carbon particle diameter, m}$;
- $D_{Cl} = \text{Diffusivity of Cl}_2 \text{ in the melt, m}^2 \text{ min}^{-1}$;
- $\rho_C = \text{Carbon density, Kg m}^3$;
- $\rho_1 = \text{Melt density, Kg m}^3$;
- $g = \text{Gravitational acceleration, m sec}^2$;
- $\mu_1 = \text{Melt viscosity, g m}^{-1}\text{min}^{-1}$;

All the parameters in Equation E-5, with the exception of $u_g$, are fixed at a given temperature. The values used for calculation purposes are shown in Table E-3.
Table E-3. Parameters used to calculate $K_{Cl,ls}$

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_p$</td>
<td>$10^{-5}$ m</td>
</tr>
<tr>
<td>$D_{Cl}$</td>
<td>$6.0(10^{-7})$ m$^2$ min$^{-1}$</td>
</tr>
<tr>
<td>$\rho_C$</td>
<td>$2.35(10^3)$ Kg m$^{-3}$</td>
</tr>
<tr>
<td>$\rho_l$</td>
<td>$1.34(10^3)$ Kg m$^{-3}$</td>
</tr>
<tr>
<td>$g$</td>
<td>$3.53(10^4)$ m min$^{-2}$</td>
</tr>
<tr>
<td>$\mu_1$</td>
<td>$4.02(10^{-2})$ Kg m$^{-1}$min$^{-1}$</td>
</tr>
</tbody>
</table>

A simplified version of Equation E-5, derived from the parameters in Table E-3 is:

$$K_{Cl,ls} = 0.12 + 0.128u_g^{0.112}$$

(Simplified Equation E-5a)

Solid-liquid mass transfer is slightly dependent on the superficial gas velocity, as shown in Equation E-5a. This dependency is the result of an increase in liquid turbulence with increased gas flow rate. At a gas velocity of 12 m min$^{-1}$, $K_{Cl,ls}$ is 0.137 m min$^{-1}$, using the values shown in Table E-3.

Gas-Liquid Mass Transfer

The value of $K_{1a_1}$ is determined using Figure 18-132 from the Chemical Engineers' Handbook (18) and the suggested correction factor, which is the square root of the ratio of the diffusivities of the Cl$_2$–AlCl$_3$–NaCl system being studied and the air–water system used to generate the correlation. From this information the following relation
was developed:

\[ K_1 a_1 = 34.85 + 0.968 u_g \] (E-6)

Equation E-6 is a good approximation of the published correlation, including the correction factor, over the range of \( u_g \) from 12 to 20 m min\(^{-1}\).