CHLORINATION OF CaO IN CaCl₂ BASED MELTS

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ABSTRACT

The CaO in synthetic mixtures of CaCl₂ and KCl was successfully converted into chloride by chlorination at temperatures between 750 and 850°C. The chlorinations were carried out with chlorine, or mixtures of chlorine and argon containing up to 50 volume percent (v/o) argon, at flow rates ranging between 100 and 350 milliliters per minute (ml/min). Conversion rates of 0.23, 0.57 and 0.80 g CaO/min were successfully obtained. The stoichiometric amount of chlorine was sufficient to reduce the CaO content of the salt to ~1 weight percent (w/o) at 800°C.

INTRODUCTION

New processes for the production of the Actinide and Rare Earth metals are being developed (1-11). In these processes, metal oxide, fluoride or chloride is reduced by calcium in the presence of a salt medium such as molten calcium chloride. The metal produced is then trapped in a molten alloy pool consisting of the metal and another suitable metal such as zinc. General Motors has also developed such a process for the production of neodymium metal (6-11). In this process, fine Nd₂O₃ particles are suspended in a CaCl₂-based salt media by mechanical stirring at temperatures between 725 and 850°C. The suspended Nd₂O₃ reacts with CaCl₂ to form CaO and NdOCl which in turn is reduced by calcium to produce fine neodymium powder and additional CaO. The calcium reductant can either be added directly, or generated in situ by the reaction of less costly sodium with CaCl₂. The neodymium is extracted from the salt phase by dissolving it in a Nd-Zn or Nd-Fe pool at the bottom of the reactor.

The flow diagram for the neodymium production process is given in Figure 1. As shown in this diagram, the salt is presently being discarded, but may be regenerated for recycling. The amount of salt discarded is approximately four times the weight of neodymium theoretically produced.

In all the above processes, regeneration of the spent salt can further reduce the metal production cost and high temperature chlorination of the CaO by-product appears to be a promising method. Therefore, feasibility studies on this high-temperature chlorination process to regenerate the spent salt were conducted and the results of preliminary tests are communicated in this report.
THEORETICAL CONSIDERATIONS

Chlorination of CaO in the spent salt is proposed to be carried out by the following reaction

\[ \text{CaO} + \text{Cl}_2 \rightarrow \text{CaCl}_2 + \frac{1}{2} \text{O}_2 \] (1)

The standard free energy change of this reaction, \( \Delta G^* \), as shown in Figure 2, is negative at all temperatures of interest indicating it should proceed spontaneously in the forward direction. In addition, the magnitudes of this negative standard free energy change (\(-26.5 \text{ kcal at 1000 K}\)) should be sufficient to overcome the effect of lower CaO activity in the final stages of chlorination.

The standard free energy change of the reaction

\[ \text{MgO} + \text{Cl}_2 \rightarrow \text{MgCl}_2 + \frac{1}{2} \text{O}_2 \] (2)

is positive at chlorination temperatures (Figure 2). In addition, MgO does not form any solid solution or compound with CaO and is practically insoluble in the salt phase. Likewise, the standard free energy change of the reaction

\[ \frac{1}{3} \text{Al}_2\text{O}_3 + \text{Cl}_2 \rightarrow \frac{2}{3} \text{AlCl}_3 + \frac{1}{2} \text{O}_2 \] (3)

is positive at the temperatures of interest (Figure 2), and \( \text{Al}_2\text{O}_3 \) is also practically insoluble in the salt. Therefore, containers of either MgO or \( \text{Al}_2\text{O}_3 \) (if CaO does not appreciably react with \( \text{Al}_2\text{O}_3 \)) can be used for the chlorination process.

EXPERIMENTAL

Materials

Potassium chloride of 99.7% purity, anhydrous calcium chloride of 99.9+% purity and calcium oxide of 98% purity were used to make the synthetic spent salt mixtures. Prior to use, the chlorides were oven baked for 2 h at 500°C and the oxide for 2 h at 1000°C to remove moisture and other volatiles.

High purity chlorine (99.9%) and argon (99.999%) were used for the chlorination reactions and to purge the reactor, respectively.

Apparatus

The synthetic salt mixtures were prepared inside a helium-atmosphere drybox furnace well (9). The chlorination reactions were carried out in alumina crucibles (5.5 cm OD by 18 cm deep by 0.3 cm wall thickness) inside closed quartz containers (7 cm OD by 65 cm deep
by 0.2 cm wall thickness) fitted with gas and outlet ports (Figure 3). A tubular clam-shell heating element furnace (7.5 cm ID by 46 cm long) regulated by means of a programmable temperature controller was used to heat the test reactor. The temperature was monitored by a calibrated thermocouple positioned adjacent to the furnace wall at mid-melt level. Alumina sparge tubes (0.6 cm OD by 76 cm long by 0.15 cm wall thickness) were used to bubble the gases through the salt mixtures, while a mass flow controller and a dual tube mixing rotameter were used to regulate the chlorine and argon flow rates, respectively.

Procedures

The preweighed chloride salt mixture was melted at 850°C in an alumina crucible. The calcium oxide was slowly stirred into the molten salt, and then the mixture was slowly cooled (<3°C/min) overnight.

The alumina crucible was positioned inside the closed quartz container. Quartz felt thermal insulation was wrapped around the crucible to protect the quartz from splashing of the salts. The alumina sparge tube was positioned above the solid salt surface and sealed into the inlet port with a rubber stopper. This assembly was positioned in the furnace and hooked up to the facilities gas lines. The unit was purged with argon (~50 ml/m) as it was slowly heated (~3°C/min) to the reaction temperature.

Upon reaching thermal equilibrium, the sparge tube was lowered to within 1 cm of the crucible bottom. The chlorine was turned on at the required flow rate and allowed to pass through the melt for a predetermined time interval. At the completion of the chlorination reaction, the melt was purged with argon at 200 ml/m for ~15 min, the sparge tube was lifted out of the melt and the reactor was slowly cooled (~2.5°C/min) under a reduced argon purge rate (~25 ml/min) overnight.

The reactor was disassembled and the alumina crucible was transferred into a drybox where a 1 cm diameter core sample (~20 g) was taken for chemical analysis. The remaining salt was dissolved in ~3.5 liters of deionized water and the residual solids were filtered out, calcined weighed and reported as gravimetric CaO. In all cases, the alumina crucibles were not noticeably attacked by CaO during these experiments.

RESULTS AND DISCUSSION

The results of initial chlorination experiments are given in Table I. Synthetic salt mixtures consisting of 270 g of CaCl₂, 30 g of KCl and 50 g of CaO (14.3 w/o CaO) were used in these experiments. The effects of chlorine flow rate, temperature, excess chlorine (over the stoichiometric amount) and dilution of chlorine were studied. As can be seen from the first five experiments in Table I, the results appear to be fairly reproducible.
Effect of Chlorine Flow Rate

As shown in Table I, the CaO content of the synthetic salts was reduced to ~1 w/o at 800°C using the stoichiometric amount of chlorine at flow rates ranging between 100 and 350 ml/min. On the average, the amount of CaO remaining in the salt was ~4 g, which agrees with the solubility of CaO in CaCl₂ at 800°C (13). Apparently the soluble CaO was not easily chlorinated under these experimental conditions. However, the suspended particles of CaO were converted into CaCl₂ at conversion rates of 0.23, 0.57 and 0.80 g/min. As shown in Figure 4, the rate of CaO conversion is proportional to the chlorine flow rate. This means the rate of chlorination, within the flow rates studied, is controlled by the availability of chlorine gas.

Effect of Temperature

Chlorination with the stoichiometric amount of chlorine at a flow rate of 100 ml/min reduced the gravimetric CaO content of the synthetic salt mixtures to 0.57, 0.98 and 1.09 w/o as indicated by the gravimetric analysis at 750, 800 and 850°C, respectively. At the corresponding temperatures, the amount of residual CaO remaining in the salt increased from 2.29 to 3.89 to 4.13 g. Since the solubility of CaO in CaCl₂ also increases with temperature, it appears that the soluble CaO is comparatively more difficult to chlorinate than the CaO particles suspended in the salt.

Effect of Excess Chlorine

The effect of the amount of chlorine on CaO conversion was studied at 800°C at a chlorine flow rate of 100 ml/min. The CaO in the salt as indicated by gravimetric analysis decreased from 0.98 to 0.58 w/o when the amount of chlorine was increased from the stoichiometric amount to 10% excess, while the CaO was 1.23 and 1.98 w/o when the amount of chlorine was 10 and 20% less than stoichiometric, respectively. This trend is as expected, however, the average rate of CaO conversion increased slightly with a decrease in the amount of chlorine from the stoichiometric amount (Figure 5). This indicates when the amount of chlorine supplied is less than the stoichiometric amount, it is more efficient in converting CaO into chloride.

Effect of Diluting Chlorine

The effect of diluting chlorine with argon on CaO conversion was studied at 800°C using the stoichiometric amount of chlorine at a total flow rate of 250 ml/min. The CaO content of the salts was reduced from 14.3 to ~1 w/o (Table I), while the rate of CaO conversion was found proportional to the volume percent of chlorine in the gas phase (Figure 6). This again indicates the rate of CaO conversion is controlled by the availability of chlorine in the gas phase.
Further Interpretation of Results

The chlorination reaction can be basically represented as

$$0^2 + \text{Cl}_2 + 2\text{Cl}^- + \frac{1}{2} O_2$$

(4)

However, in the chlorination process, three phases exist; gaseous chlorine with oxygen, solid CaO (during most of the process), and a liquid solution of CaO in the CaCl₂ based salt. As the chlorine gas is bubbled through the melt, reaction (4) most likely takes place at the interface between the gas bubble and the melt. Oxide ions react with chlorine at this interface; the chloride ions formed pass into the melt, while the oxygen formed passes into the bubble. Due to high interfacial surface energy and agitation provided by gas bubbling, CaO particles will probably collect at the gas bubble-melt interface. In this way, the melt at the interface will be saturated with oxide ions and they will be available to react with chlorine until all the solid CaO particles are consumed. On the other hand, after a certain period, the oxide ions dissolved in the melt will have to migrate to the bubble surface to react with chlorine. The rate of oxide ion migration may be slow and could be the reason that it is comparatively more difficult to chlorinate the CaO in solution than CaO particles in suspension. To facilitate the chlorination of the dissolved CaO, it may be necessary to agitate the melt.

Since the melt at the bubble interface remains saturated with oxide ions when CaO particles are present, it may then be concluded that the rate of chlorination is not limited by the transport of oxide ions. In other words, the rate of reaction is controlled by the rate at which chlorine is available. Under such conditions, the amount of chlorine passed can be totally consumed due to sufficient residence time (determined by the chlorine flow rate and melt height) in the molten salt. Therefore, with proper design of experiments, all the chlorine can be used to convert CaO to CaCl₂, and chlorine corrosion problems can be avoided. This will require a reactor having the proper aspect ratio and chlorine flow patterns. However, oxygen corrosion problems must still be faced.

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### TABLE I
Results of Preliminary Chlorination Tests

| Experiment | Temp (°C) | Total Ar (ml/m) | Total Cl₂ (ml/m) | Time (min) | Vol Cl₂ (% | Excess Cl₂ (%) | Core-S CaO (% | Grav. CaO (% | Residual CaO (g) | Conversion Rate (g/min) |
|------------|-----------|-----------------|------------------|------------|-------------|----------------|---------------|---------------|---------------------|-------------------------|
|            |           |                 |                  |            |             |                |               |               |                     |                         |
| 1          | 800       | 100             | -                | 100        | 200         | 20.0           | 0             | 1.09          | 0.99               | 3.93                   | 0.23                    |
| 2          | 800       | 100             | -                | 100        | 201         | 20.1           | <1            | 1.10          | 0.98               | 3.80                   | 0.23                    |
| 3          | 800-      | 250             | -                | 250        | 80          | 20.0           | 0             | 0.61          | 1.23               | 4.72                   | 0.57                    |
| 4          | 800       | 350             | -                | 350        | 57          | 20.0           | 0             | 0.82          | 1.21               | 4.68                   | 0.80                    |
| 5          | 800       | 350             | -                | 350        | 57          | 20.0           | 0             | 1.20          | 1.11               | 4.43                   | 0.80                    |

**Experimental Reproducibility and Effect of Chlorine Flow Rate**

| Experiment | Temp (°C) | Total Ar (ml/m) | Total Cl₂ (ml/m) | Time (min) | Vol Cl₂ (% | Excess Cl₂ (%) | Core-S CaO (% | Grav. CaO (% | Residual CaO (g) | Conversion Rate (g/min) |
|------------|-----------|-----------------|------------------|------------|-------------|----------------|---------------|---------------|---------------------|-------------------------|
| 6          | 750       | 100             | -                | 100        | 200         | 20.0           | 0             | 0.70          | 0.57               | 2.29                   | 0.24                    |
| 7          | 850       | 100             | -                | 100        | 200         | 20.0           | 0             | 0.19          | 1.09               | 4.13                   | 0.23                    |

**Effect of Temperature**

| Experiment | Temp (°C) | Total Ar (ml/m) | Total Cl₂ (ml/m) | Time (min) | Vol Cl₂ (% | Excess Cl₂ (%) | Core-S CaO (% | Grav. CaO (% | Residual CaO (g) | Conversion Rate (g/min) |
|------------|-----------|-----------------|------------------|------------|-------------|----------------|---------------|---------------|---------------------|-------------------------|
| 8          | 800       | 100             | -                | 100        | 201         | 20.1           | <1            | 1.10          | 0.98               | 3.89                   | 0.23                    |
| 9          | 800       | 100             | -                | 100        | 220         | 22.0           | 10            | 0.44          | 0.58               | 2.28                   | 0.22                    |
| 10         | 800       | 100             | -                | 100        | 180         | 18.0           | (-10)         | 1.22          | 1.23               | 4.83                   | 0.25                    |

**Effect of Excess Chlorine**

| Experiment | Temp (°C) | Total Ar (ml/m) | Total Cl₂ (ml/m) | Time (min) | Vol Cl₂ (% | Excess Cl₂ (%) | Core-S CaO (% | Grav. CaO (% | Residual CaO (g) | Conversion Rate (g/min) |
|------------|-----------|-----------------|------------------|------------|-------------|----------------|---------------|---------------|---------------------|-------------------------|
| 11         | 800       | 250             | 125              | 125        | 160         | 20.0           | 0             | 0.56          | 1.03               | 3.96                   | 0.29                    |
| 12         | 800       | 250             | 50               | 200        | 100         | 20.0           | 0             | 0.30          | 1.13               | 4.30                   | 0.45                    |

**Effect of Diluting Chlorine**

* See appendix.
Fig. 1 Flow diagram of the Nd$_2$O$_3$ reduction process.

Fig. 2 Standard free energy change of reactions, $\Delta G^\circ$, versus temperature (12).

Fig. 3 Schematic diagram of the chlorination apparatus.
Fig. 4 Rate of CaO conversion versus chlorine flow rate.

Fig. 5 Rate of CaO conversion versus chlorine in excess of stoichiometry.

Fig. 6 Rate of CaO conversion versus volume percent chlorine in the gas phase.
Determination of the CaO Content in the Chlorinated Salt

The synthetic salt mixtures contained 270 g of CaCl₂, 30 g of KCl and 50 g of CaO before chlorination.

After chlorination, a 20 g core sample of the salt was taken for chemical analysis of CaO. The results of these analyses on the core samples are reported in Table I as Core-S CaO (w/o).

The remainder of the chlorinated salt sample was dissolved in water and the precipitate calcined and weighed. The calcined precipitate is reported in Table I as Gravimetric CaO (w/o). These values were calculated as follows:

\[
\text{Grav. CaO (w/o)} = \frac{100 (x)}{300 g + \frac{(50 g - x)(110.99)}{56.08} - 20 g + x}
\]

where \(x\) = the amount (g) of calcined CaO precipitate, and 20 g is the portion of the salt mixture used for chemical analysis.

The residual CaO reported in Table I is the sum of the CaO obtained from the gravimetric analysis (calcined precipitate) and the chemical analysis, or

\[
\text{Residual CaO (g)} = x + \frac{20 g \times \text{Core-S CaO}}{100}
\]