DIFFUSION COEFFICIENT OF OXYGEN IONS IN MOLTEN CALCIUM CHLORIDE

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ABSTRACT
Calciothermic reduction of metal oxides in a molten salt media is a commercial process for the production of certain actinides and lanthanides which produces a calcium oxide saturated calcium chloride salt mix as the process waste. Electrolytic reduction of calcium oxide (CaO) has been carried out in a molten calcium chloride (CaCl₂) medium to produce calcium metal cathodically and to regenerate the chloride. A porous ceramic anodic sheath has been used which allows the diffusion of ions from the catholyte into the anolyte. Diffusion of oxygen ions has been found to be the rate controlling step in the electrowinning of calcium metal. The diffusion coefficient of oxygen ions in molten CaCl₂ has been measured in the temperature range of 800 - 900°C. The data has been used to design the cell for optimizing the cell efficiency.

INTRODUCTION
Industrial processes must strive to mitigate wastes where the wastes are generated. Reactive metal production using molten salt electrolysis is an example of an industrial process which has progressed towards achieving value-recovery through hazardous waste mitigation. CaO saturated CaCl₂ salts are a by-product of the calciothermic reduction of plutonium oxide in the presence of CaCl₂, referred to as the Direct Oxide Reduction [DOR] process (Reaction [1]).

\[ \text{PuO}_2 + 2Ca \rightarrow \text{Pu} + 2\text{CaO} \]  

The effluent salt is radioactively contaminated and can not be discarded as such. This investigation was aimed at the electroreduction of CaO component of the salt to cathodically produce calcium metal for subsequent reduction of reactive metal oxides and an oxide free CaCl₂ for recycling in the DOR process. A summary of the previous work in this area and the results of the extensive investigations have been comprehensively discussed (1,2).

Conclusions regarding the feasibility of electrowinning calcium suggest that (i) atmosphere control is essential to the recovery of calcium, due to its highly reactive nature and strong thermodynamic tendency to form stable compounds, (ii) a net gain of calcium is possible if the rate at which calcium is electrowon is greater than the rate at which calcium is 'lost' due to chemical reactions, (iii) porous ceramic diaphragms must
be used to separate anode and cathode products, and thus improve the overall efficiency of the cell and (iv) the transport rate coefficients of ionic species in the molten salt needs to be determined if the kinetics of winning calcium is to be modeled and the processes, which include cell configuration and materials, are to be optimized (3,4). This study has identified the controlling factors for enhancing the calcium deposition rate by placing a ceramic diaphragm between the electrodes which provides the ionic conductivity but keeps the reaction products separated.

The porous sheath requires sufficient porosity to allow transport of specific ionic species, sufficient mechanical integrity to withstand the thermal shock and agitation in the molten salt and sufficient corrosion resistance in the aggressive, high-temperature molten salt environment. The sheath must not react with the ionic species to a degree which causes ionic transport to cease.

An investigation which has relevance to the present study was concerned with the measurement of effective diffusion coefficient in porous media (5) where the effect of path-tortuosity of the porous media on diffusion has been shown. Bouhroum et al.(6) have studied the effect of concentration and viscosity on the effective ionic diffusion. Some of the techniques which have been used to determine diffusion coefficients for particular species include radiotracer methods, chronopotentiometry, and diaphragm cell methods. In this work, the electrolytic recovery rate of calcium was found to depend on the ionic diffusion through the porous membrane. Therefore, measurement of the diffusion coefficient of oxygen ions has been made as a function of cell temperature and membrane porosity. Suggestions for the modification of cell design have also been made to enhance the rate of metal deposition.

**EXPERIMENTAL PROCEDURE**

The objective of these trials was to demonstrate the process of depositing calcium on the cathode by dissociating CaO, to determine the operating parameters (temperature, voltage, current densities, electrolyte composition) necessary and to investigate the problem areas in calcium recovery. The arrangement of the cell components in a typical cell is shown in Figure 1 and Table I lists the various process parameters used in the experiments.

The furnace and the cell were contained within an argon atmosphere glovebox with a slightly positive argon pressure. The atmosphere was circulated and kept within acceptable purity limits ($O_2 < 50 \text{ ppb}$). 5.0 wt. pct. CaO was dissolved in CaCl$_2$ at 900°C in a magnesia crucible. A stainless steel backup liner was used to protect the furnace well in the event of a crucible failure. A thermocouple was immersed in the salt bath and contained within an alumina sheath. Consumable graphite anodes and a stainless steel cathode were used for electrolysis. Magnesia porous sheaths (52 mm diameter and 2 mm wall thickness) were used to protect the anode, with a porosity ranging between 20 and 32 percent which allowed the ionic infiltration into the sheath. The porous sheath worked as the anolyte compartment. The initial level of oxygen concentration (calculated from the measured CaO content) was measured. A known weight of salt-mix is dissolved in water and titrated against hydrochloric acid. The dc current was applied to the cell and the anodic gas composition was monitored. The current was interrupted once an
appreciable level of chlorine was detected in the anodic gas. Intermediate and final levels of oxygen were recorded by the titration method as a function of time. The cell was held at a set temperature and oxygen ions were allowed to diffuse in and replenish the anolyte. The replenishment was also monitored as a function of time at a given temperature. Once the concentration of oxygen levelled off, current was reapplied and calcium was won at a different temperature. This sequence was continued for four more times at 875, 850, 825 and 800 °C for a given sheath porosity. Equivalent amount of calcium was dissolved in the catholyte and samples from different regions of the solidified catholyte salt were analyzed. Analytical method, based on hydrogen evolution upon water dissolution, was used as the technique to establish the amount of calcium. The collected data is in the form of a concentration measurement in the anolyte chamber as a function of time along with the physical characteristics data of the cell components and the diaphragm. The data was analyzed to obtain a diffusion coefficient of oxygen ions in molten CaCl₂-CaO system as a function of temperature.

RESULTS AND DISCUSSION

It was determined that the primary difficulty in obtaining a cathodic calcium deposit is due to the use of graphite anode and the evolution of carbonaceous anodic gases. These gases encourage various back-reactions in the cell through which the deposited calcium is lost (2). Therefore, in this work a porous ceramic anode-sheath was incorporated. Electrowinning under non-steady state conditions (until the point of chlorine gas generation) is performed to achieve a concentration gradient between the anolyte and catholyte. The concentration gradient which is established allows for quantifying the transport rate coefficient across the porous diaphragm. A model was used on the basis of Fick's 1st Law which relates the measured flux of oxygen into the anolyte with the diffusion coefficient:

\[
D_{\text{eng}} = \frac{c_t - c_{\min}}{c_t - \frac{1}{2}(c_t + c_{\min})} \cdot \frac{V \delta}{A \cdot t} \quad [2]
\]

where, \(D_{\text{eng}}\) is the engineering diffusion coefficient for oxygen ions in CaCl₂ diffusing through a porous sheath in \(m^2\cdot s^{-1}\), \(c_t\), \(c_i\) and \(c_{\min}\) are the bulk composition of electrolyte, the changing anolyte composition as a function of time, \(t\) (sec) and the minimum oxide concentration of anolyte (concentration at the start of diffusion), respectively, in \(mol\cdot m^3\), \(\delta\) is the sheath wall thickness in \(m\), \(A\) is the active area of inside wall of porous cylinder in contact with the salt in \(m^2\) and \(V\) is the volume of cylinder that is filled with salt in \(m^3\). In the present investigation, the effective or engineering diffusion coefficient is related to the diffusion coefficient for oxygen ions (\(D_{O_2}\)) as:

\[
D_{\text{eng}} = D_{O_2} - \frac{f \cdot \phi}{q} \cdot \beta \quad [3]
\]

where \(\phi\) is the void fraction of the porous medium calculated by subtracting from unity the ratio of the measured density of the sheath and the theoretical density for magnesia [3.58 \(x\) \(10^3\ kg\cdot m^3\) (7)], \(q\) is the tortuosity factor, \(\beta\) takes into consideration possible chemical interactions between diffusing ionic species and the porous media and \(f\) is the
open porosity fraction. Typical values of tortuosity factor range between unity and two for various media (8). For a perfectly inert media, \( \beta \) would have a value of unity. Because the possible chemical interactions are dependent on the amount of surface area available in the porous microstructure, \( \beta \) is a function of porosity fraction \( \phi \), tortuosity factor \( q \) and sheath wall thickness \( \delta \). The chemical interaction parameter, \( \beta \), is an adsorption dependent quantity. The open porosity fraction \( f \) is the fraction of the voids fraction that are open. The open porosity fraction is dependent on the ceramic manufacturing process. In equation (3), \( D_{02} \) represents the diffusion coefficient for oxygen ions in liquid calcium chloride which is a fundamental property and is only a function of the temperature and the partial pressure of oxygen.

Figure 2 shows a plot of \([C_t-C_{\text{min}}]/C_t\) versus time, where \( C_t = [(C_i+C_{\text{min}})/2 - C_{\text{in}}] \), and the slope of the line is used to calculate the engineering diffusion coefficient at different temperatures. The diffusion coefficients, as a function of temperature have been plotted in Figure 3. The use of Fick's first law is valid only as a first approximation as the driving force changes constantly with time. The measurement of \( C_t \) is made in the bulk anolyte which is assumed to be same as the concentration at the inner sheath surface, i.e. \( C_{x,t} = C_{d,t} \).

The purpose of this work is to determine a rate at which calcium may be electrowon from the present experimental system. The model uses Faraday's law modified for the rate limiting process in the system, which is diffusion of oxygen ions into the anolyte. The constraint that oxygen is the rate limiting species in the system is based upon the facts that there is a relatively small quantity (3.3 atom pct.) of oxygen present in the system, the anolyte volume is relatively small \((1.28 \times 10^4 \text{ m}^3\) compared with \(4.5 \times 10^3 \text{ m}^3\) for the catholyte) and the cell is operated at an applied potential such that oxygen, carbon monoxide or carbon dioxide gases are evolved, and chlorine gas is not evolved at the anode. The rates of ionic diffusion and electrowinning are linked by:

\[
R_{\text{max}} = -D_{02} \cdot \frac{1.789}{0.0254 - r} \cdot \left[ 2\pi r l + \pi r^2 \right] \cdot \frac{f \phi}{q} \cdot \beta
\]

where \( R_{\text{max}} \) is the maximum rate of winning in kg-moles of calcium per second, \( r \) is the inside radius of the sheath and \( l \) is the salt height in the anolyte. Thus, the maximum rate of electrowinning can be simulated using Equation (4). Figure 4 shows the relationship of \( R_{\text{max}} \) and sheath porosity for a given void fraction, \( \phi \) and tortuosity, \( q \). Knowing the maximum rate of electrowinning, the limiting current density can be estimated, using Faraday's law. Assuming favorable conditions for a high rate of calcium electrowinning, a cell can be designed, as shown in Figure 5. The optimization of porosity is essential since large porosity adversely affects the mechanical integrity of the sheath. However, small porosity levels of the sheath make the transport extremely difficult. Since one has to wait for oxygen transport, the transport through the sheath is the rate limiting process. The sheath size, geometry and porosity must be optimized to achieve a calcium winning electrolytic cell. The favorable conditions for a higher flux of oxygen ions into the anolyte are (i) thin walled porous membrane, (ii) high surface area, (iii) high open porosity and (iv) small anolyte volume. Open porosity and wall thickness are factors that, in general, compromise with the mechanical strength of the sheath. A high flux of oxygen ion allows a high current density, thereby increasing the metal recovery efficiency.

700
Cell Temperature

A high cell temperature in excess of 900°C is desired due to the following factors associated with the cell operation:

[i] High diffusion coefficient for ionic migration.
[ii] High dissolution kinetics for calcium oxide in calcium chloride.
[iii] High fluidity for salt and calcium metal.
[iv] Low dissociation potential for calcium oxide and chloride.
[v] Instability of calcium carbonate - a possible back-reaction product.

The results show that calcium can be cathodically electrowon by effectively shielding the anode with a porous membrane and by optimizing the sheath parameters to enhance the dissociation rate. The process will be most effective when the electrowon calcium will be used in situ, to reduce another metal oxide, which will, in turn, maintain a low desired activity of calcium in the cell. These investigations offer potential improvements in waste management in the reactive metal production and provide an accurate mechanistic understanding of the electrolytic calcium metal production process.

CONCLUSIONS

Calcium can be electrowon from calcium oxide-calcium chloride salt mixture by the dissociation of calcium oxide. However, the recovery as a mass requires the use of a porous anodic sheath with over 30 vol. pct. porosity.

Ionic diffusion through the sheath is the rate controlling step. A diffusion coefficient in the range of $10^{4.6}$ to $10^{5.6} \text{cm}^2/\text{sec}$ is obtained for a thirty percent porous magnesia sheath for cell temperatures between 800°C and 900°C.

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**TABLE I: CELL OPERATING DATA FOR CALCIUM ELECTROWINNING**

| Electrolyte | CaCl₂, 0-5 wt. pct. CaO |
|-------------|-------------------------|
| Cell Parameter | Figure (1) |
| atmosphere: | argon |
| crucible: | MgO |
| operating temp.: | 800-900°C |
| current: | 15 A |
| voltage: | 5-15 V |
| time: | variable |

**Anode**

| material: | graphite |
| size: | 12.7 mm x 305 mm |
| active area: | 11.4-26.6 cm² |
| current density: | 2.3-8.8 KA.m² |

**Cathode**

| material: | high purity iron |
| size: | 273 x 152 mm |
| active area: | 0.0173-0.0312m² |
| current density: | 0.40-1.44KA.m² |
Figure 1: Schematic diagram of the cell showing the 50 mm diameter ceramic sheath around the 13 mm diameter graphite anode-rod.

Figure 2: Oxygen ion concentration in the anolyte as a function of time
Figure 3: Diffusion coefficient as a function of temperature

Figure 4: Simulation studies to predict the maximum rate of calcium electrowinning as a function of the sheath porosity

Figure 5: Schematic Diagram of an advanced cell designed to enhance the rate of calcium electrowinning.