APPLICATION OF MOLTEN SALTS IN PYROCHEMICAL PROCESSING OF REACTIVE METALS

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ABSTRACT

Various mixes of chloride and fluoride salts are used as the media for conducting pyrochemical processes in the production and purification of reactive metals. The direct oxide reduction [DOR] process for the extraction of certain reactive metals utilizes calcium as the reductant which produces calcium oxide saturated calcium chloride salt as the waste product. A method has been studied to recover calcium by electrowinning it from the molten salt-mix. The recovery of calcium is characterized by the process efficiency to overcome back reactions in the electrowinning cell. A need to enhance the deposition rate by controlling the cell design and process parameters has been identified. Therefore, a theoretical analysis, based on fundamental rate theory, has been performed to understand the process parameters controlling the metal deposition rate, behavior of the ceramic anode-sheath and influence of the back-reactions. It has been observed that the deposition of calcium is dependent on the ionic diffusion through the sheath. It has also been evidenced that the recovered calcium is completely lost through the back-reactions in the absence of a sheath. The importance of anode/cathode area ratio has been highlighted. A practical scenario has also been presented where the electrowon metal can be used in situ as a reductant to reduce another reactive metal oxide.
INTRODUCTION

Direct oxide reduction, molten salt extraction, electrorefining and salt scrub reduction are some of the pyrochemical processes that use molten salt medium in the production and purification of certain reactive metals. Various salt mixtures of chlorides with additions of fluorides are used as the media which generates a considerable amount of contaminated waste that has to be processed before recycling or disposal. The commercial production of reactive metals often utilizes the direct oxide reduction (DOR) process, according to the following reaction (1):

\[ \text{MeO}_2 + 2\text{Ca} = \text{Me} + 2\text{CaO} \]  \[1\]

Reactive metal oxide is reduced with calcium to produce reactive metal and calcium oxide. The calcium oxide is dissolved by molten calcium chloride as it forms at the operating process temperatures between 850 and 900 °C. The present investigation focuses on separating the salt into calcium metal and calcium oxide-free calcium chloride, both of which can be recycled in the process.

In 1954, Threadgill (2) developed a process for electroreducing calcium from calcium chloride/calcium oxide electrolytes. Calcium oxide levels studied in this early investigation were below 2 wt. pct., and calcium electrowinning was achieved with the rising cathode technique. This technique was based upon continually pulling an electrolyte-covered calcium 'carrot' out of the molten salt. Threadgill reported that calcium electrowinning at calcium oxide concentrations higher than two wt. pct. was not possible because the viscosity of the salt decreases with increased calcium oxide levels. With lower viscosity levels, electrolyzed calcium does not remain covered with frozen electrolyte and ignites in air. Also, lower viscosity levels produce convection currents which were believed to wash calcium back into the bath. The optimal electrowinning conditions, for that system, therefore were calcium oxide content between 0.5 and 1 wt. pct., and electrolyte temperature between 788°C and 816°C.

Lukasko and Murphy (3) have recently developed a method for electrolytically producing calcium metal using an electrowinning/electrorefining sequence. In the initial electrowinning step, a calcium-tin alloy is produced in a molten cathode type of cell using a potassium chloride/calcium chloride electrolyte at 650°C. Tin was chosen as the cathode material due to its high solubility for calcium. The calcium-tin product (~7.5 wt. pct. Ca) of electrowinning is then used as the anode in the subsequent electrorefining step. Electrorefining was done in a calcium chloride/calcium fluoride electrolyte at 850°C. One of the advantages of producing calcium by this two-step method is a lower energy requirement, compared with present commercial production methods (3). The major advantage of using a liquid tin cathode is that free calcium is not available to reoxidize or form other compounds in the system, thus improving the efficiency and enabling the use of graphite as an anode.
Poa, Mulcahey and Johnson (4) have reported the results of calcium oxide dissociation experimentation from calcium chloride electrolyte with 15 wt. pct. calcium fluoride, using a liquid zinc cathode and a consumable graphite anode at 785°C. Calcium fluoride is present in certain reactive metal oxide reduction fluxes, since it lowers the melting point of calcium chloride and thereby lowers the necessary operating temperature. Preliminary results indicate that calcium oxide dissolved in molten calcium chloride/calcium fluoride can be electrolyzed to produce calcium dissolved in a liquid zinc cathode. Oxygen gas reacts with the consumable graphite anodes, and is driven out of the cell as carbon dioxide and carbon monoxide. Final calcium weight percentages in the zinc cathode range between 0.27 and 2.28 wt. pct.

Kipouros and Sharma (5) have studied electrolytic regeneration of neodymium oxide (Nd₂O₃) reduction salt, and have reported successful calcium oxide dissociation with calcium recovery in the range of ten to twenty wt. pct. The investigation involved the use of calcium chloride with calcium fluoride levels near fifteen wt. pct. Calcium oxide levels ranged between 4.74 and 8.38 wt. pct. According to the investigators, low calcium recovery levels were due to calcium carbonate and calcium carbide formation at the anode.

Steele (6) has reported the results of calcium oxide electroreduction using a calcium chloride-based electrolyte with 35.4 wt. pct. lithium chloride (LiCl) and 8.4 wt. pct. calcium oxide. Steele concludes that although this electrolyte has several advantages over pure CaCl₂, as a flux for a calcium electroreducing cell, the advantages do not outweigh the major disadvantage of anodic corrosion. The advantages of calcium chloride/lithium chloride-type electrolytes, relative to pure calcium chloride, include lower calcium solubility levels, slower reaction rates for recombination, and lower vapor pressure levels for calcium chloride above the melt.

The solubility of calcium in calcium chloride-based systems at temperatures between 760 and 950°C has been well characterized (7). The reported calcium solubility at these temperatures ranges between 2.1 and 16 wt. pct. Peterson and Hinkelbein (8), Sharma (9), Dworkin, et al.(10), Shaw and Perry (11) and Staffanson (12), however, report a maximum solubility level of about 3 - 4 wt. pct., indicating that the early reported value of 16 wt. pct by Cubiciotti and Thurmond (13) is high due to the influence of other calcium products in the salt. Figure 1 shows the collective plot for the available calcium solubility data.

A comprehensive survey of the calcium electrowinning work done in the past and its limitations has been described (14). The analysis of this earlier work indicates that two systems have been successfully used: (1) rising cathode technology, and (2) liquid cathode technology. Both of these methods suggest that calcium should leave the system either through a physical withdrawal, or by using a molten metal cathode. These methods have the advantage of enhancing the recovery rate by lowering the activity of calcium in the cell. The attempts to deposit calcium in the elemental form within the system, using graphite anodes, have met with little success in the past (6), essentially due to its reactive nature and readiness to form very stable compounds with other components in the system, such as carbon, oxygen and carbon dioxide.
This work describes the modelling of the various reaction rates involved in the cell for electrowinning calcium from the waste salt, to achieve expressions which relate rates to physical and chemical parameters, such as the voltage, current density and activities of various liquid and gaseous species. The study has identified the controlling factors and attempted to overcome the back reactions by enhancing the calcium deposition rate, removing the anodic gaseous products quickly and by placing a ceramic diaphragm between the electrodes which provides the ionic conductivity but keeps the deposited calcium away from the anode. One of the goals of the present investigation is to develop a technology to allow for simultaneous calcium electrowinning and reactive metal oxide reduction. In such a scenario, the reactive metal oxide would be chemically reduced to metal by calcium in a cell which electrolyzes the resulting calcium oxide back into calcium metal and oxygen gas.

EXPERIMENTAL

The following sections describe the materials, apparatus, and procedures used in the calcium electrowinning trials completed thus far (15). The objective of these trials was to demonstrate the process of depositing calcium on the cathode by electrolytically dissociating calcium oxide, to determine the operating parameters (temperature, voltage, current densities, electrolyte composition) necessary to dissociate calcium oxide, and to investigate the problem areas in calcium recovery.

Materials

Calcium chloride and calcium oxide used in the experiments were received in pellet and powder form, respectively. To ensure that moisture was not present, calcium chloride and calcium oxide were dried at 250°C and 900°C respectively, both for twelve hours under a nitrogen cover. The presence of water (from hydrated CaCl₂) in some of the earlier experiments essentially changed the primary cathodic reaction from calcium deposition to hydrogen evolution. After drying, these materials were kept in an inert atmosphere until ready for use.

Consumable graphite anodes and a stainless steel cathode have been used for electrolysis. The anodes were of AGKS (moderate) purity, and had dimensions of 6 mm diameter and 305 mm length. The cathode was cylindrically shaped, with dimensions of 102 mm diameter and 1.6 mm thickness. The immersion depth in the salt for the cathode ranged between 32 mm and 108 mm, in order to vary the active cathodic area.

Magnesium oxide crucibles were used to contain the molten salt. The crucibles had dimensions of 130 mm diameter, 305 mm height, and 3 mm wall thickness. Alumina sheaths were used to protect the thermocouple. Alumina and magnesia sheaths were used to protect the anode, in several configurations. Porous and dense sheath materials were tried in both closed- and open-ended sheath configurations. The arrangement of the cell components in a typical cell is shown in figure 2.
Apparatus

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 with a Vac Systems model MO40-H Dri Train.

The temperature of the resistance furnace was controlled with a temperature controller, and a current limiting SCR power controller. Furnace temperature was measured with a chromel-alumel thermocouple placed next to the elements. The temperature of the salt was also monitored with a chromel-alumel thermocouple immersed in the salt bath and contained within an alumina sheath. The graphite anode and stainless steel cathode were connected to a 10 V-50 A max. controllable DC power supply. A stainless steel backup liner was used to protect the furnace well in the event of a crucible failure.

Dense open-ended alumina sheaths were used to shield the anode in certain trials. The sheaths had an outside diameter of 22 mm, wall thickness of 2.6 mm, and the lengths ranged between 229 mm and 413 mm. A flared-end version of the tube was also tried to enhance oxygen gas collection at the anode. The maximum outside diameter of the flared end of these sheaths was 35 mm.

Porous alumina and magnesia closed-end anode sheaths with the same size as the dense sheaths were tried on various trials as the open-ended sheaths were found to be ineffective in maintaining the ionic flow or in preventing the graphite from mixing in the salt. Porosity levels ranged near 20 percent. Sheaths were evaluated for their ability to allow molten salt to infiltrate, to prevent graphite contamination of catholyte and their ability to enable electrolysis in the cell by providing a conductive path for the ions.

Based on the observations made on the first set of trials with the 6 mm dia. anode rods and narrow sheaths, the sheath and anode configurations were modified to accommodate wider sheaths (50 mm dia.) and 13 mm dia. anode [Figure (3)].

Procedure

All operations were performed in an argon atmosphere glovebox. Calcium chloride and calcium oxide were mixed in a magnesium oxide crucible, to make a simulated DOR salt mixture. The salt mixture was melted in the crucible, and then held at the desired electrolysis operating temperature.

Cathodic current density ranged between 0.40 KA m\(^{-2}\) and 1.44 KA m\(^{-2}\) for the electrolysis trials conducted. Current was held constant at 25 Amperes during these trials, while the voltage varied between 5 and 25 V. The voltage started to fluctuate once the anode surface area in the salt changed due to thermal erosion and reaction with oxygen. The voltage was around 25 V when the anode rod reduced to a pin.
Electrowinning times ranged between 1.0 and 10.6 hours, and integrated current for the trials ranged between 25.0 A·h and 265.8 A·h. Average anode life was 84 minutes. The criterion for replacing an anode during cell operation was the cell voltage level ranging between 10 and 15 volts, to maintain a constant current level of 25 Amperes. Cell operating data for the electrolysis trials are listed in Table I.

After electrolysis, salt samples from different regions of the solidified salt were analyzed for calcium and calcium oxide. Analytical methods similar to those reported by Threadgill (2) and Axler (7) were used for these analyses. Hydrogen evolution and alkalinity determination (titration with hydrochloric acid) were used as techniques to establish the respective amounts of calcium and calcium oxide in each sample.

RESULTS AND DISCUSSION

The electrowinning trials with 6 mm dia. anode were performed to determine the parameters necessary to dissociate calcium oxide and to win calcium metal. The results indicate from current and time measurements that calcium was present at the cathode during electrolysis for several of the trials, but was not recoverable. Calcium at the cathode has the possibility of reacting with oxygen, carbon dioxide, or carbon to form calcium carbonate or calcium carbide if the anodic and cathodic products are allowed to come in contact. Some pertinent observations have been made:

Proper handling of the graphite anodes, ceramic sheaths and the crucible are of utmost importance, particularly under high temperature conditions, since many trials had to be terminated due to component breakage during the melting or electrowinning. Since the salt is in a pellet form, subsequent additions of cold charge became necessary during melting to have an adequate level of molten salt. These additions caused thermal shock to the crucible in some experiments which had to be terminated.

The dissolution of calcium oxide in calcium chloride has an extremely slow kinetics at temperatures below 900°C, although 18 wt. pct. solubility is predicted by the phase diagram at the temperature. The salt-mix needs to be molten at 1000°C to take the oxide completely into solution. The experiments done at lower temperatures showed an incomplete solutionizing and had high concentrations of calcium oxide in the bottom of the crucible. The cell operating temperature should be maintained around 850°C due to various reasons:

(1) lower the solubility of calcium in the salt
(2) slow down the kinetics of other chemical reactions within the cell.
(3) lower the thermal stress on the cell components and the furnace.

A temperature of 850°C is sufficient to keep the molten salt fluid and produce liquid calcium. However, a higher temperature has distinct advantages of faster kinetics of oxide dissolution and lowers thermodynamic dissociation potential for the
oxide which can improve the cell efficiency. Calcium carbonate is also unstable preventing the reaction between calcium oxide and carbon dioxide. However, dissolution of calcium oxide can also be enhanced by stirring or sparging the molten salt by an inert gas (11).

Since it was determined that calcium is getting deposited on the cathode and subsequently participating in back reactions, three distinct possibilities existed besides dissolution in the salt, viz. calcium oxide, calcium carbonate and calcium carbide. Therefore, qualitative tests were performed and the presence of calcium carbonate was confirmed. There is also a known solubility of carbon dioxide (16) in similar salt systems, which supports at least the concept of calcium carbonate formation. Also, in the absence of hydrogen evolution on the cathode, the presence of calcium carbonate confirms the dissociation of calcium oxide and, therefore, the winning of calcium (15,17).

Besides calcium oxide and calcium carbonate, it is possible that calcium and carbon are reacting to form calcium carbide. Although the salt was not specifically analyzed for calcium carbide, previous investigations have shown that this compound may form under similar conditions (5).

The solubility of calcium in the salt, shown in figure (1), accounts for the poor recovery efficiencies observed. The aspect of calcium solubility in the salt mix is of utmost importance, since it not only affects the electrolyte characteristics in terms of ionic conductivity, transport and salt viscosity, etc., it also interferes with the electrode processes by altering the established double layers and concentration gradients. The solubility of calcium in calcium chloride is a strong function of calcium oxide in the salt and has been found to vary inversely (7). The solubility is also affected by the use of graphite as the anode where oxygen is released as a result of the anodic reaction and causes the formation of carbonates (11). The dissolved calcium, however, is useful in the in situ reduction.

Experiments were carried out using alumina (both close-end porous and open-end dense) and magnesia (closed-end porous) sheaths around the 6 mm anode graphite rod. Alumina sheaths reacted with the salt and perhaps were reduced by calcium producing calcium oxide and aluminum, as significant erosion was observed on all the alumina components in the cell. The closed-end porous (20 pct. porosity) alumina sheaths took prohibitively long hours for the salt to infiltrate. The 33 pct. porous sheath had very poor mechanical strength and were damaged during or within short time of insertion.

It was demonstrated that molten calcium chloride at 900°C adequately infiltrates porous magnesia sheaths of thirty percent porosity, within an hour of immersion. Some electrowinning experiments were conducted with magnesia sheaths, where the following observations were made:

(1) The cell voltage was higher in experiments with the sheath than without, for a given current supply.
(2) Graphite anode did not erode and the salt outside the sheath was clean.
(3) Calcium dissolved in the salt was detected by hydrogen evolution test.
(4) Chlorine gas was also detected during these experiments.

Based on the above observations, it can be concluded that a high voltage is achieved in the cell which causes the calcium chloride dissociation and chlorine gas evolution, once the concentration of calcium oxide gets close to 500 ppm. The rate of flow of chlorine ions to the anode through the sheath configuration used, is faster than oxygen ions. Therefore, (a) chlorine gas is produced, (b) calcium is deposited on the cathode and (c) carbon anode does not oxidize. A wider and more porous sheath could, therefore rectify this situation and allow the cell to operate at lower voltage.

The analyses of the data obtained from the experiments with 6 mm dia. anodes and narrow sheaths show no evidence of any significant calcium recovery, either as a separate phase on top of the salt or in the dissolved form. It has been conclusively shown that electrowinning occurred, calcium oxide dissociated and transfer of ions took place. However, calcium could not be recovered as a mass on the cathode in its elemental form. Various possibilities exist for the absence of calcium, which provide an insight into the process in the cell and also direct the future course of research.

**Back Reactions with oxygen, carbon and carbon dioxide**

If it is assumed that calcium chloride does not participate in the chemical or electrochemical reactions in the cell and is only an inert electrolyte, then the only other chemical species present in the cell are calcium, carbon and oxygen. The source of calcium is the calcium oxide and of carbon is the graphite. Oxygen is present from the dissociation of the oxide and from the ingress into the cell through leakages and as an impurity in commercial argon gas. The various possible reactions in the cell in a complete absence of moisture are:

**CELL REACTIONS**

\[
\begin{align*}
2\text{CaO} & \rightarrow 2\text{Ca} + \text{O}_2 \\
\text{C} + \text{O}_2 & \rightarrow \text{CO}_2
\end{align*}
\]

**BACK REACTIONS**

\[
\begin{align*}
\text{Ca} + \text{CO}_2 & \rightarrow \text{CaO} + \text{CO} \\
\text{CaO} + \text{CO}_2 & \rightarrow \text{CaCO}_3 \\
\text{Ca} + 2\text{C} & \rightarrow \text{CaC}_2 \\
\text{Ca} + \text{CaCl}_2 & \rightarrow \text{Solution} \\
2\text{Ca} + \text{O}_2 & \rightarrow 2\text{CaO}
\end{align*}
\]
Calcium is produced through reaction [2] and is lost through reactions [4] through [8]. Reactions [3,4,5 and 8] involve gaseous phases and their rates can be controlled by (a) the removal of anodic gases efficiently, (b) use of a lower cell temperature and (c) prevention of oxygen ingress in the cell. The presence of calcium carbonate has been confirmed by silver nitrate test which also confirms the existence of reactions [3-5]. There is also a solubility of carbon dioxide in the salt which can readily form carbonate in the presence of calcium oxide (16). Reaction [6], which is simply a measure of the calcium solubility in calcium chloride, is known to be a function of temperature and calcium oxide content and is found to range between two to four weight percent (8-12). The solubility of calcium can only be lowered by a decrease in the process temperature. The formation of calcium carbide (reaction [6]) can also potentially cause the absence of calcium at the end of the experiments. The formation of calcium carbide can be prevented by placing a sheath around the graphite anode and keeping the calcium and carbon apart. A sheath around the anode is also necessary to prevent the carbon from disintegrating and floating over the salt layer, creating a short-circuiting situation. Disintegration of the graphite anode also causes the voltage to fluctuate as the tip of the anode reduces to a pin.

Thus, to be able to produce calcium it is necessary that the rate for reaction [2] (the electrochemical cell reaction) is maximized, which can be done by increasing the cathodic current density. This practice can be achieved in three ways:

1. Increase the cell current, which will also require an increase in the cell voltage for a given resistance.
2. Decrease the cathodic area.
3. Increase the anodic area, since the anode is consumable and reduction in area to a large extent causes the anodic current density to surge very high.

The cell configuration was modified to allow the above changes [Figure (3)]. An optimum anode to cathode area ratio has to be maintained before the current can be increased. Experiment conducted with the 13 mm dia. anode and 50 mm dia. porous magnesia sheath has shown that metallic calcium is collected on the cathode and is recoverable as a mass. The porosity of the anodic sheath, however, has to be optimized to maintain an ionic flow through the sheath. The rate of flow determines the cell efficiency since the sheath acts as an additional resistance in the cell.

The rate of reactions [4-8] can be effectively lowered by lowering the temperature, quickly removing the anodic gases and using an appropriate sheath around the anode as observed during the trial with 50 mm dia. sheath. An analysis based on the fundamental rate theory shows the critical parameters that control the electrode reactions and the metal deposit.

Theoretical Rate Expression

Fundamental reaction rate theory can be applied to predict the rate of calcium deposition rate on the cathode for a given current density and to determine the cell
potential required. As discussed earlier, the deposited calcium can be lost within the system through a series of backward reactions.

**FORWARD REACTIONS IN THE CALCIUM ELECTROWINNING CELL:**

\[
\begin{align*}
2\text{CaO} & = 2\text{Ca}^{2+} + 2\text{O}^{2-} & \text{(electrolyte)} \\
2\text{Ca}^{2+} + 4\text{e}^- & = 2\text{Ca} & \text{(cathode)} \\
2\text{O}^- & = \text{O}_2 + 4\text{e}^- & \text{(anode)} \\
\text{C} + \text{O}_2 & = \text{CO}_2 & \text{(reaction at anode)} \\
\hline
2\text{CaO} + \text{C} & = 2\text{Ca} + \text{CO}_2 & \text{(cell reaction)} \\
\text{CaCl}_2 & = \text{Ca}^{2+} + 2\text{Cl}^- & \text{(electrolyte)} \\
\text{Ca}^{2+} + 2\text{e}^- & = \text{Ca} & \text{(cathode)} \\
2\text{Cl}^- & = \text{Cl}_2 + 2\text{e}^- & \text{(anode)} \\
\hline
\text{CaCl}_2 & = \text{Ca} + \text{Cl}_2 & \text{(cell reaction)}
\end{align*}
\]

**Boundary Condition:**

\[ r_{\text{Ca}} = 2r_{\text{O}_2} + r_{\text{Cl}_2} \]

where all the rates are in moles/sec.

Figure (4) shows the dependence of equilibrium cell potential on the calcium oxide content of the salt. The dissociation of calcium chloride (Reaction [14]), an undesirable reaction in the present cell, is thermodynamically feasible only below a calcium oxide content of 0.04 wt. pct. in the salt, when an inert anode is used for oxygen evolution. However, the use of carbon anode makes it even more difficult for the chloride to dissociate, since the equilibrium potential of reaction (13) is significantly lower than the potential for reaction (14) if an infinitely small amount of calcium oxide is present in the salt. Therefore, it is possible to dissociate all the calcium oxide in an inert calcium chloride salt medium. Accordingly, the boundary condition would reduce to:

\[ r_{\text{Ca}} = 2r_{\text{O}_2} \]

**Calculation of \( r_{\text{Ca}} \): (Based on equation 10 and 15)**

\[
\begin{align*}
\nu_{\text{fwd}} & = \nu_o \cdot e^{-\Delta G^*/RT} \\
\nu_{\text{bkwrd}} & = \nu_o \cdot e^{-\Delta G^*/RT}
\end{align*}
\]

where \( \nu_o \) is the atomic vibrational frequency, sec\(^{-1}\)
\( v_{net} = v_{fwd} - v_{bwd} = v_0 \cdot e^{-\Delta G^* / RT} [ e^{-\Delta G^* / RT} - 1 ] \)  \[22\]
\( v_{net} = v_0 \cdot e^{\Delta S^*/R} \cdot e^{-\Delta H^*/RT} [ e^{-\Delta G^* / RT} - 1 ] \)  \[23\]

where \( v_{net} \) is the net jump frequency of calcium ions that produce metal on the cathode [Figure (5)] and \( \Delta G^* \) is the Free energy activation barrier/mole. The driving force/mole, \( \Delta G^* \), can be expressed as:

\[ \Delta G^* = nF \eta_{Ca} + RT \ln ([\text{Ca}]/[\text{Ca}^{++}]) \]  \[24\]
\[ \eta_{Ca} = E_{applied} - E_{Ca} \]  \[25\]
\[ E_{Ca} = E_{o, Ca} - \frac{RT}{nF} \ln ([\text{Ca}]/[\text{Ca}^{+}]) \]  \[26\]

where \( \eta_{Ca} \) is the cathodic over-potential in (-) volts [Figure (6)]; \( E_{applied} \) is the cathodic applied potential; \( E_{o, Ca} \) is the Standard calcium half-cell potential (-2.87 volts) and \( E_{Ca} \) is the Equilibrium calcium half-cell potential.

\[ e^{-\Delta G^*/RT} = e^{-nF \eta_{Ca}/RT} \cdot e^{\ln ([\text{Ca}^{+}]/[\text{Ca}])} \]  \[27\]
\[ = [\text{Ca}^{2+}]/[\text{Ca}] \cdot e^{-nF \eta_{Ca}/RT} \]  \[28\]

where \( nF \) is 2 x 96500 amp-sec/mol, \( R \) is the Universal Gas Const. (8.314 joules/K-mole) and \( T \) is the cell temperature at 950 °C [1223 K].

\( v_{Ca} = \text{mole/sec} = \frac{v_{net}}{\text{Av. No.}} \)
\( = 1.66 \times 10^{-24} \cdot v_{net} \)
\( = 1.66 \times 10^{-24} \cdot v_0 \cdot e^{\Delta S^*/R} \cdot e^{-\Delta H^*/RT} [ e^{-\Delta G^*/RT} - 1 ] \)
\( = 1.66 \times 10^{-24} \cdot v_0 \cdot e^{\Delta S^*/R} \cdot e^{-\Delta H^*/RT} [ [\text{Ca}^{+}]/[\text{Ca}] \cdot e^{-nF \eta_{Ca}/RT} - 1 ] \)

\[ r_{Ca} = A' \cdot e^{-nF \eta_{Ca}/RT} \]  \[29\]

where \( A' \) is a coefficient = \( 1.66 \times 10^{-24} \cdot v_0 \cdot e^{\Delta S^*/R} \cdot e^{-\Delta H^*/RT} \cdot [\text{Ca}^{2+}]/[\text{Ca}] \) in moles/sec. and \( -nF \eta_{Ca}/RT > 1 \).

For a cell current efficiency of 100 percent and a given current of \( I \) amperes:

\[ r_{Ca} = 5.2 \times 10^6 \cdot I \text{ mole/sec} \]  \[30\]
\[ r_{Ca} = 5.2 \times 10^6 \cdot i_c \cdot C_{area} \]  \[31\]
where $i_c$ is the cathodic current density in amps/cm² and $C_{\text{area}}$ is the cathodic area.

Combining equations [29] and [31]:

$$i_c = A^* \cdot e^{-\frac{F\eta_{\text{Ca}}}{RT}} \quad [32]$$

where $A^*$, in amperes/cm², is a new coefficient and incorporates the cathodic area. Equation (32) is the familiar Tafel Equation and can be expressed in the form:

$$\log i_c = \beta - \frac{nF\eta_{\text{Ca}}}{RT} \quad [33]$$

where $\beta = \log A^*$. Equation (33) can be rearranged as:

$$-\eta_{\text{Ca}} = \alpha \log i_c + \beta' \quad [34]$$

where $\alpha$ is $RT/nF = 0.0527$ volt, $\beta'$ is $-\alpha \beta$ and $\beta$ is dependent on the atomic jump frequency of calcium ions, the free energy activation barrier, $\Delta G^*$, and the cathodic area. Thus, $\beta$ is a constant at a given temperature and cathode area. For a given cathodic current density, $i_c$ (i.e. rate of calcium deposition), $\eta_{\text{Ca}}$ can be thus calculated.

**Calculation of $r_{O_2}$:** (based on equation [11])

A similar analysis can be done to develop a rate equation for the anodic reaction of oxygen evolution and an equation similar to equation (29) can be obtained:

$$r_{O_2} = A'' \cdot e^{\frac{nF\varphi}{RT}} \quad [35]$$

where $A''$ is a coefficient $= 1.66 \times 10^{-24} \cdot \varphi_0 \cdot e^{\Delta V^R} \cdot e^{-\frac{\Delta G^*}{RT}} \cdot ([O_2^2]/pO_2)$ in moles/sec.

For a cell current efficiency of 100 percent and given current of $I$ amperes:

$$r_{O_2} = 2.6 \times 10^{-6} \cdot I \text{ moles/sec} \quad [36]$$

$$r_{O_2} = 2.6 \times 10^{-6} \cdot i_a \cdot A_{\text{area}} \quad [37]$$

where $i_a$ is the anodic current density in amps/cm² and $A_{\text{area}}$ is the anodic area.

Combining equations [35] and [37]:

$$i_a = A''' \cdot e^{\frac{nF\varphi}{RT}} \quad [38]$$
where \( A^{**} \), in amperes/cm\(^2\), is a new coefficient incorporating the anodic area. From equation (38):

\[
\log i_a = \beta^* + nF\eta_{O_2}/RT \quad [39]
\]

where \( \beta^* = \log A^{**} \). Equation (39) can be rearranged as:

\[
\eta_{O_2} = \alpha^* \log i_a + \beta'' \quad [40]
\]

where \( \alpha^* = RT/nF = .0263 \) volt, \( \beta'' = -\alpha^* \beta^* \) and \( \beta^* \) is a function of the atomic jump frequency of oxygen ions, the free energy activation barrier, \( \Delta G^* \), and the anodic area. Thus \( \beta^* \) is a constant at a given temperature and anode area. For a given anodic current density, \( i_{a0} \) (i.e rate of oxygen evolution), \( \eta_{O_2} \) can be thus calculated.

Equations (34) and (40) have been plotted in Figure (6). The required applied potential of the cell can be calculated for a given applied current density for the two electrodes [figure (6)].

Total applied potential,

\[
E_{\text{appl.}} = E_{Ca} + E_{O_2} + \eta_{Ca} + \eta_{O_2} + IR_{\text{drop salt}} + IR_{\text{drop sheath}} \quad [41]
\]

where \( E_{Ca} + E_{O_2} = E_{Ca}^0 + E_{O_2}^0 + 0.029 \log Q \) and \( \eta_{Ca} \) and \( \eta_{O_2} \) are given by equations [34] and [40].

\[
\eta_{Ca} + \eta_{O_2} = \log \left( i_{a0}^{*a} / i_{c}^{*c} \right) + (\beta'' - \beta^*) \quad [42]
\]

The current densities, \( i_a \) and \( i_c \), and, therefore, the cell efficiency or the calcium deposition rate is not only driven by the applied over-potentials, \( \eta_{Ca} \) and \( \eta_{O_2} \), but the respective anodic and cathodic areas, \( A_{area} \) and \( C_{area} \). In other words, the cell behavior can be controlled by controlling the electrode configurations, sheath porosity and applied potential. Under standard condition, i.e. \( Q = 1 \); the applied cell potential can be accurately calculated by equation [41]. The term, \( \log \left( i_a / i_c \right) \) in equation [42] translates to a function of the ratio of cathode to anode areas for a given applied current, \( I \). However, as discussed earlier, \( \beta'' - \beta^* \), also has an equal but opposite dependency on the respective electrode areas and, therefore, the over-potentials are independent of the electrode areas. In a practical situation in a cell, where the electrode areas are different, the over-potential can be determined by using Figure (6). Equation (41) completely describes the cell reactions. It illustrates the importance of individual voltage components and criticality of the sheath behavior in not only controlling the cell potential but the flow of ionic species to the anode. The voltage components can be described separately for the two conditions of inert anode application and a graphite anode application:

**Inert anode:** [950 C]

\[
E^{Ca} + E^{O_2} = 2.65 \text{ volts} \quad Q = (a_{Ca} \cdot P_{O_2}^{1/2} / [Ca^{2+}] \cdot [O^{2-}]) \quad [43]
\]
Carbon anode: [950 C]

\[
E^{\text{Ca}} + E^{\text{O2}} = 1.62 \text{ volts}
\]

\[
Q = \left( a_{\text{Ca}} \cdot \frac{P_{\text{CO2}}^{1/2}}{[\text{Ca}^{2+}] \cdot [\text{O2}^{-}]} \right)
\]  \hspace{1cm} \text{[44]}

It is evident from the above analysis that the rate of flow of ions through the sheath will have a major influence on the cell potential, since it will determine the values of \( \text{IR}_{\text{drop}} \) and \( Q \). The activity of calcium ions can be assumed as unity, since both the oxide and chloride electrolyte provide the source for calcium ions. The activity of calcium metal will be determined by the solubility of the metal in the salt which is found to be 2 - 4 wt. pct. (7), depending on the oxide content and the cell temperature. Beyond the solubility limit of calcium in the salt, the metal will have an activity of unity. It is important to note that the dissolution of calcium in the electrolyte is the only feasible back reaction in the presence of a sheath. Therefore, the constitutive constant, \( Q \), will depend on the flow of oxygen ions through the sheath and the efficiency of removal of oxygen or carbon dioxide gas from the anode and will be a function of time. The removal of the anodic gases is controlled by the flow of argon gas within the cell enclosure at one atm. pressure. This discussion, therefore, suggests that a near total depletion of oxygen ions within the sheath (lack of flow of oxygen ions through the sheath) can raise the equilibrium potential of the cell to a level where the evolution of chlorine becomes feasible thermodynamically and chlorine gas would then start to evolve on the anode [Figure (6)]. In an event, where chlorine depletion also takes place within the sheath, the cell will effectively shut off.

**In situ electrowinning and direct oxide reduction**

If calcium metal is electrowon and back reactions are minimized by the steps mentioned above, then it will be possible to carry out an in situ direct oxide reduction of the metal oxide by the following reaction:

\[
\text{MeO}_2 + 2\text{Ca} \rightarrow 2\text{CaO} + \text{Me}\downarrow
\]

\[
2\text{CaO} \rightarrow 2\text{Ca} + \text{O}_2
\]  \hspace{1cm} \text{[2]}

Reactions [1] and [2] give a net reaction of:

\[
\text{MeO}_2 = \text{Me} + \text{O}_2
\]  \hspace{1cm} \text{[45]}

The rate of reaction [45] is directly linked with reaction [2]. If the rate for reaction [2] is increased, the rate for reaction [45] will increase significantly as the reduced high density metal will settle in the bottom of the cell. The rates for back reactions will also be lowered by the presence of in situ reduction using calcium. Calcium oxide will be continuously generated keeping its concentration in the salt at near constant level, which will aid in keeping the salt density and fluidity as well as the calcium solubility constant. Such a process has been successfully developed for producing neodymium from its oxide (5).
The present results suggest that the in situ cell is feasible, since electrolytic dissociation of calcium oxide is observed. Cell improvements have been incorporated to design a system which allows for calcium recovery. Such a cell system has been tested with 50 mm dia. ceramic low-density Magnesia flat-bottom crucible as anode sheath stock (Figure 3). The outside diameter of these crucibles is in the range of 50 mm which will allow the use of up to 25 mm round graphite anode rods. The results show that metallic calcium can be deposited and maintained at the cathode.

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.

**Future Directions**

To recover calcium, under DOR conditions with 10 wt. pct. calcium oxide, it is apparently necessary to remove electrowon calcium away from the system immediately after its formation. Since calcium has a strong thermodynamic driving force to react with other species in the system, it is necessary to design the cell and operating parameters to allow for winning the calcium faster than it is being lost. Possible ways of overcoming the fast kinetics for back reactions include using a high cathode current density or a high active anode area, or both. For example, arranging the anode and cathode in such a manner as to achieve a high anode area to cathode area ratio, as well as operating at a relatively high current level, may result in a net accumulation of calcium. Also an optimization of the porosity and evaluation of the closed-end porous anode sheaths and reduction in the cell operating temperature needs to be investigated.

**CONCLUSIONS**

1. Calcium can be electrowon from 10 wt. pct. calcium oxide-calcium chloride salt mixture by the dissociation of calcium oxide. However, the recovery as a mass requires cell modifications to control the back reactions. The modifications are:

   [a] Use of 30-40 vol. pct. porous close-end MgO anodic sheath.
   [b] Quick removal of anodic gases.
   [c] Complete isolation of cell atmosphere.
   [d] Optimization of temperature.
   [e] Increase in the cathodic current density.

2. The electrode reaction rates have been analyzed to derive a constitutive process equation which shows the importance of anodic sheath and the electrode areas in controlling the cell potential.
(3) The application of electrowon calcium to perform an insitu reduction of another reactive metal oxide has been analyzed.

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Table I - Cell Operating Data Calcium Electrowinning Trials.

| Electrolyte | CaCl₂, 0-10 wt. pct. CaO |
|-------------|-----------------------------|
| **Cell**    |                             |
| atmosphere: | argon                       |
| crucible:   | magnesium oxide             |
| operating temp.: | 850-970°C               |
| current:    | 25 A                        |
| voltage:    | 5 - 25 V                    |
| time:       | 3.5 - 10.6 h                |
| **Anode**   |                             |
| material:   | graphite                    |
| size, cm:   | 6.4 mm dia x 305 mm length  |
| active area:| 0.0005 - 0.0011 m²          |
| current density: | 20 - 50 KA m²          |
| **Cathode** |                             |
| material:   | stainless steel             |
| size, cm:   | 273 x 152 mm                |
| active area:| 0.0173 - 0.0312 m²          |
| current density: | 0.40 - 1.44 KA m²          |
Figure 1 - Solubility of calcium in calcium chloride

![Graph showing solubility of calcium in calcium chloride.](image)

Figure 2 - Schematic diagram of the cell configuration with a ceramic anode sheath.

![Schematic diagram of cell configuration.](image)
Figure 3: Schematic diagram of the cell showing the arrangement for 13 mm diameter anode rod and 50 mm diameter sheath.

Figure 4: Dependence of equilibrium cell potential on calcium oxide content.

Equilibrium Potential, $E$ (Volts)

$\text{CaCl}_2 = \text{Ca} + \text{Cl}_2$
$2\text{CaO} = 2\text{Ca} + \text{O}_2$
$2\text{CaO} + \text{C} = 2\text{Ca} + \text{CO}_2$
Figure 5: Activation energy barrier for the ionic jump

\[ \Delta G^* = E_0 - RT \ln \frac{\nu_{\text{prod}}}{\nu_{\text{reo}}}, \]

\[ E_{\text{appl}} = E + \eta + IR, \]

\[ E = E_0 - RT \ln \frac{\nu_{\text{prod}}}{\nu_{\text{reo}}} \]

850°C

Figure 6: Cell potential Vs. applied current density