Conf-9206163--1

PROCESSING OF EFFLUENT SALT FROM THE DIRECT OXIDE REDUCTION PROCESS

RFP--4572

DE92 013400

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ABSTRACT

The production of reactive metals by Direct Oxide Reduction [DOR] process using calcium in a molten calcium chloride salt system generates significant amount of contaminated waste as calcium oxide saturated calcium chloride salt mix with calcium oxide content of up to 15 wt. pct. Fused salt electrolysis of a simulated salt mix [$CaCl_2$ + 10 wt. pct. CaO] has been carried out to electrowin calcium, which can be recycled to the DOR reactor along with the calcium chloride salt or may be used in-situ in a combined DOR and electrowinning process. Many reactive metal oxides could thus be reduced in a one-step process without generating a significant amount of waste. The technology will resolve a major contaminated waste disposal problem, besides improving the cost and process efficiency in reactive metal production. The process has been optimized in terms of the calcium solubility, cell temperature, current density and the cell design to maximize the current efficiency. Based on the information available regarding the solubility of calcium in calcium chloride salt in the presence of calcium oxide, and the back reactions occurring insitu between the electrowon calcium and other components present in the cell, e.g. carbon, oxygen, carbon dioxide and calcium oxide, it is difficult to recover elemental calcium within the system. However, a liquid cathode or a rising cathode has been used in the past to recover calcium. The solubility has also been found to depend on the use of graphite as the anode material as evidenced by the presence of calcium carbonate in the final salt. The rate of recovery for metallic calcium has to be enhanced to levels that overcome the back reactions in a system where quick removal of anodic gases is achieved. Calcium has been detected by the hydrogen evolution technique and the amount of calcia has been determined by titration. A porous ceramic sheath has been used in the cell to prevent the chemical reaction of electrowon calcium to produce oxide or carbonate and to prevent the contamination of salt by the anodic carbon. Cell design, temperature and current density has been investigated to adopt proper methods for quickly removing the anodic gases and also to maintain a high rate of calcium deposition to discourage back reactions.

INTRODUCTION

The commercial production of reactive metals often utilizes the direct oxide reduction (DOR) process , according to the following reaction [1]:

$$MeO_2 + 2Ca \rightleftharpoons Me + 2CaO \tag{1}$$

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. In the current practice the used salt is stored as a contaminated waste. The present investigation focuses on separating the salt into calcium metal and calcium oxide-free calcium chloride, both of which can be recirculated into the process stream.

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 two 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 this system, therefore are 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.

Mulcahey, Poa, and Johnson [4] have reported the results of calcium oxide dissociation experimentation from calcium chloride electrolyte with fifteen wt. pct. calcium fluoride, using a liquid zinc cathode and a consumable graphite anode at 785°C. Calcium fluoride is present in certain plutonium 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 (Nd_2O_3) 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 $CaCl_2$, 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 three to four 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 their limitations have 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. 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.

Figure 1 - Solubility of calcium in calcium chloride

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 twenty one calcium electrowinning trials completed thus far. The objective of these trials was to demonstrate the process of depositing calcium on the cathode by electrolytically dissociating calcium oxide, determine the operating parameters (temperature, voltage, current densities, electrolyte composition) necessary to dissociate calcium oxide, and to investigate the problem areas in calcium recovery. Table 1 lists the oxide levels, cell temperature and salient observations of these trials.

Materials

Calcium chloride and calcium oxide used in the experiments were received in pellet and powder form, respectively. During experiments 1 through 8, excessive moisture was present in the starting materials. For runs 9 through 21, to ensure that moisture is 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 $CaCl_2$) in the earlier experiments essentially changed the primary cathodic reaction from calcium deposition to hydrogen evolution. A vacuum system was developed for periodic removal of collected water during drying [Figure 2]. 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.

Figure 2 - Schematic diagram for the apparatus used for drying calcium chloride and calcium oxide

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 3.

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 for trials 7-8 and 12-15. 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. For trials 12 and 19, a flared-end version of the tube was tried to enhance oxygen gas collection at the anode. The maximum outside diameter of the flared end of these sheaths was 35 mm.

Table 1 - Salient observations in calcium electrowinning

Test no.	Init. CaO (wt. pct.)	Final CaO (wt. pct.)	Cell Temp. (°C)	Observations
Ca001	19.2	19.2	700	Too low temperature
Ca002	<1.0	<1.0	924	anode failure
Ca003	<1.0	<1.0	777	calcium not recovered
Ca004	<1.0	<1.0	876	anode dissolved
Ca005	5.1	2.2*	831	CaO not dissolved
Ca006	5	5	n/a	crucible broke
Ca007	5	5	no T/C	anode erosion
Ca008	5	0.41*	846	H_2O present
Ca009	0	0	936	sparging expt.
Ca010	9.1	6.2	883	calcium not recovered
Ca011	9.1	7.1*	872	Dri-Train failure
Ca012	10	7.4	970	calcium not recovered
Ca013	10	9.2	970	calcium not recovered
Ca014	10	8.1	970	calcium not recovered
Ca015	10	7.3	970	calcium not recovered
Ca016	10	8.3	901	Iron anode
Ca017	10	-	810	crucible broke
Ca018	5	2.7	870	sheath broke
Ca019	5.5	4.9	877	Cl_2 detected
Ca020	6	5.8	881	3 sheaths used
Ca021	5.8	4.8	857	sheath broke

* CaO not completely dissolved in $CaCl_2$

Porous alumina and magnesia anode sheaths were tried on experiments 1,2 and 17-21. 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.

Figure 4 shows a schematic diagram of the hydrogen evolution apparatus used to determine the amount of calcium present in a salt sample. Dissolving a known quantity of salt in water and measuring the volume of hydrogen gas evolved allows for calculation of the molar quantity of calcium present in the known amount of salt, according to the following reaction:

$$Ca + 2H_2O \rightleftharpoons Ca(OH)_2 + H_2 \qquad (2)$$

To determine the amount of CaO present in a salt sample, the sample was dissolved in distilled water and titrated with hydrochloric acid. The quantity detected by acid titration accounts for the calcium hydroxide found by reaction (2) and also by reaction (3):

$$CaO + H_2O \rightleftharpoons Ca(OH)_2 \qquad (3)$$

Therefore, undissociated calcium oxide was obtained by the difference in the amounts of calcium detected by the hydrogen evolution and titration techniques.

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.

As a verification on the time-temperature conditions necessary to dissolve ten wt. pct. calcium oxide in calcium chloride, a solubility test was run, using 50 g of calcium chloride and 5 g of calcium oxide in a small alumina crucible. The mixture was heated to 1000°C, and held at temperature for twenty four hours. Post test analysis showed that the calcium oxide level in the final sample was uniform, indicating that calcium oxide dissolution in calcium chloride can be achieved with sufficient time at 1000°C.

During trials 1 and 3, calcium oxide was not sufficiently dissolved, as evidenced by calcium oxide-rich regions at the bottom of the solidified salt, since the time and temperature allowed for dissolution was inadequate. Approximately one hour prior to electrolysis, the molten salt was manually stirred for one minute, to ensure complete solubility of calcium oxide.

Figure 3 - Schematic diagram of the cell configuration with a ceramic anode sheath.

Figure 4 - Schematic diagram of the hydrogen evolution apparatus for the determination of calcium dissolved in the salt.

Cathodic current density ranged between 0.40 KA m^{-2} and 1.44 KA m^{-2} for the seven 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 ten and fifteen volts, to maintain a constant current level of 25 Amperes. Cell operating data for seven electrolysis trials are listed in Table 2.

Table 2 - Cell Operating Data Calcium Electrowinning Trials.

Electrolyte	
$CaCl_2$, 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 m^2
current density:	20 - 50 KA m^{-2}
Cathode	
material:	stainless steel
size, cm:	273 x 152 mm
active area:	0.0173 - 0.0312 m^2
current density:	0.40 - 1.44 KA m^{-2}

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

Twenty one electrowinning trials have been thus far 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 may have reacted with oxygen, carbon dioxide, or carbon to form calcium carbonate or calcium carbide. The information gathered during the experiments completed have been described in this section. Even though the primary objective of obtaining electrowon calcium has not been achieved under the present set of parameters, some very 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 two distinct advantages, besides the faster kinetics of oxide dissolution. It lowers the thermodynamic dissociation potential for the oxide which can improve the cell efficiency and it makes calcium carbonate unstable preventing the reaction between calcium oxide and carbon dioxide. However, the advantages of low temperature operation around 850°C out-weigh the benefits of raising the cell temperature, since the rate of dissolution of calcium oxide can also be enhanced by stirring or sparging the molten salt by an inert gas [11]. It is, therefore, important to optimize the cell temperature.

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 to see if calcium carbonate was present. Calcium carbonate may form through a reaction between calcium oxide and carbon dioxide. Salt from trial 14 was dissolved in excess water to separate the carbonate and the residue was filtered. Effervescence was observed when this residue was reacted with 0.1 N hydrochloric acid, indicating the possible existence of calcium carbonate in the salt. In a separate test, a sample of the residue was stirred into 0.1 N silver nitrate and allowed to settle. A gray precipitate was obtained which is another positive indication of calcium carbonate in the salt. There is also a known solubility of carbon dioxide [15] 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.

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 salt and the oxide must be completely dry to be able to produce any calcium through electrolysis. Any presence of moisture in the salt can change the cathodic reaction from calcium deposition to hydrogen evolution and can completely ruin the atmosphere in the glovebox. While a current will flow through the cell its efficiency will be lowered due to hydrolysis reaction. Such a behavior was observed in the earlier experiments. When a completely dried salt was used in the experiment using an iron anode, iron was deposited on the cathode with an efficiency of approximately 95 percent.

The analyses of the data obtained from all the experiments thus far 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. 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

$$2CaO \Rightarrow 2Ca + O_2 \qquad (4)$$
$$C + O_2 \Rightarrow CO_2 \qquad (5)$$

BACK REACTIONS

$$Ca + CO_2 \Rightarrow CaO + CO \qquad (6)$$
$$CaO + CO_2 \Rightarrow CaCO_3 \qquad (7)$$
$$Ca + 2C \Rightarrow CaC_2 \qquad (8)$$
$$Ca + CaCl_2 \Rightarrow \text{Solution} \qquad (9)$$
$$2Ca + O_2 \Rightarrow 2CaO \qquad (10)$$

Calcium is produced through reaction (4) and is lost through reactions (5) through (10). Reactions (5,6,7 and 10) 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 (5-7). There is also a solubility of carbon dioxide in the salt which can readily form carbonate in the presence of calcium oxide [15]. 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 (8)) can also potentially cause the absence of calcium at the end of the experiments. Formation of calcium carbide can not only account for the lack of calcium deposit, it can also interfere with the determination of calcium and calcium oxide due to the following reaction with water:

$$CaC_2 + H_2O = CaO + C_2H_2\uparrow \qquad \mathbf{(11)}$$

Acetylene gas will appear along with the hydrogen gas in the hydrogen evolution test and calcium oxide obtained through the above reaction will also be detected in the titration test. 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 (4) (the cell reaction: electrochemical) 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 has to be modified to allow the above changes. An optimum anode to cathode area ratio has to be maintained before the current can be increased.

The rate of reaction for reactions (5-10) (the back reactions: chemical) can be lowered by lowering the temperature, quickly removing the anodic gases and using a sheath around the anode. The experiments done with a sheath have shown that carbon and calcium can be kept apart. Various reaction rates for the electrochemical and chemical reactions have to be carefully studied to obtain the optimum temperature and current density to produce a net amount of calcium metal. Such a rate analysis is being conducted.

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:

$$MeO_2 + 2Ca \rightarrow 2CaO + Me\downarrow \qquad (12)$$

$$2CaO = 2Ca + O_2 \qquad (13)$$

Reactions (12) and (13) give a net reaction of:

$$MeO_2 = Me + O_2 \qquad (14)$$

The rate of reaction (14) is directly linked with reaction (4). If the rate for reaction (4) is increased, the rate for reaction (14) 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].

Experiments have been carried out using alumina (both close-end porous and open-end dense) and magnesia (closed-end porous) sheaths around the 6.3 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 was detected in the salt 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 in the cell also causes the calcium chloride salt to dissociate along with calcium oxide which causes the chlorine ions to move to the anode. 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 can rectify this situation and allow the cell to operate at lower voltage.

Future Directions

To recover calcium, under DOR conditions with ten 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 evaluation of the closed-end porous anode sheaths and reduction in the cell operating temperature needs to be investigated.

The present results suggest that the in situ cell is feasible, since electrolytic dissociation of calcium oxide is observed. Cell improvements are necessary, however, to design a system which allows for calcium recovery. Such a cell system has been designed, fabricated and tested which utilizes wider ceramics low-density Magnesia flat-bottom crucible as anode sheath stock (Figure 5). The outside diameter of these crucibles is in the range of 50 mm which will allow the use of 25 mm round graphite anode rods.

Development of rate theory for the system is required to optimize the cell conditions, i.e. temperature and current density, to achieve a net gain of calcium while minimizing the back reactions with oxygen, carbon dioxide and carbon.

Figure 5: Schematic diagram of the cell showing the arrangement for 13 mm diameter anode rod and 50 mm diameter sheath

CONCLUSIONS

The experiments carried out thus far and the results discussed lead to the following conclusions:

(1) Calcium can be electrowon from ten wt. pct. calcium oxide-calcium chloride salt mixture by the dissociation of calcium oxide.

(2) The removal of moisture from the salt and oxide and the complete dissolution of oxide in the salt is critical, which must be assured prior to the start of electrolysis.

(3) The cell reaction of calcium deposition has to be enhanced and the back reactions have to be discouraged for a net cathodic deposition of calcium. This result can be achieved by incorporating the following steps:

[a] Use of 30-40 pct. porous close-end magnesia sheath around the anode.

[b] Quick removal of anodic gases, i.e. oxygen, carbon dioxide, chlorine, by properly designing the gas exit system.

[c] Complete isolation of cell atmosphere and use of oxygen-free argon gas by installing oxygen-traps on the argon inlet.

[d] Optimization of temperature to be optimized for oxide dissolution, salt fluidity, rate of back reactions, calcium solubility, thermal stresses and theoretical dissociation voltage for the oxide.

[e] Increase in the cathodic current density by increasing the supply current, decreasing the cathodic area or increasing the anodic area.

(4) In situ DOR experiments can be conducted using a surrogate heavy metal oxide in the modified cell combining electrowinning and reduction steps in one operation.

Acknowledgement

The authors appreciate and acknowledge the support of the U.S. Department of Energy and EG&G Rocky Flats, Inc.

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