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Molten salt applications in materials processing

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Abstract

The science of molten salt electrochemistry for electrowinning of reactive metals, such as calcium, and its in situ application in pyroreduction has been described. Calcium electrowinning has been performed in a 5–10 wt% calcium oxide–calcium chloride molten salt by the electrolytic dissociation of calcium oxide. This electrolysis requires the use of a porous ceramic sheath around the anode to keep the cathodically deposited calcium and the anodic gases separate. Stainless steel cathode and graphite anode have been used in the temperature range of 850–950 °C. This salt mixture is produced as a result of the direct oxide reduction (DOR) of reactive metal oxides by calcium in a calcium chloride bath. The primary purpose of this process is to recover the expensive calcium reductant and to recycle calcium chloride. Experimental data have been included to justify the suitability as well as limitations of the electrowinning process. Transport of oxygen ions through the sheath is found to be the rate controlling step. Under the constraints of the reactor design, a calcium reductant produced electrolytically within the same reactor, has been shown in a hybrid process. Several processes are currently under investigation to use this electrowon calcium for in situ reduction of metal oxides.

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1. Introduction

Molten salt processing provides a unique opportunity to process and produce metals where gas-based pyro-reduction, metallothermic reduction, hydrometallurgical methods or aqueous electrochemical techniques are not feasible due to thermodynamic or kinetic constraints. Industrial applications of molten salts have been well recognized for more than a century. In spite of the use of high temperature corrosive liquids, molten salts offer unique opportunities. The steel and other non-ferrous metal industries make use of molten salts and slags for refining and precision heat treatment. Commercial production of aluminum, magnesium, sodium, potassium, lithium, beryllium, etc. make use of molten salt reduction or electrolysis, since any other method is technoeconomically not feasible. Several other reactive metals, such as lanthanides and actinides make use of molten salt processing for extraction and refining. Additionally, the high temperature carbothermic or metallothermic smelting reduction methods for metal production are associated with the generation of significant quantity of waste as slags. There is a need to develop alternative processes that have low waste or ideally a 'zero-waste' generation. Low temperature multicomponent molten salts [1], as well as room temperature ionic liquids [2] have been developed for materials processing. Molten salts are also finding applications in fuel cell technology. The process described in this paper for producing metals is primarily aimed at complete recycling of process waste. It is also anticipated that the suggested scheme will lower the production cost, since the reductant is electrolytically generated. Significant research effort has been invested in recent times for producing titanium and other refractory metals by molten salt processing. Implementation of this scheme with respect to titanium production is demonstrated [3–5].

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Direct oxide reduction (DOR), molten salt extraction (MSE), and salt scrub (SS) reduction are some of the pyrochemical processes that use molten salt medium in the production and purification of certain actinide metals. Various salt mixtures of chlorides with additions of fluorides are used as the media that generates a considerable amount of contaminated waste that has to be processed before recycling or disposal. Direct oxide reduction produces calcium oxide saturated calcium chloride salts as a contaminated by-product of the calciothermic reduction of actinide oxide. Since calcium chloride is the primary constituent of the salt, these processes typically operate in the temperature range of 850–950 °C.

A number of research studies have been initiated to prepare a waste-minimization strategy [6–9]. This work describes two aspects of the overall metal production program: (a) electrolytic recovery of calcium metal from the DOR process effluent salt comprising calcium oxide and calcium chloride and (b) use of electrolytically recovered calcium metal in situ as a reductant in a hybrid reactor.

There are several advantages of the suggested hybrid process. The process ideally produces 'zero' waste and the metals can be recovered from inexpensive oxides/chlorides without the need for an expensive reductant. Oxygen, carbon dioxide and chlorine gases are the only process effluent which can be easily contained. Operational costs include graphite anode, electric power and recyclable salt only. The process is also amenable to alloy production directly by incorporating co-reduction of respective oxides.

2. Electrochemical principles

The principles are similar to the Hall cell for aluminum production but the aluminum process is essentially restricted by the solubility of alumina in cryolite. A molten flux electrolyte consisting of commercial grade calcium chloride and 10 wt% [20 at.%] calcium oxide, with additions of potassium and sodium chlorides for lowering the melting point, density and viscosity of the salt, has been used in the range of 825–950 °C. The oxide is electrolytically dissociated on a graphite anode and steel cathode:

$$CaO = Ca^{2+} + O^{2-}$$
(1)

 $Ca^{2+} + 2e^- = Ca$ (on cathode) (2)

$$O^{2-} = 1/2O_2 + 2e^-$$
 (on inert anode) (3)

$$C + 2O^{2-} = CO_2 + 4e^-$$
 (on graphite anode) (4)

Calcium has 4–6 at.% solubility in the salt depending on the composition and temperature [10]. Therefore, the deposited calcium metal is initially dissolved in the salt and is subsequently deposited on the cathode. Calcium has a very low density (1.55 g/cm³; melting point 805 °C) and the liquid deposited calcium floats up along the cathode on the salt (approx. density; 2.0 g/cm^3). The dissolved, as well as the deposited calcium metal can be used in situ to reduce another metal oxide:

$$M_x O_v + y Ca = xM + y CaO$$
⁽⁵⁾

However, if the metal exists as a chloride or has been converted to a chloride form, calcium oxide will not be required in the cell. Calcium chloride could be dissociated (NaCl and KCl are more stable than CaCl₂) by a similar scheme as Eqs. (1)–(3), producing chlorine gas on the anode and using calcium according to the following equation:

$$\mathbf{M}_{x}\mathbf{Cl}_{2y} + y\mathbf{Ca} = x\mathbf{M} + y\mathbf{Ca}\mathbf{Cl}_{2} \tag{6}$$

Thus, besides the collected metal, M, the only by-product of the entire process is the anodically generated gas, viz. oxygen, carbon dioxide or chlorine. The other product of calcium oxide (Eq. (5)) or calcium chloride (Eq. (6)) will be further dissociated electrolytically (Eq. (1)), thus forming a closed cycle. The metal, M, could theoretically be any metal, since calcium oxide is one of the most stable oxides and, therefore, calcium can reduce most other metals, including actinide, lanthanides, refractory metals, rare earths and various other reactive and precious metals such as, titanium, lead, silver, tin, bismuth, etc. However, the following restrictions would apply:

- 1. Metal M should be insoluble in the salt.
- 2. Metal M should not alloy with calcium.
- 3. A solid deposit of M will form if its melting point is higher than the cell temperature, e.g. silver, neodymium, silicon, titanium, etc.
- 4. Metal will settle at the bottom if its density is greater than 2 g/cm^3 .
- 5. Liquid metal pool can be deposited for low melting metals, thus the process could be continuous.

The behavior of calcium electrowinning cell and the parameters relating to metal halide and oxide reduction with calcium have been discussed in this work. A schematic hybrid cell design has been developed which will allow both, electrowinning and thermal reduction. The features of this cell have been described. Use of this scheme to produce titanium has been originally developed as OS process [11].

3. Experimental

Fig. 1 shows the schematic diagram of the electrowinning cell used for calcium recovery. The distinctive feature of this cell is the ceramic diaphragm shown around the anode. This sheath is required to prevent the anodic carbon and the gases from mixing with the catholyte and lowering the cell efficiency. It is also required to keep the deposited calcium away from the anodic gases. Table 1 lists the various process parameters used in the experiments.



Fig. 1. Schematic diagram of the cell showing the arrangement for 13 mm diameter anode rod and 50 mm diameter sheath.

Five weight percent of calcium oxide was dissolved in calcium chloride at 900 °C in a magnesia crucible. Magnesia is generally stable if it is not exposed to calcium directly at high temperatures over a prolonged period of time. Initial deposition of calcium is soluble in the salt and the subsequent deposition adheres to the stainless steel cathode near the top of the salt bath due to its low density. A ceramic sheath with known porosity was inserted in the molten salt and the salt was allowed to infiltrate into the sheath. The porous sheath worked as the anolyte compartment. The dc current was applied to the cell and the anodic gas composition was monitored for the evolution of chlorine. The current was interrupted once an appreciable level of chlorine was detected in the anodic gas. The cell was held at a set temperature and oxygen ions were allowed

 Table 1

 Cell operating data calcium electrowinning trials

Electrolyte	CaCl ₂ , 0–5 wt% CaO	
Atmosphere	Argon	
Crucible	MgO	
Operating temperature	825–900 °C	
Current	5–15 A	
Voltage	5–25 V	
Time	Variable	
Anode		
Material	Graphite	
Size (cm)	12.7 mm dia.×305 mm long	
Active area	11.4–26.6 cm ²	
Current density	$2.3-8.8 \text{ kA m}^{-2}$	
Cathode		
Material	Stainless steel	
Size (cm)	273×152 mm	
Active area	0.0173–0.0312 m ²	
Current density	$0.40-1.44 \text{ kA m}^{-2}$	

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 leveled off, current was reapplied and calcium was won. This sequence was continued for three to four times at different temperatures for a given sheath porosity. Data was analyzed to obtain a diffusion coefficient as a function of temperature for a given porosity. Equivalent amount of calcium was dissolved in the catholyte.

4. 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 [4]. However, very few metals lend themselves as electrode materials in a molten chloride salt without corroding severely and, therefore, in this work a novel technique of incorporating a porous ceramic anode-sheath was adopted. The surface area, volume and porosity of the sheath were found to be the critical parameters in controlling the rate of electrowinning. The rates of calcium deposition and oxygen evolution are given by the following Eq. [5]

$$r_{\rm Ca} = 5.2 \times 10^{-6} \times i_{\rm c} C_{\rm area} \tag{7}$$

$$r_{\rm O2} = 2.6 \times 10^{-6} \times i_{\rm a} A_{\rm area} \tag{8}$$

where r_{Ca} and r_{O2} are the rates in moles/s for calcium deposition and oxygen evolution, respectively, i_c and i_a are

the cathodic and anodic current densities and C_{area} and A_{area} are the cathode and anode areas, respectively.

The applied voltage of the cell, $V_{appl.}$ can be represented as

$$V_{\text{appl.}} = E_{\text{O2}} - E_{\text{Ca}} + \eta_{\text{Ca}} + \eta_{\text{O2}} + \text{IR}_{\text{drop}}^{\text{salt}} + \text{IR}_{\text{drop}}^{\text{sheath}}$$
(9)

where $E_{O2} - E_{Ca} = E_o^{O2} - E_o^{Ca} + 0.029 \log Q$ at 950 °C cell temperature and η_{Ca} and η_{O2} are the cathodic and anodic over-potentials, respectively. The IR drops due to electrolyte and ceramic sheath directly influence the cell voltage. For a dissociation reaction with graphite anode (activity of carbon = 1)

$$2CaO + C = 2Ca + CO_2 \tag{10}$$

and at a cell temperature of 950 °C, $E_{o}^{O2} - E_{o}^{Ca} = 1.62$ V and $Q = (a_{Ca} \times p_{CO2}^{1/2} / [Ca^{2+}] \cdot [O^{2-}]).$

The rate of flow of ions through the sheath has a major influence on the cell potential, since it determines the values of IR^{sheath} and Q. The activity of calcium ions is assumed as unity, since both the oxide and chloride electrolyte provide the source for calcium ions. The activity of calcium metal is determined by the solubility of the metal in the salt which is found to be 2–4 wt%, 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. The constitutive constant, Q, depends on the flow of oxygen ions through the sheath and the efficiency of removal of oxygen or carbon dioxide gas from the anode and is a function of time. It was found that the rate of oxygen ion replenishment in the sheath is the rate-controlling step.

A simple model, based on Fick's first law, was applied to calculate the diffusion coefficient of the porous ceramic sheath. Experiments were conducted as a function of temperature. Five weight percent of calcium oxide was used as the starting concentration, $C_{\rm B}$, for electrowinning, which has been assumed constant in the bulk catholyte. The electrolysis was terminated when the concentration of oxide in the anolyte reached a minimum value, $C_{\rm min}$. The minimum level was ascertained by the initiation of chlorine



Fig. 2. Plot of $[C_t - C_{min}]/C_f$ versus time. Slope of the line is used to calculate diffusion coefficient *D* at different temperatures.

Table 2Diffusion coefficient of ceramic sheath [7]

Parameter	825 °C	875 °C
Anolyte volume (cm ³)	98.54	113.32
Sheath surface area (cm ²)	104.19	117.49
Porosity (%)	30	30
Sheath thickness (cm)	0.3302	0.3302
Bulk conc. (wt%) CaO	5.0	5.0
Min. conc. (wt%) CaO	0.12	0.20
Diff. coeff. (cm ² /s)	8.12×10^{-6}	11.7×10^{-6}

evolution at the anode. Once the current was interrupted, the oxide concentration, C_t , was monitored as a function of time till the rate of 'back-fill' was too slow and the concentration driving force diminished. An average compositional driving force, C_f , between a small time interval, t, was used to calculate an approximate diffusion coefficient, D_{eng} . According to Fick's first law:

$$D_{\rm eng} = [C_t - C_{\rm min}] / [C_{\rm B} - 1/2(C_t + C_{\rm min})] [V\delta/At]$$
(11)

where $C_f = [(C_t + C_{min})/2 - C_B]$, *V* is the volume of molten anolyte, *A* is the surface area of the sheath, and δ is the thickness of the sheath. Fig. 2 shows a plot of $[C_t - C_{min}]/C_f$ versus time and the slope of the line is used to calculate diffusion coefficient *D* at different temperatures. Table 2 shows the values for *V*, *A*, δ , temperature, *C*_B, *C*_{min} and the diffusion coefficient. 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. Table 2 shows that the diffusion coefficients are typical for ions in molten salts. Since one has to wait for oxygen transport, the transport through the sheath is the rate controlling process. The sheath size, geometry and porosity must be optimized to achieve a calcium winning electrolytic cell.

5. Hybrid process

The technique applied for calcium deposition has been optimized as a combination of two steps; (STEP A) electrowinning to a desired low level of oxygen ion concentration within the anolyte and (STEP B) holding for a known length of time for oxygen ion diffusion through the sheath. The technology for calcium oxide dissociation and recovery of calcium has thus been developed. The reduction of lead, tin, bismuth and silver compounds by calcium in a calcium chloride salt medium has also been investigated as a preliminary evaluation of the concept. It has been stated that the CaO-CaCl₂ salt mixture is generated as a result of the direct oxide reduction of reactive metals. In the present investigation, this reactive metal oxide is also a radioactive metal. Therefore, lead oxide, tin oxide, bismuth chloride and silver chloride were used to surrogate for the radionuclide due to their



Fig. 3. Schematic diagram of a hybrid reactor for electrowinning and metal oxide reduction.

similarities of certain chemical and physical behavior. These metals were not chosen on the basis of their reactivity or as potential metals for calciothermic reduction. However, investigations have been carried out to produce several other metals, such as titanium, tantalum, niobium, neodymium, etc. by other researchers [12]. The hybrid process is a combination that essentially addresses the issue of utilization of cathodically deposited calcium as an in situ reductant for another metal compound. Fig. 3 shows a schematic reactor design that was used to increase the calcium deposition rate by increasing the sheath diffusivity and the anolyte volume. For the given reactor design, a calcium winning rate of 140 g/h was estimated at 100% current efficiency for electrowinning. The winning rate is estimated using the following equation based on oxygen ion diffusion into the anolyte:

$$R_{\text{max}} = [1.2 \times 10^{-6} \exp(-6.0 \times 10^4 / \text{RT})](f\phi/q)[(C_{\text{B}} - C_{\text{min}})/\delta](2\pi r l + \pi r^2)$$
(12)

This rate of calcium electrowinning is based on the availability of maximum oxygen into the anolyte via sheath diffusion. The modified reactor outer dimensions were maintained for use in the same furnace chamber. The parameters used for the modified hybrid reactor (Fig. 3) are listed in Table 3 in comparison to the original reactor (Fig. 1). These parameters are used in determining the rate using Eq. (12). The reactor, shown in Fig. 3, allows the two processes of electrowinning and calciothermic reduction to be combined into one. The process was identical to the scheme used for calcium electrowinning except that metal chloride/oxide powders were added through a ceramic tube into the catholyte chamber and the reduced metallic button was collected after the salt was cooled and separated from the metal. The reduction of metal compound can be accomplished by following two different schemes:

(A) $M_x O_y$ soluble in CaCl₂–CaO salt system. In this case, the reactive metal oxide will be introduced into the reactor

through the charge hopper, during the period (STEP B) where the current supply is turned off and oxygen ions are diffusing through the sheath. Calcium reduction will occur during this period and metal, M will settle in the reactor bottom.

(B) M_xO_y insoluble in CaCl₂–CaO salt system. In this case, the metal oxide can be introduced at any stage (STEP A and/or STEP B) through the hopper in the catholyte compartment depending on the level of calcium dissolved in the salt. The metal, M will also settle in the reactor bottom. It is important to introduce the metal oxides after a delay, since sufficient calcium must exist in the system for the reaction with oxides.

The process could be conducted under a cover of nitrogen gas in the electrowinning and reduction chamber, since the metals are not exposed to high temperature atmosphere and are always contained within the salt phase. Fig. 4 shows two such possible designs that have been adopted to produce titanium metal (OS Process) by electrolytically winning calcium and using it simultaneously to reduce titanium oxide [11]. In Fig. 4a, the calcium chloride salt with electrodeposited calcium is transferred into another reactor where the reduction of titania takes place. In the design shown in Fig. 4b, titania is

Table 3			
Cell parameters	for the	hybrid cel	1

Cell parameters	Calcium win- ning cell (Fig. 1)	Hybrid cell (Fig. 3)
Sheath radius, $r(m)$	2.25×10^{-2}	1.5×10^{-1}
Sheath height, l (m)	0.10	0.20
Sheath thickness, δ (m)	2.9×10^{-3}	1.0×10^{-3}
Sheath porosity, ϕ	0.32	0.40
Open porosity fraction, f	0.85	0.90
Tortuosity factor, q	1.5	1.5
Cell temperature, $T(K)$	1123	1273
Diffusion coefficient, D_{O2-} (m ² s ⁻¹)	2.0×10^{-9}	4.2×10^{-9}
Bulk concentration, $C_{\rm B}$ (kg mole m ⁻³)	1.85	3.70
Min. anolyte conc., C_{\min} (kg mole m ⁻³)	0.07	0.07



Fig. 4. Two reactor designs describing the OS Process for titanium production; (a) separate chamber for titanium reduction and (b) single chamber for electrowinning and reduction [11].

introduced in the same chamber and the reduction id affected by the calcium deposited on the iron cathode.

6. Conclusion

Calcium can be electrolytically produced by dissociating calcium oxide in a molten calcium chloride electrolyte. A porous ceramic diaphragm around the anode is essential for separating the anolyte and catholyte to be able to cathodically deposit calcium. The cell temperature, fluidity of salt and porosity of the sheath are critical in recovering calcium. Ionic diffusion through the sheath is the rate-controlling step. A diffusion coefficient in the range of 10^{-5} to 10^{-6} cm²/s is obtained for a 30% porous alumina sheath for cell temperatures between 800 and 900°C.

A hybrid process is investigated consisting of electrowinning calcium from calcium oxide and in situ utilization of calcium as a reductant within the same reactor. Silver, tin, lead and bismuth can be produced by pyrochemical reduction of their respective chlorides and/or oxides with calcium in a calcium chloride medium. These metals were produced as a surrogate for a certain radioactive metal.

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