

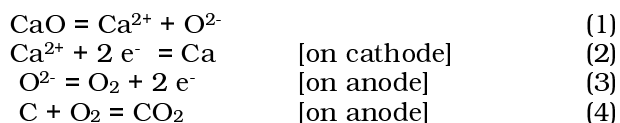
## PRODUCTION OF REACTIVE METALS BY MOLTEN SALT PROCESSING

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Molten Salt electrolytic processes offer unique opportunities to extract and refine reactive metals where gaseous or metallothermic reduction, hydrometallurgical extraction and aqueous electrolytic methods are thermodynamically constrained. Production of aluminum and magnesium by molten salt electrolysis are well known commercial processes. Several other reactive metals, such as lanthanides and actinides, as well as beryllium and calcium, make use of molten salt processing for extraction and refining.

This paper describes the science of molten salt electrochemistry for electrowinning and electrorefining. In addition, recovery of metals from waste process salts by molten salt reduction as well as oxidation have been discussed. Material issues in design of molten salt reactors have been included. Case studies presented in this paper include (i) recovery of calcium metal from molten salt waste forms and (ii) separation of cerium oxide by oxygen sparging of molten salts. Experimental data have been included to justify the suitability as well as limitations of these specific processes.

The principles of calcium electrowinning 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 ten wt. pct. [20 at. pct.] calcium oxide, with additions of potassium and sodium chlorides for lowering the melting point, density and viscosity of the salt, has been used at 825-900°C temperatures. The oxide is electrolytically dissociated on a graphite anode and steel cathode:



Calcium has 4-6 at. pct. solubility in the salt depending on the composition and temperature. 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/cc; melting point 805 °C] and the liquid deposited calcium floats up along the cathode on the salt [approx. density; 2.0 g/cc]. The dissolved, as well as the deposited calcium metal can be used insitu to reduce another metal oxide:



An ion-conducting ceramic porous barrier around the graphite anode is necessary in molten salt electrolytic cells where reactive metals, such as calcium, are produced to minimize the possibility of back reactions, as

shown in Figure 1. The maximum calcium electrowinning rate in the experimental cylindrical cell is limited by the rate of oxygen ion diffusion through the porous cell barrier, assuming that oxygen diffusion through the anolyte and the discharge reaction on the anode are rapid. The work suggests a novel cell design and its parameters that must be used to win calcium at an acceptable rate of approx. 140 g/h from a feed-stock of 10 wt. pct. CaO in CaCl<sub>2</sub>.

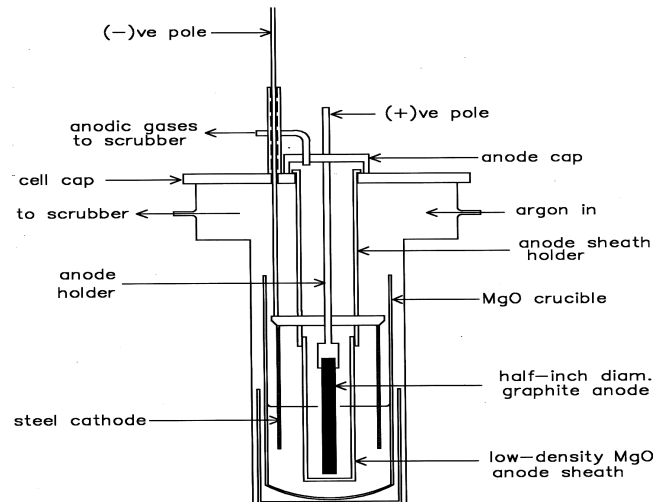


Figure 1: Schematic Diagram of the Calcium Electrowinning Cell

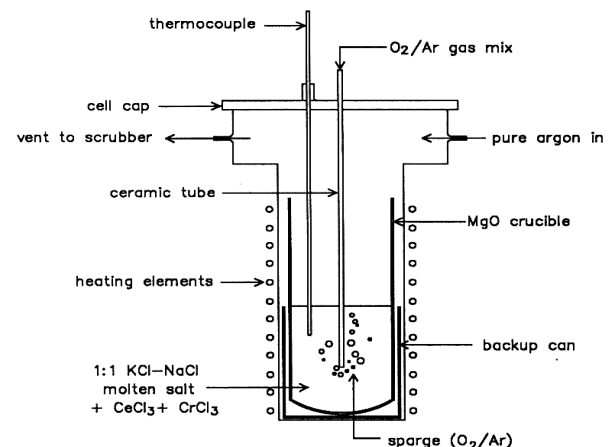


Figure 2: Schematic Diagram of the Oxygen Sparging Reactor for Metal Recovery

The work on oxygen sparging was conducted to convert the soluble chlorides in molten salts into insoluble oxides, thereby recovering reactive metals. Cerium chloride was used as a surrogate for radioactive metal chloride and chromium chloride was added as a RCRA constituent. Oxygen sparging performed in the reactor [Figure 2] showed that chromium chloride conversion can be achieved with over 99 percent efficiency. Cerium chloride conversion is 95 percent efficient but its recovery is limited to 80 percent, as the balance cerium metal in the form of converted oxide as well as unconverted chloride is mixed with the residual clean salt. It was determined that the flow rate of oxygen gas was critical to CeCl<sub>3</sub> conversion. The process was optimized at 700°C temperature in a 40% Oxygen-Argon gas mix at a flow rate of 1.25 l/min. The sparging is also sensitive to the location of gas release.