

NEW OPPORTUNITIES FOR WASTE TREATMENT BY  
ELECTROCHEMICAL PROCESSING IN MOLTEN SALTS

Donald R. Sadoway

Department of Materials Science and Engineering  
Massachusetts Institute of Technology  
Cambridge, Massachusetts 02139-4307

Abstract

Molten salt electrolysis is a proven technology for the extraction of metals -- all the world's primary aluminum is produced in this manner. The unique properties of molten salts make them excellent media in which to treat a variety of forms of waste. Of special note in this regard is electrolysis in molten oxides, a concept put forward by the author, initially as a "clean technology" for producing primary metal while generating pure oxygen gas as the main by-product. However, in the context of waste treatment, electrolysis in molten oxides is a process offering the prospect of changing the valence of dissolved heavy metals while making pure oxygen gas as the main by-product. Laboratory tests conducted at a temperature of 1550 °C on chromate sludge dissolved in an electrolyte composed of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{CaO}$ , and  $\text{MgO}$  have confirmed oxygen evolution on a carbon-free anode.

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## Introduction

Molten salt electrolysis is the electrolytic decomposition of a compound dissolved in an ionic melt. The prime example of this process can be found in the production of aluminum. The compound, alumina ( $\text{Al}_2\text{O}_3$ ) derived from the mineral bauxite, is dissolved in an ionic melt comprising a multicomponent solution of cryolite ( $\text{Na}_3\text{AlF}_6$ ), aluminum fluoride ( $\text{AlF}_3$ ), and calcium fluoride ( $\text{CaF}_2$ ). The products of electrolysis are molten aluminum and carbon dioxide, the latter due to the attendant consumption of the carbon anode. Electrolysis is conducted in a reactor called an electrochemical cell. Primary aluminum is produced in a reactor known as the Hall cell.<sup>1</sup> Alternatively, the compound undergoing electrolytic decomposition can be derived from waste. Processing in molten salts, with their capacity to dissolve materials to very high concentrations as compared with that of aqueous solutions, can be rather advantageous. High solubilities lead to high limiting current densities, and this, in turn, results in high productivities. For a primer on molten salt electrolysis and a review of the basic literature in the field of molten salts the reader is directed to an earlier publication of the author (1).

## Processing of Waste by Molten Salt Electrolysis

Exploratory research has been conducted in this laboratory to assess the viability of processing chromate sludge by electrolysis in melts composed of oxides as distinct from the melts traditionally employed in industrial molten salt electrochemistry, namely chlorides and fluorides. The work has been described in a recent publication, portions of which are reproduced here for the convenience of the reader (2). Secondary residue or waste mud produced in the course of chromate chemical production is the focus of attention in this work. The goal is to reduce the water soluble hexavalent chromium either to insoluble trivalent chromium or to chromium metal. The use of an oxide melt for the electrolyte establishes the conditions for the production of oxygen gas as the anodic reaction. This is very attractive from an environmental standpoint where the cost of treating byproducts can be a deciding factor in determining the profitability of a process.

## Treatment of Chromate Sludge

Chromate residue, like much of the solid industrial waste in this country, is in the form of oxidized metal, some of which is water soluble and thus poses a threat to the environment. Treating this stuff to make it chemically inert is an enormous task. Processes doing so must not only be energy efficient but also have acceptable productivity, i.e., space/time yields. One practice is to leach out the hexavalent chromium for subsequent electrochemical treatment. This requires vast quantities of water, and one cannot be certain of the extraction efficiency of the leaching operation. Molten salt electrolysis in a fused oxide electrolyte can be viewed as a potential alternative to the aqueous chemistry cited here. The high-temperature approach not only may reduce hexavalent chromium but also may recover the iron and chromium metal contents of the

<sup>1</sup> The extraction of aluminum by the electrolysis of alumina was invented in 1886 independently by Charles Martin Hall in the U.S. and by Paul Héroult in France. The reactor for this process is known as the Hall cell in North America and as the Hall-Héroult cell in Europe.

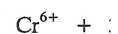
waste material. In special cost of remediation.

Direct electrolysis carbon anodes (3). What This is critical to the success a methodology developed nonconsumable anode for a systems view of the reactions that occur between electrolyte and cell product metal recovery in the high free direct electrolysis. Technology.

These are the keys to treatment of chromate high level of electronic chromate melts as a function technical viability of the design of the industrial electrolysis function as an oxygen-evolving what are the overvoltages:

Tests have begun sludge (2). What has been and will sustain faradaic production in response to the passage held at this temperature is important, as many molten ferrites and chromites, a processing is impossible. composition one can dissolve

Possibly, the cathode to lower valent forms, as



More work is necessary chronoamperometry and this author recommends direct electrolysis in molten Clearly, from a commercial as metal. Perhaps by current density and temperature,

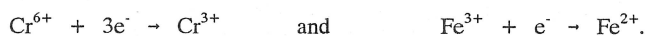
waste material. In special circumstances the value of the metal so produced may even offset the cost of remediation.

Direct electrolysis in molten oxides has been tried in the past but relied on the use of carbon anodes (3). What is new and unique in the present concept is the absence of carbon (4). This is critical to the successful implementation of the concept. Materials selection derives from a methodology developed by the author in connection with the problem of finding a carbon-free nonconsumable anode for use in aluminum electrolysis cells (5). The methodology is based upon a systems view of the process and therefore takes into full consideration the types of chemical reactions that occur between the key elements of the cell (cathode, anode, sidewall) and the electrolyte and cell products. A fresh look at the use of molten oxides as electrolytic media for metal recovery in the light of the above cited methodology gave birth to the concept of carbon-free direct electrolysis. Treatment of waste represents what should be an adaptation of the same technology.

These are the key issues in the relevant high temperature physical chemistry as they apply to treatment of chromate residue. Are chromate bearing melts ionic or is there an unacceptably high level of electronic conduction, i.e., what is the electrical conductivity of multicomponent chromate melts as a function of temperature and composition? The answer helps assess the technical viability of the concept (including the energy consumption) and leads directly to the design of the industrial electrolyte. Do the selection criteria call out a suitable material that will function as an oxygen-evolving anode, i.e., in the candidate electrolyte what is the emf series and what are the overvoltages associated with various suspected anodic processes?

Tests have begun to examine the technical feasibility of direct electrolysis of chromate sludge (2). What has been demonstrated thus far is that it is possible to design a melt that is ionic and will sustain faradaic processes as evidenced by the presence of oxygen which was detected only in response to the passage of electric current. When the melt was simply heated to 1550°C and held at this temperature for several hours, no oxygen was detected. This observation is extremely important, as many molten oxides containing substantial amounts of transition-metal oxide, e.g., ferrites and chromites, are known to be electronic conductors. In such melts, electrochemical processing is impossible. This experiment then demonstrates that by judicious choice of melt composition one can dissolve transition-metal oxides and retain ionicity.

Possibly, the cathodic reaction was the reduction of iron and chromium from higher to lower valent forms, as for example,



More work is necessary to reveal the true nature of the cathodic reaction. Stepped potential chronoamperometry and electrochemical impedance spectroscopy are the electrokinetic techniques this author recommends for such a study. If the reactions proposed above in fact do occur, then direct electrolysis in molten oxides is a means to immobilize the toxic hexavalent chromium ion. Clearly, from a commercial standpoint it would be desirable to be able to extract the chromium as metal. Perhaps by changes in electrolyte chemistry and processing conditions, e.g., current density and temperature, this goal can be reached.

### References

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