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Methods and Materials

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FOREWORD

In the perspective of the United States, this International Symposium on Actinides occurs as the goals of actinide processing are changing rapidly. For the past fifty years the majority of actinide research was done to support processing for the nuclear weapons program. Important to that research was the development of purification and recovery processes with optimal actinide usage and throughput. Now actinide process development emphasizes waste minimization, waste treatment and the ultimate disposal and/or storage of actinides. These same considerations also are integral to the actinide process development done to support the nuclear reactor programs.

The papers presented in this symposium demonstrate this transition in actinide research. Material development efforts reported in this symposium are examples of research efforts focused on the needs to minimize the waste associated with actinide processing. In tandem with the waste minimization efforts, is research into characterizing and treating any wastes which are generated in the actinide processing. Environmental regulations require a better understanding of the wastes and the development of efficient, yet permissible, waste treatment processes. Several papers in this symposium reflect these waste considerations. Finally the ultimate disposal and/or storage of actinide must be resolved. This symposium includes reports in this area.

This symposium also considers the continued research efforts in understanding the fundamental properties of elemental actinides and of actinide compounds. Some basic research is a necessary component to the successful development of processes which meet the new targets of waste minimization, waste treatment, and actinide disposal and/or storage.

In summary, this symposium presents deliberations on the new goals for actinide processing. These new directions are found not only in the United States but throughout the international actinide research community as environmental concerns become a critical component in the assessment of which proposed actinide processes will be implemented.

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CONTINUOUS OXIDATION/

REDUCTION SYSTEM (CORS)

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Abstract

A Continuous Oxidation-Reduction System (CORS) is being developed at Lawrence Livermore National Laboratory (LLNL). The CORS combines reduction and oxidation reactions within a single reactor. The materials being processed are fed continuously while the products are continuously removed. The system is being developed for the continuous oxidation and/or reduction of reactive metals, salts, oxides, and other compounds. Recent feasibility tests reducing cerium oxide were successful. Two applications of this system currently being examined are: actinide oxide reduction and the separation of radionuclides from wastes and residues. In comparison to traditional processes such as fluorination/bomb reduction and Direct Oxide Reduction (DOR), CORS reduces operator radiation exposure, waste, processing time and equipment requirements. A patent has been filed for this process.

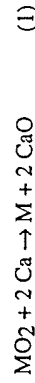
Introduction

Actinide and lanthanide metals are produced by pyrochemical (high temperature) reduction of oxides, chlorides or fluorides in a molten salt. These reductions are frequently performed in batch processes which are characterized by manual operations (e.g., equipment set-up, reagent loading and product unloading); low throughput due to long heat-up and cool-down times; and significant production of wastes and residues (e.g., spent salts and expendable crucibles). In the calcium reduction of plutonium, cerium, and neodymium oxides; large amounts of waste salt are produced⁽¹⁾. The calcium oxide by-product is solvated into a calcium chloride flux in order to perform the reduction at moderate temperatures (< 1000 °C). Conversion of the calcium oxide in the waste salt to calcium chloride by chlorine sparging has been used^(2,3) to regenerate the salt flux and significantly decrease the amount of salt waste.

A Continuous Oxidation-Reduction System (CORS) is being developed at Lawrence Livermore National Laboratory (LLNL). The CORS contains a reduction zone for converting actinide or lanthanide oxides to metal and an oxidation zone for converting the product calcium oxide to calcium chloride. The system can also be used as a single zone reactor for various reduction or oxidation reactions. Through continuous operations, significant reductions in operational and capital costs can be achieved. Continuous processes are readily adaptable to automation thus eliminating manual operations. In addition, the generation of waste ceramic can be decreased by the elimination of expendable crucibles. For actinide metals, a continuous operation can also significantly decrease operator radiation exposure and radioactivity contaminated waste.

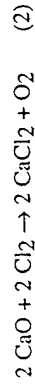
Process Description

The production of several reactive metals from their oxides is performed in a molten calcium chloride salt using calcium metal as the reductant. The metal oxide (MO₂) reacts with calcium (Ca) to form metal (M) and calcium oxide (CaO) by the following reaction:



Calcium oxide is nearly the most stable metal oxide with a free energy of -531 kJ/gram atom oxygen at 1000 °C. Therefore calcium will reduce almost all other metal oxides. Calcium oxide, however, has a very high melting point (2572 °C) making recovery of the metal product difficult without a fluxing agent. Calcium chloride (CaCl₂) has been found to be a good flux for the CaO with a solubility of 18.5 mole % CaO at 835 °C. Fluxing the CaO into molten CaCl₂ allows the higher density molten product metal to separate from the molten salt and form a button at the bottom of the reaction crucible.

To minimize process waste the salt can be "regenerated" by sparging with chlorine gas (Cl₂) releasing oxygen (O₂). Due to the inherent thermodynamic stability of calcium chloride compared to calcium oxide the following reaction proceeds nearly quantitatively at 900 °C.



This reaction converts the calcium oxide product to calcium chloride thus allowing the salt flux to be reused. Excess calcium chloride is periodically removed and discarded. Current production and development systems perform the reduction and salt regeneration in batch mode.

The objective of the CORS is to perform continuous oxidation and reduction in a single reactor. The reactor (see Figure 1) consists of two zones: a reducing zone and an oxidizing zone. In the reducing zone, the metal oxide reacts with calcium metal in the molten calcium chloride salt. The calcium oxide by-product dissolves into the salt and the metal forms droplets that fall to the bottom of the reactor due to density differences.

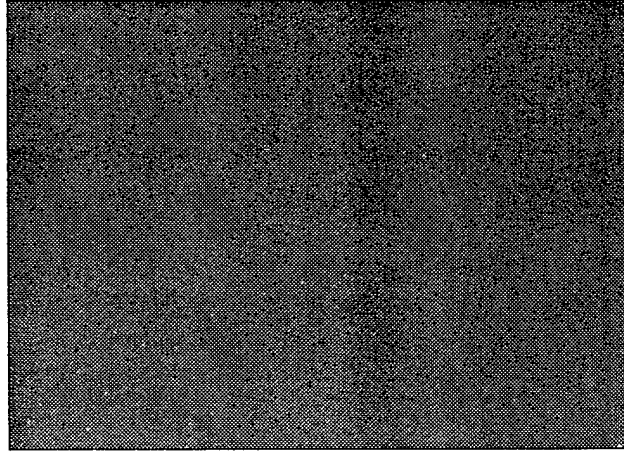


Figure 1. Conceptual Drawing of CORS Reactor

The metal collects at the bottom of the reactor and is removed continuously by overflowing the metal weir. In the oxidizing zone, the by-product CaO is converted to CaCl_2 by sparging the salt with chlorine gas. Excess CaCl_2 is removed from the reactor by a salt overflow. A block diagram of the system is given in Figure 2.

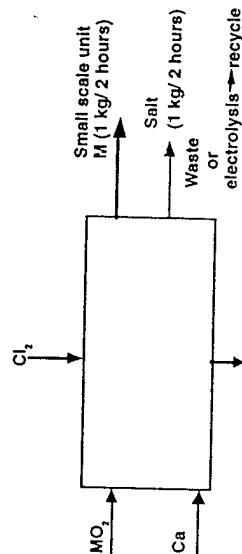


Figure 2. CORS Metal Oxide Reduction Flowsheet

Because each zone is operating under different chemical and physical conditions, different materials of construction are used. The reducing environment containment is a metal, such as tantalum (Ta). A metal is used to minimize attack by the highly reducing calcium metal. The oxidizing zone is enclosed by a ceramic, such as alumina (Al_2O_3) or magnesia (MgO). These ceramic materials are resistant to the highly oxidizing chlorine and oxygen gases.

Applications

There are two types of applications for the CORS that are currently being investigated. They are oxide reduction and residue recovery/waste reduction. The candidate oxides for reduction are uranium (UO_2), plutonium (PuO_2), neodymium (Nd_2O_3), and oxide nuclear fuels. The candidate residues and wastes for recovery are: residue salt from plutonium and uranium processing and waste calcine from the Idaho National Engineering Laboratory (INEL) Idaho Chemical Processing Plant (ICPP).

Uranium oxide residues are generated in the fabrication of nuclear weapons components. The current process used to convert this oxide back to metal is fluorination and metallothermic (bomb) reduction. The CORS is being examined to replace this process thus eliminating multiple steps and the use of hydrogen fluoride (HF) gas.

General Motors is reducing neodymium oxide in the patented NEOCHEM process (4). This process is similar to methods used in the DOR process, used to reduce plutonium oxide. The CORS could be used to increase throughput and eliminate multiple operations.

The Rocky Flats Plant (RFP) has a large quantity of spent salt that requires disposal.(5) These salts contain actinides and reactive metals. Before disposal, the reactive metals need to be passivated. The current technology sparges air into a batch of salt to oxidize the reactive metals. It is estimated that it will require 9 years to complete. Using the CORS technology, it is expected to take about 2.5 years.

Feasibility testing using the CORS with INEL ICPP calcine is ongoing at LLNL. The INEL ICPP calcine is produced from the calcination of liquid waste from the dissolution of nuclear fuel assemblies.(6,7) The calcine contains less than 1 wt% long-lived radionuclides. Without reprocessing, the calcine would require 40,000 cubic meters in a costly geological disposal site such as Yucca Mountain. If the long-lived radionuclides can be separated from the remaining chemicals, the amount of long-lived waste could be reduced by 99%. A flowsheet (Figure 3) based on the CORS has been developed that achieves a 98% volume reduction and a 90% mass reduction (4260 metric tons to 426 metric tons) in the long-lived radionuclide stream.

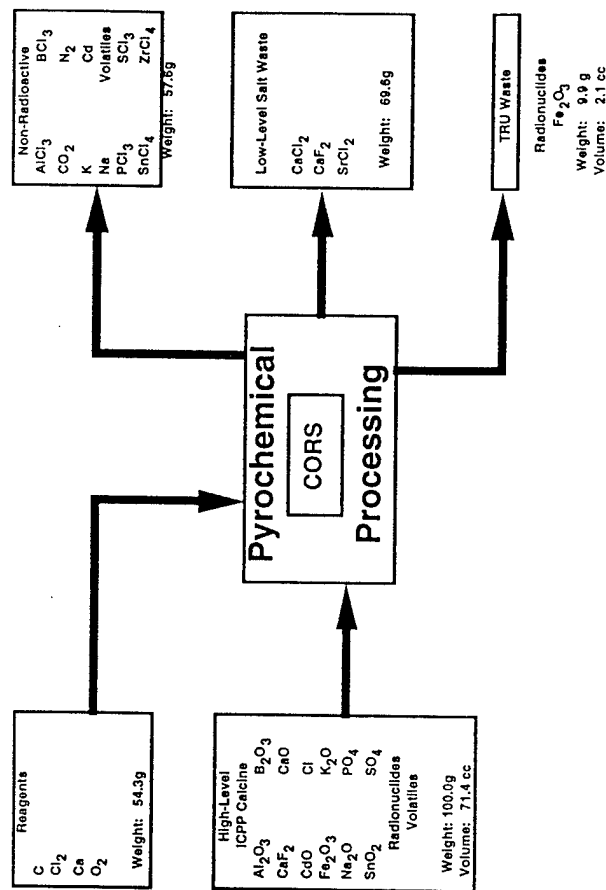


Figure 3. CORS Processing flowsheet for INEL ICPP Calcine

Experimental Work

A diagram of the experimental equipment is shown in Figure 4. This design is different from Figure 1, in respect that the oxidizing (chlorinating) zone is in the middle and the reducing zone is around the outside. The oxidizing zone, that contains the chlorine gas, is constructed of magnesia (MgO). The reducing zone consisting of the reactor shell, salt overflow, metal weir, and stirrer, is constructed of tantalum. This design fits within existing furnaces at LLNL and is being used for feasibility demonstrations.

In initial feasibility demonstrations, cerium oxide was reduced to cerium metal. The reactor was operated at 900-1000 °C in an argon glovebox at slightly above atmospheric pressure (2" of water). The dry argon glovebox eliminates parasitic reactions between atmospheric moisture and oxygen and the reactive metals (calcium and cerium) and hygroscopic salts. The reactor components were first tested independently with the calcium reduction, salt regeneration, and product removal operations. The cerium oxide and calcium metal were feed at the rate to generate about 300 g of cerium per hour. This is equivalent to a generation rate of 500 g of plutonium per hour. The chlorine gas flow was 2 standard liters per minute.

Following the demonstration of separate operations, the reactor was tested as an integrated unit. Initially there was some operational difficulty due to the molten salt and metal freezing on the heat shield. The heat shield was removed and the system was operated successfully. The loaded system has been held at temperature for over 500 hours. The feed addition and salt regeneration have operated for about 40 hours. There has been no evidence of corrosion on the Ta reactor. The MgO did have some corrosion around the tip of the chlorine sparge tube. Other materials such as yttria (Y_2O_3) are being examined for the oxidation zone.

Conclusion and Future Plans

Initial feasibility studies have shown that a dual zone reactor can be used to continuously reduce cerium oxide to metal with minimal salt waste. The system will be tested in the future with other reactive metals (e.g., uranium, gadolinium, neodymium). Alternate materials of construction will be evaluated (e.g., tantalum carbide and yttria). Feasibility studies have been initiated to examine the CORS for processing INEL ICPP calcine.

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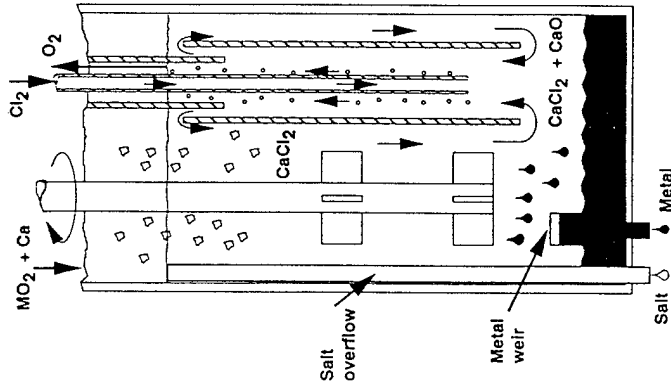


Figure 4. Conceptual Diagram of Experimental CORS Reactor

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PYROCHEMICAL SALT SCRUB

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Abstract

A pyrochemical salt scrub process for calcium chloride based salts, that eliminates the waste generated during aqueous processing and the associated chloride corrosion problem, is being developed and tested at Lawrence Livermore National Laboratory. In the scrub process, calcium metal is used to reduce the actinide chlorides present in residue pyrochemical salts to a metal product, called a metal button. The metal button can be stored, converted to an oxide for storage, recycled, or further refined using aqueous processing to separate the plutonium from the americium, if plutonium recovery is required. It has been determined that a calcium titration of molten salt extraction and electrorefining residue salts can be used to determine reaction completion and to prevent the addition of excess calcium to the process. An automated calcium feeder and associated control system have been designed and built to monitor the salt scrub process and to determine when calcium metal should be fed.