Conf-940602--21

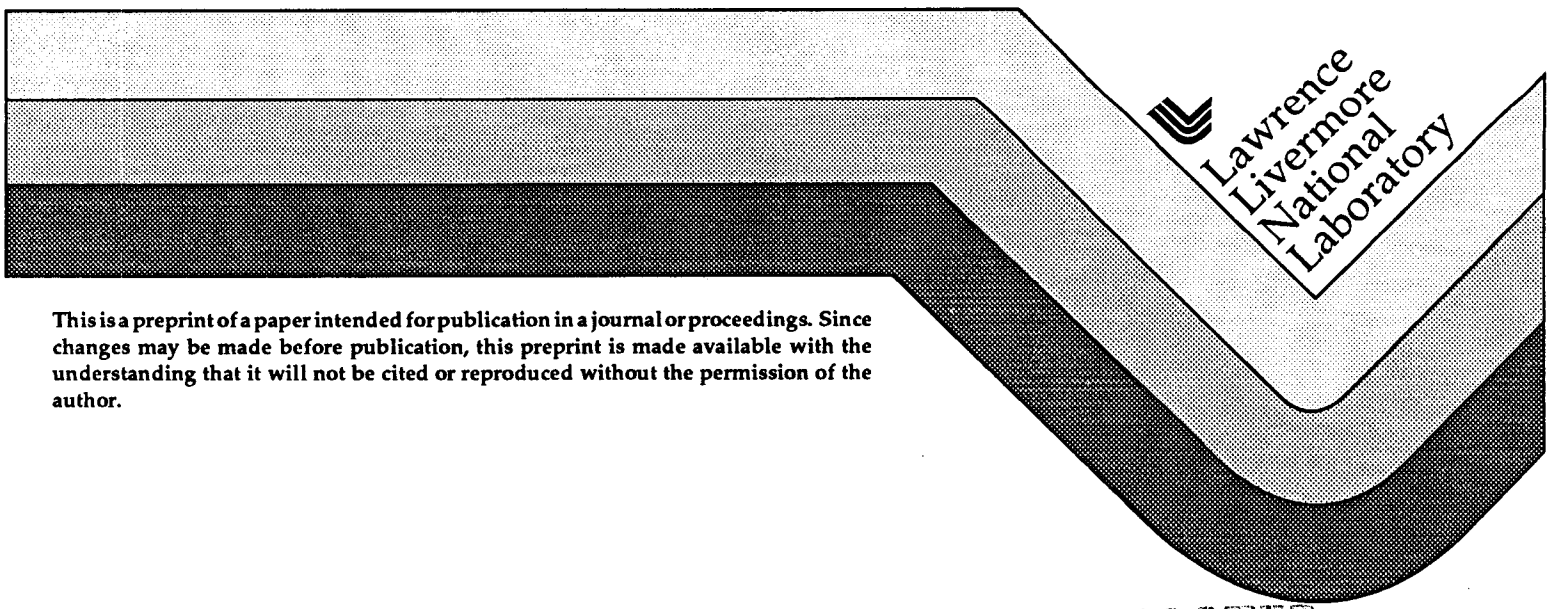
UCRL-JC-116202
PREPRINT

Advanced Pyrochemical Technologies for Minimizing Nuclear Waste

M. C. Bronson
K. E. Dodson
D. C. Riley

This paper was prepared for submittal to the
American Nuclear Society 11th Topical Meeting
on the Technology of Fusion Energy
New Orleans, Louisiana
June 19-23, 1994

June 1, 1994



DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Advanced Pyrochemical Technologies for Minimizing Nuclear Waste*

Mark C. Bronson
Karen E. Dodson
David C. Riley
Lawrence Livermore National Laboratory
Livermore, California 94550

Introduction

The Department of Energy (DOE) is seeking to reduce the size of the current nuclear weapons complex and consequently minimize operating costs. To meet this DOE objective, the national laboratories have been asked to develop advanced technologies that take uranium and plutonium, from retired weapons and prepare it for new weapons, long-term storage, and/or final disposition. Current pyrochemical processes generate residue salts and ceramic wastes that require aqueous processing to remove and recover the actinides. However, the aqueous treatment of these residues generates an estimated 100 liters of acidic transuranic (TRU) waste per kilogram of plutonium in the residue. Lawrence Livermore National Laboratory (LLNL) is developing pyrochemical techniques to eliminate, minimize, or more efficiently treat these residue streams. This paper will present technologies being developed at LLNL on advanced materials for actinide containment, reactors that minimize residues, and pyrochemical processes that remove actinides from waste salts.

Materials for actinide containment

Ceramic (Al_2O_3 and MgO) crucibles are currently used in many of the pyrochemical operations for processing uranium and plutonium. After each use the ceramic crucibles are broken to remove product and processing salt, thus producing a ceramic waste and adding ceramic shards to residue salts. In addition, process cycle times are relatively long in order to minimize thermal shock. These limitations can be overcome if crucibles were constructed of non-brittle and reusable materials that are not wetted by molten actinides. Refractory metals such as tungsten and tantalum are used for pyrochemical plutonium processing but are susceptible to wetting and intergranular attack.

A tantalum-carbon alloy has been developed that is not wetted and is resistant to intergranular attack by plutonium. This alloy is formed by gas-phase carburization of the tantalum followed by a high temperature annealing step. The carburization step forms a carbide coating. High temperature annealing diffuses carbon into the bulk of the material. Carbon content of the material is about 0.02 weight percent. The interior microstructure consists of continuous grain boundary carbides and dispersed carbide particles within the grains.

Several tantalum-carbon components have been successfully tested in plutonium pyrochemical processes. A carbide coated stirrer has been used repeatedly with no signs of deterioration and is still in use, whereas untreated tantalum metal stirrers previously failed at the welds after only a few cycles. A tantalum-carbon alloy crucible has shown promising results in small scale testing with molten plutonium and molten salt. The plutonium button and salt were easily removed from the crucible after repeated melting and cooling cycles.

Advanced pyrochemical reactors

Pyrochemical reactors for plutonium and uranium processing are typically vertical tube furnaces that incorporate ceramic crucibles for molten metal and salt containment. Operations that use these simple furnaces have long cycle times and generate ceramic wastes. Tilt-pour and bottom pour reactors have been developed for actinide processing. These reactors provide a means to remove the molten product metal and salts from the reaction crucible thus allowing crucible recycle and short cycle times. Extensive testing of these reactors has been performed with an actinide surrogate (cerium metal). A Continuous Oxidation/Reduction Systems (CORS) reactor is being developed for uranium oxide reduction. This reactor consists of two zones: a reducing zone and an oxidizing zone. In the reducing zone actinide oxides are reacted with calcium metal at 850 to 950 C to produce calcium oxide and actinide metal(1). The calcium oxide dissolves in a calcium chloride solvent salt. The actinide metal settles out by density difference and collects at the bottom of the CORS reactor where it is continuously removed. In the oxidizing zone, the by-product CaO is converted to $CaCl_2$ by chlorine gas sparging.

Excess $CaCl_2$ is removed from the reactor by a salt overflow. In a recent feasibility demonstration using a laboratory scale reactor, cerium oxide was reduced to cerium metal. The reactor produced 300 g of cerium metal per hour with a chlorine gas flow of 2 standard liters per minute. The loaded system has been held at temperature for over 500 hours, and the feed addition and salt regeneration have operated for about 40 hours.

Treatment of waste salts

Residue salts containing actinides are produced during pyrochemical processes. Residue salt from uranium fluoride reduction contains several percent of the feed uranium, and salt from pyrochemical plutonium processing may contain substantial amounts of plutonium and americium. The pyrochemical salt scrub process recovers the residual actinides, produces a salt that can be recycled, and eliminates excessive waste production associated with aqueous processing of the salts. In addition the need to construct aqueous systems to treat the salt residues is eliminated. For a proposed future plutonium plant this would result in an estimated savings of about 6% in construction costs.

An automated salt scrub system is being developed that titrates the actinides with calcium metal. Heat is released with each addition of calcium due to the exothermic reaction between calcium and the actinide halides to produce actinide metal and calcium halide salt. The extent of the reaction is monitored by the thermal response of the system due to calcium additions. Recently this automated salt scrub system was demonstrated with residue salts containing plutonium and americium. The salts were successfully scrubbed of actinides to the extend that they met TRU waste discard limits or could be recycled back through pyrochemical processes.

References

1. Melvin S. Coops, James B. Knighton, and Lawrence J. Mullins, "Pyrochemical Processing of Plutonium," ACS Symposium Series. No 216 Plutonium Chemistry (American Chemical Society, 1983), 381-408

* Work performed under the auspices of the Department of Energy by the Lawrence Livermore National Laboratory under Contract W7405-ENG-48

Technical Information Department · Lawrence Livermore National Laboratory
University of California · Livermore, California 94551