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TITLE: REGENERATION OF RECYCLE OF SPENT OXIDE REDUCTION SOLVENT SALTS  
USED IN PYROCHEMICAL PLUTONIUM RECOVERY OPERATIONS AT LOS ALAMOS

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REGENERATION AND RECYCLE OF SPENT OXIDE REDUCTION  
SOLVENT SALTS USED IN PYROCHEMICAL PLUTONIUM  
RECOVERY OPERATIONS AT LOS ALAMOS

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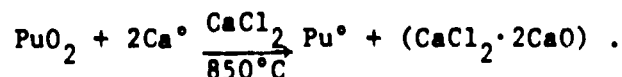
ABSTRACT

One method used at Los Alamos for producing plutonium metal is to chemically reduce the oxide with calcium metal in molten  $\text{CaCl}_2$  at  $850^\circ\text{C}$ . The solvent  $\text{CaCl}_2$  from this reduction step is currently discarded as low-level radioactive waste because it is saturated with the reaction by-product,  $\text{CaO}$ . We have developed and demonstrated a molten salt technique for rechlorinating the  $\text{CaO}$ , thereby regenerating the  $\text{CaCl}_2$  and incorporating solvent recycle into the batch  $\text{PuO}_2$  reduction process. We discuss results from salt regeneration and recycle experiments, and present our plans for incorporating the technique into an advanced design for semi-continuous plutonium metal production.

INTRODUCTION

The Plutonium Metal Technology Group at Los Alamos National Laboratory routinely uses batch pyrochemical unit operations to produce and purify plutonium metal from a variety of impure feed sources. These pyrochemical operations consist of controlling oxidation and reduction reactions (either chemical or electrochemical) between plutonium metal and its compounds in suitable molten chloride salts.

One method for producing plutonium metal from its oxide is to chemically reduce the oxide with calcium metal in molten  $\text{CaCl}_2$  at  $850^\circ\text{C}$ . This process is called direct oxide reduction (DOR) and proceeds according to the general reaction



The DOR process is a batch operation in which the  $\text{CaCl}_2$  acts as a heat sink during the exothermic reduction of  $\text{PuO}_2$ , provides a medium to control the rate of reaction, and dissolves the  $\text{CaO}$  by-product to 18 mol%.

The process does not perform any product purification, however, and impure reagents will result in impure metal product.

Because of the limited solubility of CaO in  $\text{CaCl}_2$ , the solvent salts are discarded as low-level radioactive waste after each reduction. Developing a procedure to regenerate the spent salts offers numerous advantages; among them are the ability to reduce the volume of waste from the process by approximately 80% and to increase the overall process recovery by about 2% due to recycle.

We have determined that DOR salt regeneration and recycle is feasible. The success of this program depends not only on effective CaO rechlorination, but on maintaining or reducing the concentration of metallic impurities in the salt. This is important because plutonium metal is an active metal solvent where metal impurities concentrate during the DOR reaction.

#### Regeneration and Recycle Procedure

All research and process development for salt regeneration were carried out using synthetic, nonradioactive, spent DOR salt.<sup>4</sup> Once the technique was developed, it was transferred to a glovebox and applied to actual spent process salts.

The method used in all regeneration experiments is to place 3 to 5 kg of salt in a 15-cm-od by 38-cm-tall vitrified magnesia crucible nested in a stainless steel containment can inside a stainless steel furnace tube (Figure 1).

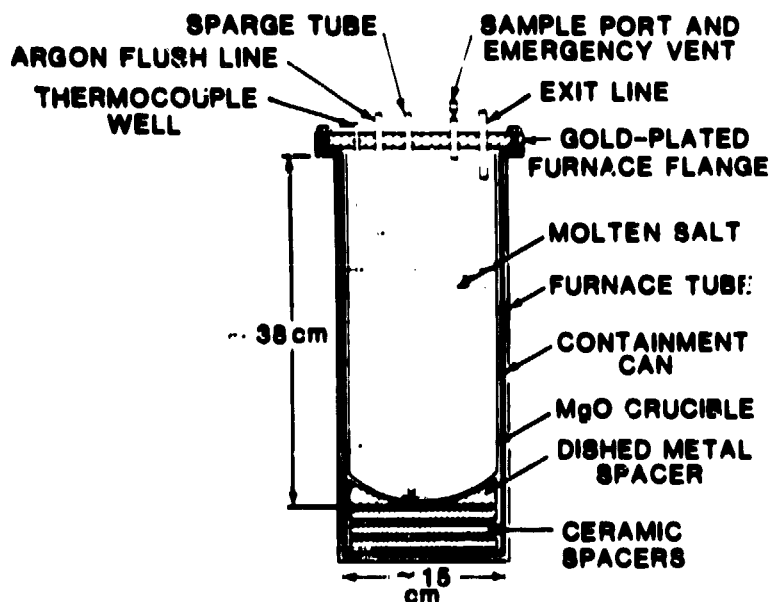


Figure 1: Apparatus for spent-salt regeneration.

After an argon atmosphere is placed above the salt, the apparatus is resistance-heated to 850°C using a Lindberg model 6015S furnace. The metal is sparged for a fixed time at a fixed flow rate with either anhydrous HCl or chlorine through alumina or magnesia tubing. Samples are withdrawn at selected intervals to determine CaO conversion profiles and residual oxygen profiles as functions of gas contact time. After chlorination, the system is purged with argon, and the salt vacuum is transferred to ambient-temperature split molds for final shaping and cooling. All off gas from regeneration is directed through a caustic scrubber system before venting to the glovebox atmosphere.

Our recycle procedure is identical to the production DOR operating procedure. When the regenerated salt has cooled under argon it is placed along with calcium metal and  $\text{PuO}_2$  into another 15-cm-od by 38-cm-tall vitrified magnesia crucible. The crucible is placed into the equipment shown in Figure 2 and covered with argon. A resistance furnace heats the reagents to 800°C and a tantalum stirrer and tantalum-nickel thermocouple well are lowered into the melt. Once stirring is initiated, the reaction proceeds to completion in about 5 min. After the temperature has stabilized, stirring is stopped and the stirrer and thermocouple well are removed from the melt. The system stays at temperature for another 10 min to allow metal coalescence before cooling and recovering the metal product.

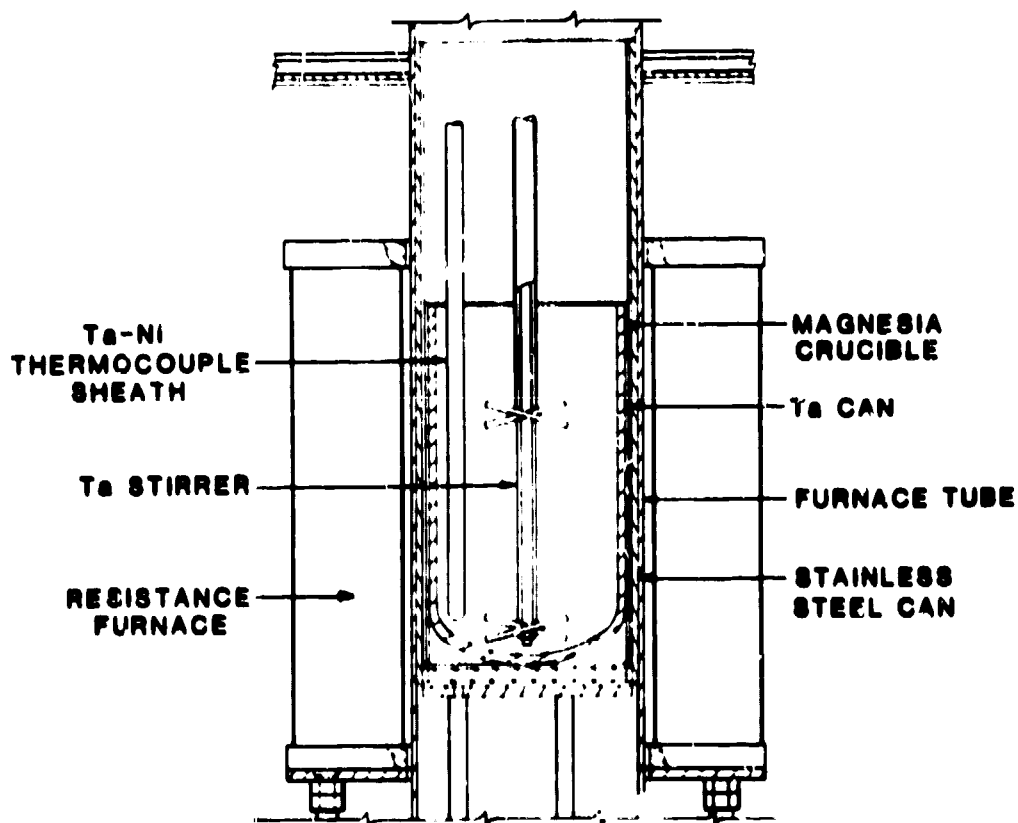


Figure 2: DOR process equipment.

### Results

We currently regenerate 5.0 to 5.5 kg of spent salt in ~2 h with chlorine or HCl at flow rates between 3 and 5 l/m. At these flow rates both reagents are effective regenerants. Chlorine produces a better quality salt based on regeneration and recycle performance, and has become our regenerant of choice (Figure 3).

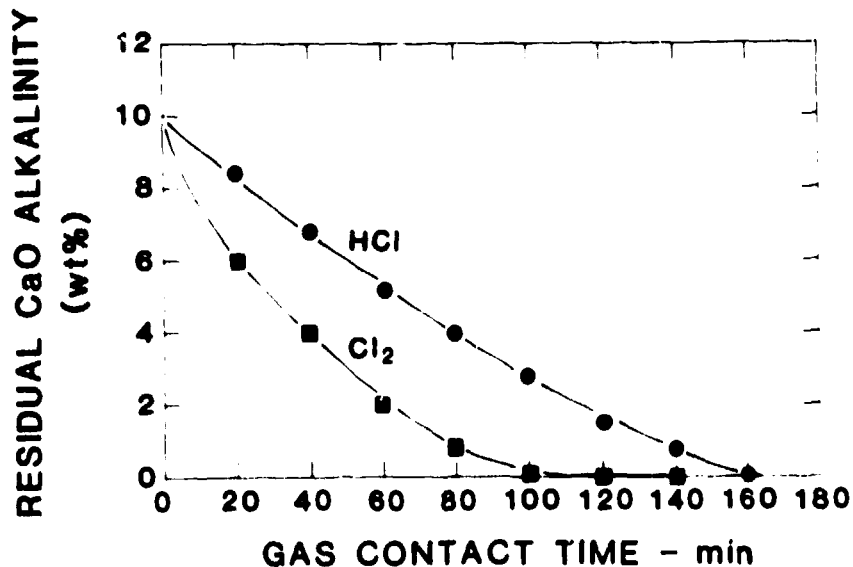


Figure: 3. Salt regeneration profiles with HCl and Cl<sub>2</sub> at 4 l/m.

After 15 months of regeneration and recycle experiments, the following summary illustrates our current status:

#### Regeneration

- 46 regenerations in the glovebox environment.
- Effective regeneration of ~5 kg salt in ~2 h with chlorine at 3-5 l/m.
- Ability to vacuum-transfer and cast regenerated salt for more effective recycle.
- Introduction of corrosion products still a problem; we have minimized concentrations, however, by system changes and good experimental technique.

#### Recycle

- Over 16 kg pure PuO<sub>2</sub> fed to the process.
- 94.1% overall plutonium metal recovery.

- 99.2% overall plutonium metal purity.
- 3.1% of feed plutonium to waste; without recycle, this would be 4.4%.
- An additional 2.8% of feed plutonium unrecoverable by current pyrochemical techniques; this material is feed, however, for aqueous processes.

Minimizing or eliminating the introduction of metallic impurities during regeneration is one of our current research topics. We are interested in maintaining salt quality to keep the purity of our final metal product high. The corrosive nature of chlorine on wetted ceramic parts results in elevated magnesium concentrations (500 ppm) and aluminum concentrations (1000 ppm) when alumina hardware is used. In addition to these elements, we have found occasional high concentrations of stainless steel components present after regeneration (500-1000 ppm Fe, Cr, Ni, Mn) and some silica and yttria, presumably from the ceramics in the system.

We believe stainless steel components result from the circulation of corrosive off gas in the vapor space above the salt; we have minimized these impurities with several minor system changes. We gold-plated the top furnace flange; raised the magnesia vessel as high as possible in the furnace tube; and introduced an argon flush line to the furnace to sweep the vapor space and force the off gas out of the system quickly. We reduced the alumina concentration by switching to an all magnesia system (this also appeared to minimize silica and yttria concentrations). The magnesia contamination continues, but is not a major concern; it reduces to magnesium during the recycle step and volatilizes, collecting in the cooler vapor space of the furnace.

The results of the recycle step were summarized earlier and are very satisfactory. Yields compare favorably to results obtained from production DOR, where the salt is discarded after each reduction. Metal purities from our experiments are higher than those from production runs, but we are using a purer grade of feed oxide. Impurities in the metal, discussed previously, are contaminants in the regenerated salt, plus carbon and americium, which are present in the feed  $\text{PuO}_2$ . The amount of unrecoverable feed plutonium is also consistent with production DOR. This type of residue is a separate processing problem that is present in some of our pyrochemical operations.

#### Future Plans

DOR salt regeneration and recycle is being developed as a stand-alone batch process capable of producing a reusable solvent salt for DOR. Our ability to vacuum-transfer and cast molten salts not only allows us to control the geometry of the DOR feed salt, but will be relied on in our advanced DOR processing concept. We are optimizing DOR and plan to convert the process from a batch to a semi-continuous operation. We plan to cluster three furnaces and tie them together with transfer tubes.

One vessel will perform oxide reduction while the other two will be regeneration vessels. This is the preferred scheme since DOR is a 20-min operation while regeneration takes 2 h. Recently we have been successful in multiple cycles of oxide reduction using lead oxide as a substitute for  $\text{PuO}_2$ . We accomplished salt transfer, regeneration, and salt transfer back<sup>2</sup> for oxide reduction without the intermittent furnace cooling necessary in the batch process. These initial experiments have also been useful in defining certain weak points in our plans, which are topics of current research. Plans include

- improving reliability in the vacuum transfer device - we must develop the capability to unplug transfer tubes in the glovebox using no water;
- investigating compatible metal reaction vessels for DOR - the breakage of ceramic DOR vessels in the semi-continuous process will interrupt continuity in salt transfer and/or plutonium metal recovery;
- considering alternatives with respect to the product metal - can it be allowed to accumulate in the DOR vessel or must it be periodically removed? How?

These three items must be resolved in order for semi-continuous DOR to become a reality. Research is well under way. Even if our semi-continuous process cannot be developed because of these problems, the batch regeneration and recycle of spent DOR salt will remain an attractive alternative for minimizing process waste and increasing overall process yields.

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