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OXYGEN SPARGING OF RESIDUE SALTS

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Oxygen sparge is a process for treating salt residues at Los Alamos National Laboratory by sparging oxygen through molten salts. Oxygen reacts with the plutonium trichloride in these salts to form plutonium dioxide. There is further reaction of the plutonium dioxide with plutonium metal and the molten salt to form plutonium oxychloride. Both of the oxide plutonium species are insoluble in the salt and collect at the bottom of the crucible. This results in a decrease of a factor of 2-3 in the amount of salt that must be treated, and the amount of waste generated by aqueous treatment methods.

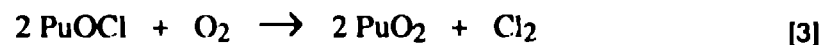
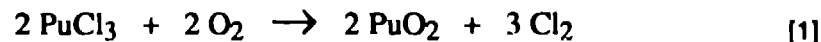
INTRODUCTION

At Los Alamos, various pyrochemical processes result in residue salts that contain plutonium in the form of plutonium trichloride. This material is soluble in the molten salts and finely dispersed in solidified salt monoliths. The plutonium value of these salts was traditionally removed by aqueous methods. However, because aqueous processes compared to molten salt processes typically produce more waste and result in increased radiation exposure to operators, an alternate means of plutonium removal was desirable.

Initial efforts focused on reduction of plutonium trichloride to plutonium metal (1). Elemental plutonium is not appreciably soluble in molten alkali chloride or alkaline earth chloride salts and should form a separate phase in a small fraction of the volume. The salt portion could then be discarded. Unfortunately, the reduction process rarely resulted in a clean separation between the metal and salt. Frequently "black salts" were produced. These so-called black salts contained uncoalesced metal and other plutonium compounds and required further treatment. In addition, some of the salts that contained plutonium trichloride consisted of equimolar sodium chloride-potassium chloride. Calcium metal will reduce these alkali metal chlorides to the metallic form producing a very pyrophoric liquid metal. The presence of this pyrophoric constituent in the discard salt presented a safety hazard and rendered the salt unacceptable according to Waste Isolation Pilot Plant (WIPP) criteria.

To meet the WIPP criteria, discard salts containing NaK were melted then sparged with air. Any pyrophoric material in the salt will be oxidized in this process, eliminating the unacceptable pyrophoric characteristic. During the course of these treatments it was noted that further plutonium was being concentrated at the bottom of the salt. Because of the problems associated with calcium metal reduction of plutonium chloride in NaCl-KCl salts and the need to air sparge discard salts it was decided to investigate a sparging process to completely replace the calcium salt strip process.

The new process was based on previous work that attempted to separate plutonium from americium by sparging a mixture of oxygen and argon into molten NaCl-KCl containing plutonium and americium chlorides (2). Plutonium was precipitated as plutonium oxide while the precipitation rate of americium was slower. Americium separation was shown to be possible but the oxygen sparge process as it was being developed was more focused on plutonium removal. Based on results obtained with oxygen sparging, the chemistry that had been presumed to be pertinent was:



EXPERIMENTAL

All handling of plutonium materials was carried out in lead-lined stainless steel gloveboxes with leaded gloves. A dried air atmosphere at negative pressure was maintained in the gloveboxes. Salts were heated by standard resistance furnaces operated by programmable LFE controllers. A stainless steel tube insert with a sealable flange was placed in the furnace to allow a controlled atmosphere at temperature. This tube was equipped with an argon gas inlet at the bottom to sweep oxygen and chlorine from the furnace tube and minimize corrosion. The salts themselves were placed in a magnesium oxide crucible. The crucible was placed in the furnace tube that was then subsequently sealed. The tube was evacuated and backfilled with argon several times then heated. The salts used consisted of either equimolar sodium chloride-potassium chloride or calcium chloride. Most of the salts were actual process residues though some experiments were carried out on pure materials added in carefully determined amounts.

After temperature had been reached a magnesium oxide sparge tube was lowered into the molten salt and the tip placed just above the crucible bottom. A mixture of argon-oxygen was controlled by Teledyne Hastings Raydist mass flow controllers. Typical mixtures were 50:50. Some experiments were carried out in which a tantalum stirrer was lowered into the molten salt after the sparge tube was withdrawn. The crucible contents were then stirred under an atmosphere of argon for a period of time. After the first two occasions in which pyrophoric material was found on the furnace tube lid, the process was modified to include a second period of oxygen sparging in which the tip of the sparge tube was located above the liquid salt level. This second sparge was effective in oxidizing the material on the furnace lid and no further pyrophoric displays were observed.

Sampling of the molten salt was accomplished by withdrawing liquid with a fused silica tube inserted through the furnace tube lid and allowing the molten salt to solidify. The samples were then analyzed for plutonium and americium by radiochemical methods or cerium titration. These were taken to determine the amount of soluble plutonium and

americium remaining in the salt as a function of time and various other process parameters.

RESULTS

In runs with equimolar sodium chloride-potassium chloride salt where no stirring was used the top layer of the solidified salt cake is the so-called "white salt". This layer may or may not be white but is the quantity of salt that has been depleted of plutonium and discardable under WIPP criteria. Under the "white salt" layer is the "black salt" portion that is further treated in aqueous recovery. This fraction of the solidified salt cake contains the great majority of the plutonium and is itself made up of two to three layers. The layer immediately under the "white salt" is a tan colored layer of salt containing plutonium oxide as identified by x-ray powder diffraction. Underneath the tan layer is a usually much thicker blue-black layer containing plutonium in the form of plutonium metal, plutonium oxychloride, and plutonium oxide(3). Finally, a coalesced metal button is sometimes found under the blue-black layer.

Experiments in which the oxygen: argon ratio was varied produced no significant changes in results of the process compared to a 50:50 mixture. Runs in which stirring was used resulted in a very different product. In the initial experiment when the furnace was opened a substantial amount of pyrophoric material had condensed on the furnace lid. The second stirring experiment also produced this pyrophoric material. Subsequent runs were modified to include a second oxygen sparge to controllably oxidize this material. The solidified salts exhibited no plutonium oxide layer. The black salt layer was not the typical blue-black color but rather a blue-green color was observed. This is the color of plutonium oxychloride. A sample of this salt was easily dissolved in a dilute aqueous hydrochloric acid solution to give a clear blue solution with no remaining solid residue. Some gas evolution was also observed. A sharp and flat dividing line separated the black salt and white salt.

An experiment was carried out in which calcium chloride was melted with plutonium trichloride. This was not a residue salt from another process but was intentionally made to exclude plutonium metal from the system. An oxygen sparge experiment was carried out and samples of the salt were taken periodically during the sparging process. The samples were analyzed for plutonium and americium and the results are shown in Figure 1. The "black salt" layer was a homogenous tan color. No black or blue color was observed.

DISCUSSION

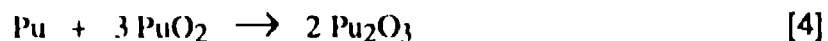
The basic oxygen sparge process had worked very well at Los Alamos for several years but there was a lack of knowledge of the chemical mechanisms and kinetics of the systems and no information, other than empirical, upon which to base modifications to the process. One of the modifications that was desired was a process that produced only plutonium oxychloride as a product because it is much easier than plutonium dioxide to dissolve in hydrochloric acid solutions. In addition there were some results that were not well understood. For example, the presence of plutonium oxychloride in a layer under a

plutonium oxide layer is counter to expectations based density properties (PuOCl - 8.3 g/cc, PuO₂ - 11.5 g/cc).

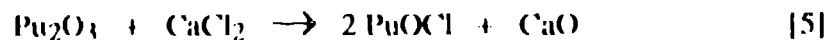
Because of the presence of plutonium dioxide and plutonium oxychloride in salts from oxygen sparging it had been thought that three reactions were of interest in the oxygen sparge system (reactions [1] - [3]). All three reactions have negative free energies of formation and theoretically could occur to some extent. A number of possible mechanisms for the process based on these can be envisioned. One of these involves [2] proceeding to completion, then reaction [3] converts some of the product oxychloride into the oxide. An obvious alternative is that all three reactions proceed with comparable rates.

If reactions [1] and [2] are proceeding at comparable rates then lowering the oxygen partial pressure should favor the production of plutonium oxychloride. Lowering the oxygen partial pressure in the sparge gas did not result in a reduction in the amount of plutonium oxide product observed. An experiment was carried in which a residue salt was stirred while oxygen sparging. This resulted in only plutonium oxychloride as a product. Reaction [3] can therefore be ruled out as significant even in cases where the salts are stirred and certainly in cases where the salts are not stirred. Oxygen sparging of plutonium trichloride in calcium chloride with no plutonium metal present produced only plutonium dioxide as the product. Since reaction [3] can be ruled out, reaction [2] cannot be occurring or plutonium oxychloride would have been observed in this experiment. The chemistry as described by [1]-[3] is inadequate to explain the ubiquitous presence of plutonium oxychloride in oxygen sparge products.

However, the species listed in reactions [1]-[3] are not the only species in the system. Plutonium metal is known to be present in certain salts and is frequently found along with plutonium dioxide in the oxygen sparge salts. An examination of the plutonium-oxygen phase diagram shows that elemental plutonium and plutonium dioxide cannot coexist in equilibrium (4). Obviously the products observed as the result of oxygen sparging are not in chemical equilibrium. The stable oxide species in equilibrium with excess plutonium metal is β -plutonium sesquioxide (β -Pu₂O₃). Plutonium metal and plutonium dioxide should react according to:



Until this point the molten salt had been considered an inert solvent for the plutonium trichloride. However it was realized that the salt could play a part in the reaction chemistry according to:



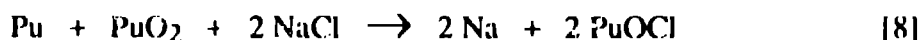
An equivalent reaction can be proposed for the sodium chloride-potassium chloride salt as well. Thermodynamic data indicate (5-7) that reaction [5] should proceed to the right but enough uncertainty exists in the free energy values for the plutonium species that the

production of plutonium oxychloride was not a certainty. Reactions [4] and [5] can be combined to give overall reactions:



However, even if $\beta\text{-Pu}_2\text{O}_3$ was the product, it was felt that this oxide would be much easier to dissolve than PuO_2 . In any case, it would be moot unless a method was found that resulted in a product that was at chemical equilibrium. The method chosen to accomplish this was the simple expedient of stirring the molten salt after the oxygen sparge process was completed.

In experiments that used calcium chloride salt residues the chemistry did proceed according to reaction [6]. However, in cases where sodium chloride-potassium chloride salts were used, metallic sodium was deposited on the furnace lid and obviously sodium chloride chemistry was not analogous to the calcium chloride chemistry. In order to gather more data the product of an oxygen sparge run that had not been stirred was used as the starting material for an experiment in which the crucible contents were stirred but not sparged. The various layers that included a "white salt", plutonium dioxide layer, black Pu-PuOCl-PuO₂ layer, and a large metal button, were separated and weighed prior to being stirred. After stirring only a blue green plutonium oxychloride layer was found along with a smaller plutonium metal button. Weight lost from the metal button indicated that plutonium metal and plutonium dioxide reacted in a 1:1 ratio rather than the 1:3 predicted by [7]. Upon further consideration another reaction was postulated:



This reaction also has a negative free energy of reaction indicating that it is thermodynamically possible and would explain the presence of the pyrophoric material: elemental sodium.

Enough information was now available to postulate a possible reaction scheme for oxygen sparging of certain salt residues. The first step occurs when the salt is melted. Any plutonium oxychloride or oxide present in the salt as a result of the pyrochemical process will tend to settle towards the bottom of the crucible. Plutonium metal is also insoluble and should coalesce into a plutonium button beneath the molten salt. However, frequently the plutonium metal fails to coalesce and merely concentrates near the bottom portion of the molten salt in a suspension of finely divided metallic "fog". When oxygen sparge is initiated plutonium trichloride is converted directly to plutonium dioxide. The plutonium dioxide precipitates, mixes with the suspended finely divided plutonium metal, and reaction [7] or [8] occurs to produce plutonium oxychloride. Some of the precipitated PuO_2 does not come into intimate contact with plutonium metal and remains unreacted. This explains the presence of plutonium metal, plutonium oxychloride and plutonium dioxide in the lower fraction of the black salt layer. As the oxygen sparge

proceeds, the bottom layer becomes more and more viscous until the precipitating plutonium dioxide accumulates on top of the layer containing plutonium metal. The plutonium dioxide cannot react with elemental plutonium and forms the tan-brown layer that constitutes the top layer of unstirred oxygen sparge black salts. This postulated reaction scheme explains why the more dense plutonium dioxide is found in a layer above that which contains plutonium oxychloride.

Information can also be gained on the kinetics of the reaction between plutonium trichloride and oxygen from the data presented in Figure 1. The data are from an experiment in which the system was open with respect to oxygen and the oxygen partial pressure was kept constant. The rate of the reaction should therefore be first order with respect to plutonium trichloride concentration. For a first order reaction it can be shown that

$$[\text{PuCl}_3] = [\text{PuCl}_3]_0 e^{-kt} \quad [9]$$

where $[\text{PuCl}_3]_0$ is the initial concentration, k is the rate constant, and t is time. A logarithmic plot of the data is shown in Figure 2. Excluding the last three points, a very good linear fit of the data yields a rate constant of 0.018 min^{-1} . The last three points fit a second linear plot with a rate constant of 0.15 min^{-1} . This phenomenon is not yet understood and must be further investigated. These rate constants can be used to determine the amount of time required to process a salt in oxygen sparge to reach a desired plutonium concentration in the discard salt. This is a recent result that has not yet been confirmed in subsequent runs but has been applied to previous runs in which the plutonium concentration of the "white salt" had been carefully determined. Predicted concentrations have been found to agree very well with those actually found.

CONCLUSIONS

Oxygen sparge of residue salts containing plutonium trichloride proceeds by a mechanism that produces plutonium dioxide. The rate constant for a first order reaction at which this occurs has been determined to be 0.018 min^{-1} for a partial pressure of oxygen of 320 torr. The plutonium dioxide then further reacts according to reactions [8] or [9] to produce plutonium oxychloride. If the molten salt is not stirred this reaction is incomplete and plutonium metal, plutonium oxychloride and plutonium dioxide are all found. If the salt is stirred plutonium dioxide can be eliminated.

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