

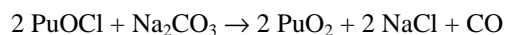
## Oxidation Of Plutonium Metal And Chloride Compounds Using Sodium Carbonate In Molten Chloride Salts

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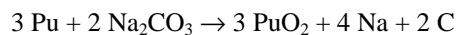
A process to separate plutonium from chloride salt residues has been developed at Los Alamos National Laboratory. The separation is based on the vapor pressure difference at elevated temperatures between the sodium chloride-potassium chloride salt matrix components and plutonium dioxide. However, plutonium is present in the salt residues in the form of plutonium trichloride, plutonium oxychloride, and plutonium metal, as well as plutonium dioxide. A method was therefore needed to convert all plutonium compounds to plutonium dioxide.

Bubbling oxygen into the molten chloride salt residue was found to effectively oxidize plutonium trichloride, but was found to be ineffective at oxidizing plutonium metal and plutonium oxychloride. The lack of reaction, even though highly thermodynamically favored, was attributed to the insolubility in the molten salt of both the oxidizing gas and reduced plutonium species. The presence of insoluble plutonium compounds could not be avoided, so a soluble oxidizing agent was sought.

One oxidizing agent investigated was sodium carbonate. This material is highly soluble in molten sodium chloride-potassium chloride, and was found to quickly and effectively oxidize all the plutonium compounds in the residues to plutonium dioxide (see Figure 1). The reaction of sodium carbonate with plutonium chloride compounds ( $\text{PuCl}_3$  and  $\text{PuOCl}$ ) could be characterized by acid-base titrations of withdrawn molten salt samples since the basic sodium carbonate is neutralized by reaction with the chloride compounds. The reactions were determined to be:



However, acid-base titrations could not be used to characterize the reaction of sodium carbonate with plutonium metal, since sodium metal was expected to be one of the products according to:



Elemental sodium placed in an aqueous solution will of course result in generation of sodium hydroxide. However, the presence of sodium was confirmed by the presence of a soft metallic pyrophoric material as a reaction product. In experiments with plutonium metal and sodium carbonate, a black foamy layer was always found floating at the top of the molten salt. EDAX analysis of this layer revealed it to be mainly carbon (Figure 2).

Characterization of experiments with each of the plutonium compounds, as well as tests with actual residues showed that oxidation with sodium carbonate met all of the requirements.

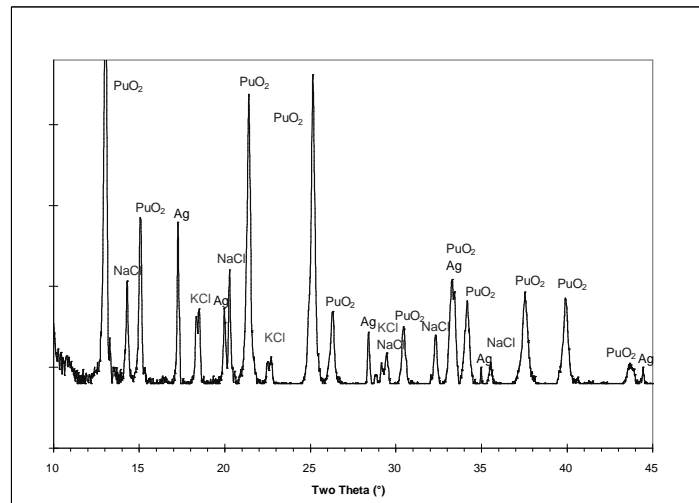


Figure 1. X-ray powder diffraction pattern of a residue salt oxidized with sodium carbonate. Only plutonium dioxide and the salt matrix were observed along with an internal silver standard.

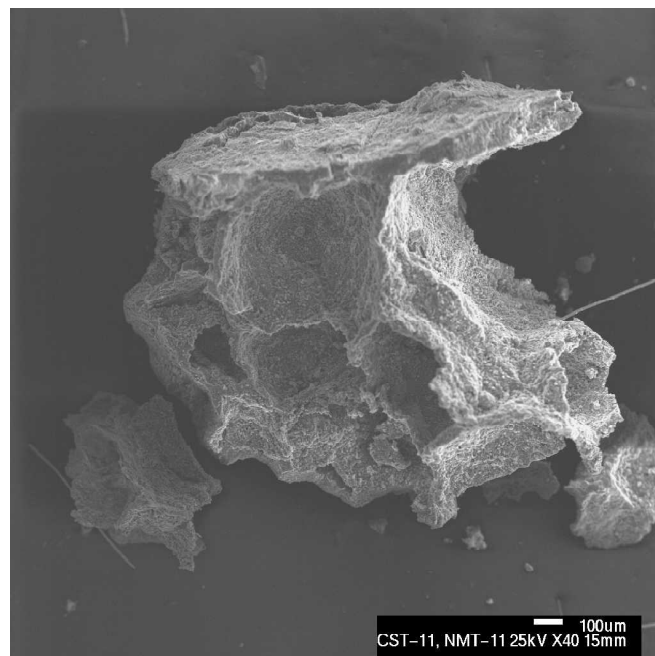


Figure 2. Scanning electron micrograph of a black foamy layer formed by reaction of plutonium metal with sodium carbonate. EDAX analysis revealed it to be mainly carbon.