

37


03-2552  
04/16/2003

## Photochemical Oxidation of Oxalate in Pu-238 Process Streams

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### Introduction

For over forty years, NASA has relied on plutonium-238 in Radioisotope Thermoelectric Generator (RTG) units and Radioisotope Heater Units (RHUs) to provide power and heat for many space missions including Transit, Pioneer, Viking, Voyager, Galileo, Ulysses and Cassini. RHUs provide heat to keep key components warm in extremely cold environments found on planets, moons, or in deep space. RTGs convert heat generated from the radioactive decay of plutonium-238 into electricity using a thermocouple. Plutonium-238 has proven to be an excellent heat source for deep space missions because of its high thermal power density, useful lifetime, minimal shielding requirements, and oxide stability.

At Los Alamos, a plutonium-238 aqueous scrap recovery facility is in the final stages of approval at Technical Area 55 (TA-55). This glovebox facility will purify Pu-238 from scrap material and residues from past production operations to provide RTGs and RHUs for additional NASA missions. The scrap material is ground to reduce its mean particle size and then dissolved in a mixture of nitric acid and hydrofluoric acid. The solution undergoes chemical pretreatment for purification using an ion exchange column, if necessary, or it is sent directly to oxalate precipitation. During the oxalate precipitation step, urea is added to scavenge nitrite, hydroxylamine nitrate is added to adjust the valence of plutonium to Pu(III), and oxalic acid is added to precipitate plutonium as  $\text{Pu}_2(\text{C}_2\text{O}_4)_3$ . The plutonium oxalate is isolated and calcined to produce the  $\text{PuO}_2$  used in the RTGs and RHUs. The filtrate after oxalate precipitation still contains a significant amount of Pu-238, most of which is precipitated by addition of sodium hydroxide to a pH of 10-13. A polymer filtration process is used to select y bind with most of

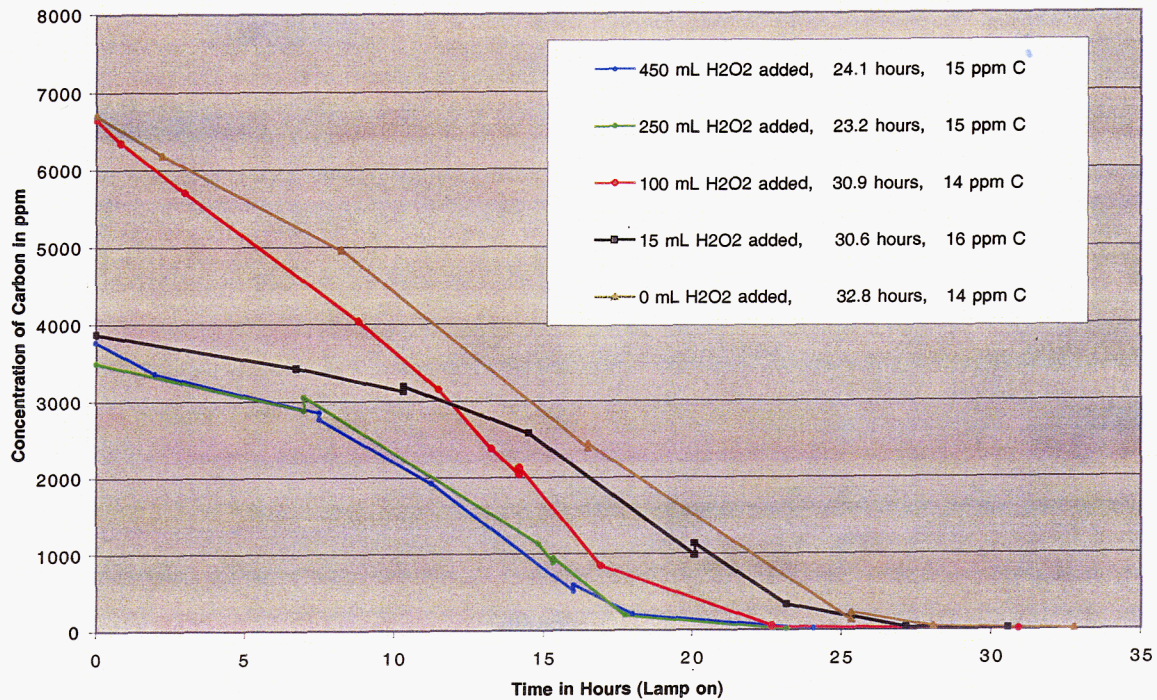


the remaining plutonium in the solution, reducing the alpha radioactivity below the TA-55 Caustic Line discard limit of 4.5 millicuries of total alpha activity / liter. The hydroxide precipitation and the polymer filtration process are both more efficient if the oxalate is not present to compete with hydroxide or polymer binding sites for the plutonium. We are investigating using UV irradiation and hydrogen peroxide to oxidize the oxalate (along with urea and hydroxylamine nitrate). Workers at Lawrence Livermore National Laboratory have reported some initial studies on oxalate destruction using this method in hydrochloric and nitric acid solutions.<sup>1</sup>

## **Results and Discussion**

A surrogate solution comprised of oxalic acid, urea, and hydroxylamine nitrate in a nitric acid matrix was used for experimentation. Two to three liters of the surrogate solution were placed in a glass reactor containing a water-cooled quartz immersion well. A 1200-watt medium-pressure mercury vapor lamp was used to irradiate the solution and compressed air was used to continuously sparge the solution. Hydrogen peroxide was pumped into the solution during irradiation and samples for analysis were removed using a peristaltic pump. The oxidation rates of oxalic acid and urea were measured throughout each irradiation period by monitoring the total organic carbon content of the solutions. The rate of oxidation has been monitored as a function of a number of variables to establish potential processing conditions including concentrations of oxalic acid, urea, hydroxylamine and hydrogen peroxide, temperature, and type of sparge gas. For example, the following graph plots the total organic carbon content of the solution as a function of irradiation time using different starting concentrations of hydrogen peroxide.

**Photochemical Destruction of 0.19M Oxalic Acid, 0.16M urea, and 0.19M Hydroxylamine Nitrate in a 2L solution of 1M Nitric Acid**



Based on initial experimentation, hydrogen peroxide does increase the oxidation rate, but the increase may not be enough to justify using hydrogen peroxide. Photochemical oxidation of the nitric acid solution alone appears to explain the bulk of the oxidation reaction. Additional results of the experimental testing of the process for use in the scrap recovery operation will be presented.

1) F.T. Wang and B.Y. Lum, "Photolytic destruction of oxalate in aqueous mixed waste," Proceedings of the ASME Biannual Mixed Waste Symposium, Aug. 7-11, 1995.