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All,

Attached is the paper about Pu oxides contaminated with chlorides within the MOX AP process.

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Dechlorination, Dissolution, and Purification of Weapon Grade Plutonium Oxide Contaminated with Chlorides: Tests Performed in the CEA Atalante Facility for the Aqueous Polishing Part of MOX Fuel Fabrication Facility

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Abstract : *During the first two to three years of operation, the MOX Fuel Fabrication Facility (MFFF) designed by Duke Cogema Stone & Webster (DCS) will receive and process low grade plutonium oxide from alternate feedstock (AFS). Some of this feedstock does not meet the specifications of material normally processed by MFFF, high grade plutonium oxide from the Pit Disassembly and Conversion Facility (PDCF). This feedstock contains in particular salt and chloride impurities at high concentration. During this time period, additional purification steps are added to remove these impurities. If chloride contaminants are above feedstock specifications they are removed by an electrochemical dissolution in nitric acid to convert the chloride to chlorine gas. The chlorine off-gas formed during this dechlorination step, is passed through a scrubber to convert the chlorine to a sodium chloride solution.*
Plutonium oxide powder (PuO_2) is then dissolved by electrolytic dissolution with silver (Ag2+) in nitric acid, at room temperature. The plutonium nitrate solution is purified in pulsed columns by solvent extraction (tri-butyl phosphate diluted at 30% in hydrogenated tetrapropylene). Nitrate impurities (americium, gallium, and silver, and all other contaminants contained in the alternative feedstock (AFS)) remain in the aqueous (raffinate) phase. To validate the process selection and design parameters, DCS has requested the CEA (Acronym for French Atomic Energy Commission) to perform laboratory scale active tests using with weapons grade Plutonium oxide contaminated with chloride and other metallic impurities. Dechlorination, dissolution and purification active tests have been performed in CEA Atalante Facility at Marcoule France with the same process parameters than the MFFF design parameters.
The aim of this paper is to present the feed characteristics, the tests conditions and the tests results.

I. INTRODUCTION

The DOE is tasked with the disposition of U.S. owned plutonium that is in excess of national security requirements into a condition that meets the spent fuel standard. This is a concept to make the plutonium as unattractive and inaccessible for retrieval and weapons use as the residual plutonium in the spent fuel from commercial reactors.

On March 22, 1999, the DOE awarded DCS a contract to support this DOE mission. The DCS Team is comprised of Duke Energy, COGEMA, and Stone and Webster (Shaw Group). Under this contract, DCS provides design, construction management, operation, and deactivation of the MOX (Mixed Oxide) Fuel Fabrication Facility (MFFF). The Mixed Oxide (MOX) Fuel Fabrication Facility (MFFF) is designed to produce completed MOX fuel assemblies for use in domestic, commercial nuclear power reactors. The feed material is uranium dioxide and surplus high grade plutonium dioxide (from the Pit Disassembly and Conversion Facility (PDCF)) or low grade plutonium oxide from Alternate Feed (AFS) supplied by the DOE

Under the Alternate Pu Feedstock (AFS) Program, the Aqueous Polishing area will have to process PuO_2 powder with variable physical and chemical properties and containing various impurities. This entails uncertainties with regard to the expected performance of the process as initially planned for MFFF baseline contract powder: high-grade plutonium dioxide (from the Pit Disassembly and Conversion Facility (PDCF)). Consequently, tests were conducted on the main aqueous polishing processes by the Commissariat à l'Énergie Atomique (CEA) in the ATALANTE facility, on the Marcoule site to validate that the polishing process produces plutonium oxide with physico-chemical characteristics meeting the MOX fuel specifications.

The alternate feed comes mainly from the plutonium that has been contacted with molten salts and one of the most significant impurities to deal with is chlorine. Thus a specific experimental program has been conducted addressing the process operations impacted by the

differences between the properties of high grade plutonium dioxide (from the Pit Disassembly and Conversion Facility (PDCF)) and properties of low grade plutonium oxide from Alternate Feed (AFS).

The selected process used to purify high grade plutonium dioxide from the PDCF low grade plutonium dioxide from alternate feed is based on a Silver(II) catalyzed Electrolytic dissolution followed by a Plutonium purification by liquid-liquid extraction.

The silver(II) dissolution process of plutonium oxide has now reached industrial maturity which has led to its implementation for the dissolution of plutonium powders and for the treatment of various solid waste at an industrial scale [1].

A derivative process was successfully tested by CEA in the 80's for the treatment of chlorinated ashes and in the 90's for hydrometallurgical treatment of Plutonium salt bearing salt baths [2, 3]. It includes a milling step, a direct electrolytic dechlorination and an electrolytic plutonium oxide dissolution.

The purification process is based on the purification flowsheets developed for the R4 facility in France (UP2 plant at La Hague) [4].

Process operations to be tested are:

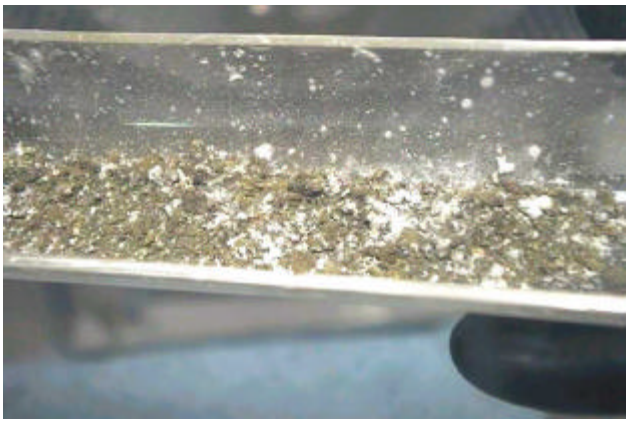
- Milling,
- Electrolytic dechlorination
- Silver II catalyzed electrolytic dissolution
- Plutonium purification by liquid-liquid extraction.

II. TEST MATERIAL

It is of primary importance to perform experiments with the most representative material. The basic material selected for the tests was a plutonium metal residue (anode heel), prepared by the Valduc CEA center by electrolysis in molten chlorides, with high gallium content (about 0,3 g/g Pu or 17 wt % , so higher than the material to be processed during the AFS phase) and about 4 wt % of chlorides. This metal residue was burned to oxide at 450 °C before being sent to Atalante facility. Picture 1 presents the powder and shows that metallic gallium was present.

Picture 1. PuO_2 sample before calcination.

The preliminary step in Atalante was calcination during 2 hours at 950 °C under an air stream to obtain a sample representative of the AFS material (i.e. thermally stabilized). These calcinations allow to produce a powder representative of alternate feed which will be calcinated at 950 °C during 2 hours to meet standard 3013-2000 requirements [9]. Picture 2 presents the powder after calcination.


Picture 2. The same PuO_2 sample after calcination.

After calcination, particle size determination on the powder showed a wide particle size distribution (from < 1 µm to 60 µm), with a mean particle diameter of 9 µm. Some aggregates (20-60 µm) were still present.

III. MILLING TEST

The main objective of this process step is to guarantee that the particle size is lower than a maximum value in order to avoid any powder settling in the dissolver while the stirring system is in operation.

Dry milling operations were performed in a remote device derived from a commercial RETSCH MM200 model. It is an oscillating/vibrating ball miller that can be used with two bowls simultaneously.

Two 25 ml stainless steel closed bowls (with 20 g of PuO_2 in each) were used with two stainless steel milling

balls in each (diameter : 10 mm). A 10 minutes milling time was applied to the 20 g PuO_2 samples, with mixing frequency of 30 Hz (usual frequency for this kind of oxide material).

After each milling operation, a particle size determination was made in order to verify the mean and maximum particle size.

After mixing all the milled powders, the mean particle size was found to be around 11 – 12 µm. The particle size distribution showed no evidence of the presence of large aggregated particles.

The specific surface area of the powder measured by a Brunauer Emmet Teller (BET) method was about 1.5 m^2/g.

The powder was weighed then analyzed to determine the main impurities content. Results are given in Table I.

Table I. Chemical composition of the PuO_2 powder used for these experiments (ppm = µg/g Pu).

Characteristics	Measured values	Uncertainties
Powder mass	185.814 g (122 g Pu)	
Cl	~ 4.1 wt %	
Ga	285000 ppm (~17,3 wt%)	8550 ppm
U	10000 ppm	500 ppm
Fe	1127 ppm	113 ppm
Ni	1300 ppm	130 ppm
Cu	2000 ppm	200 ppm
Cr	444 ppm	44 ppm
Al	2000 ppm	200 ppm
Ta	428 ppm	43 ppm
Mg	740 ppm	74 ppm
Mn	110 ppm	10 ppm

The powder sample has been separated in two parts, one with 54.378 g of Pu and the other with 57.53 g of Pu.

IV. DECHLORINATION TESTS

A schematic of the experimental device used for all dechlorination and dissolution tests of both powder samples is shown in Figure 1.

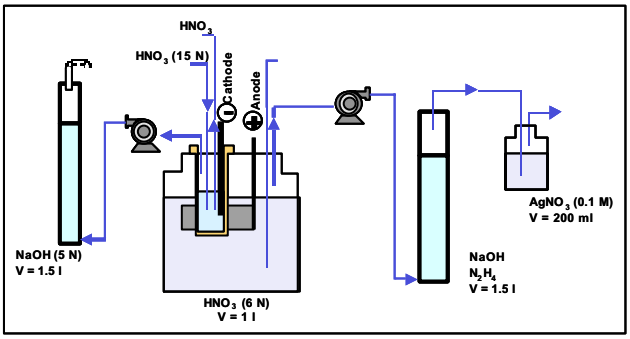


Fig. 1. Laboratory scale experimental device used for electrodissolution tests.

The electrolyzer is a jacketed glass vessel reactor that can be thermostated. It features a 2.5 L anode cell with a working volume of 1.5 L. The anode is a Pt/Ti grid. The cathode cell has a volume of 230 mL. It is separated from the anodic compartment by a SiN ceramic membrane. The hollow cathode is made of tantalum. The agitation in the anodic cell is ensured by a mechanical stirrer. The current generator is stabilized power supply (Imposed I_{max} : 80 A - V_{max} : 20 V). The anolyte is degassed by air bubbling controlled by an air flowmeter. Anodic and cathodic gas are extracted by peristaltic pumps and trapped in Plexiglas columns filled with soda solutions (a silver nitrate column is also used in line on the anodic cell gas extraction to trap the chlorine gas traces after the scrubber).

The composition of the solutions are the following :

- Anolyte : $[HNO_3] = 6$ M
- Catholyte : $[HNO_3] = 15$ M
  V = 95 mL
- Chlorine gas trapping column : NaOH 1 M – N_2H_4 0.5 M
  V = 1.5 L

For the dechlorination operations the imposed intensity has been set to 30 A and the temperature to 60 °C. These operating conditions are in agreement with operating conditions presented in reference 1 and reference 2.

During this test, 54.378g(1st dechlorination test) 57. 53 g (Second dechlorination test of PuO_2 powder was suspended in 1.5L (1st dechlorination tests) 1.2 L(2nd dechlorination tests) of a HNO_3 6 N solution and maintained at 60°C.

After two-hours electrolysis and verification of the residual chloride concentration, electrolysis was stopped and the solution left to cool to ambient temperature.

As an example of the results, at the end of the dechlorination by electrolysis step of the second lot (57.53g), the chloride concentration in solution was less than 0.001 mol/L corresponding to the elimination of

more than 99 % of the initial chlorides, as shown in figure 2.

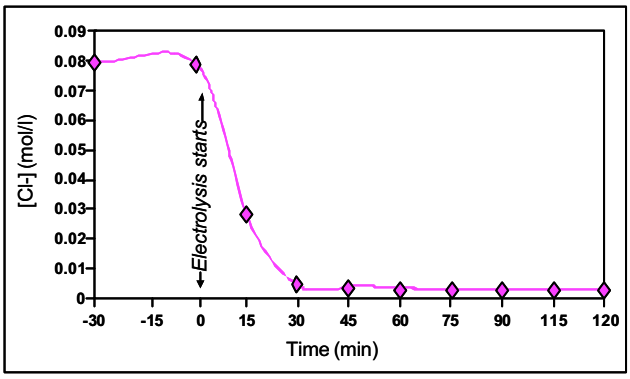


Fig. 2. Evolution of the chloride content of the anolyte during the dechlorination step of the second lot.

During the first thirty minutes, the chloride concentration decreased from 0.08 mol/L to 0.004 mol/L, with the classical kinetics limited by diffusion on the anode, which meant an elimination efficiency of about 95 % and an electrochemical efficiency of 16 % (Figure 2) compared to an electrochemical efficiency of 90 % obtained previously with the dechlorination of a pure $CaCl_2$ solution (1.5L HNO_3 6N, [$CaCl_2$] 0.8 mol/L) .

V. DISSOLUTION TESTS

V.A Dissolution tests of the powder described above

After the dechlorination step, $AgNO_3$ was added to obtain a silver concentration equal to 0.07 M [1]. The solution was maintained at about 30 °C and mechanical agitation and electrolysis were started.

Pu solubilization occurred and changes in the alpha activity of the solution were monitored. Electrolysis was carried out 180 mn until it was confirmed that the alpha activity of the solution no longer changed (Figure 3).

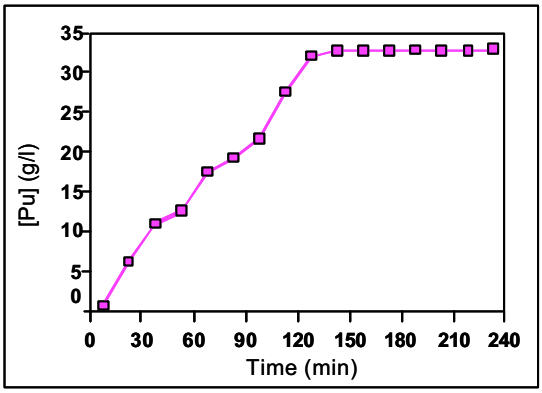


Fig. 3. Example of evolution of plutonium in solution during the plutonium dissolution step: first powder lot (54.378 g).

The analysis of the dissolution solution showed that the maximum plutonium concentration of the solution was 32.7 g/L. The following day, the electrolysis was run for one hour more (Figure 3) without higher alpha activity of the solution, thus confirming that the maximum plutonium dissolution had been reached for this type of powder.

The plutonium content of the residual undissolved powder was estimated by neutron counting. After rinsing and drying, the insoluble solid residues contained less than 210 mg of plutonium for 54.378g of Plutonium to be dissolved for this part of the tests .

For the second part of the tests the results were as follow: the plutonium content of the undissolved residue was estimated at less than 221 mg by neutron counting for 57.53g of Plutonium to be dissolved for this second part of the tests .

The global results of these test can be summarized as follows :

- Plutonium powder dissolution yield is higher than 99.6 %.
- The dissolution kinetic results in an electrochemical efficiency of 13 % (Figure 3).

Picture 3. Electrolyzer used for plutonium oxide dissolution tests.

This value is to be compared to an electrochemical efficiency of 54 % obtained with the same process conditions and the same equipment for the dissolution of plutonium oxide produced by oxalic precipitation and calcined around 650°C. This low electrochemical efficiency seemed to corroborate the hypothesis of the

presence of an impurity in the powder inducing an electrolysis loop with electron consumption.

This rather low electrochemical efficiency seems to corroborate the hypothesis of the presence of an impurity in the powder inducing an electrolysis loop with electron consumption.

After filtration and characterization of the solution, the plutonium oxidation state (VI) was reduced to (IV) using hydrogen peroxide [5]. After this adjustment step, the two dissolution solutions were mixed to form the initial solution of the extraction tests.

V.B Additional dissolution tests

Additional dissolution tests have been performed to determine if the calcination step (950°C) needed to meet the 3013-2000 requirements has an influence on the kinetic of dissolution.

The feed material was plutonium oxide obtained by plutonium metal burning at 450°C with about 3 wt% of impuritities (including about 2 wt% of Ga) and no chlorides contamination. Half of the resulting plutonium oxide has been calcined at 950 °C and ball milled as described above while the other part did not have any pretreatment step.

The global results of this test for both powder lots can be summarized as follows :

- Plutonium powder dissolution efficiency higher than 99.6 %.
- The dissolution kinetic results in an electrochemical efficiency of 24 % (Figure 4).

This value is to be compared to an electrochemical efficiency of 54 % obtained with the same process conditions and in the same equipment for the dissolution of plutonium oxide produced by oxalic precipitation and calcined around 650°C.

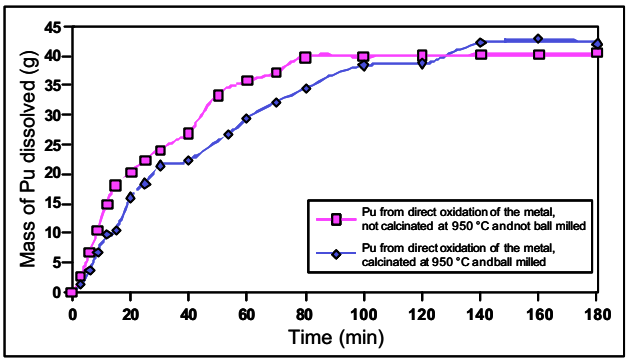


Fig. 4. Evolution of plutonium in solution during the plutonium dissolution for calcinated and non calcinated plutonium oxide.

The curves above demonstrates that the calcination temperature up to 950°C has no influence on the kinetic of dissolution of plutonium oxide produced by direct oxidation of metal and that the kinetic seems linked to the impurity content which induces an electrolytic loop with electron consumption.

This result is in agreement with results presented in the literature [6] where calcination temperatures ranges from 450°C to 800°C

VI. EXTRACTION TESTS

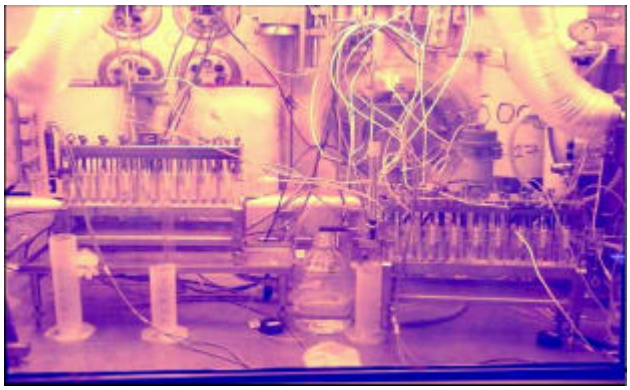
VI.A Experimentals

The experimental set-up was installed in a shielded cell of Atalante laboratory in Marcoule (Picture 4)as described below:

- Two times 16 stages of Plexiglas mixers-settlers (M-S) with perforated stainless steel blades and Teflon inter-phase level control,
- Tachometric regulation of M-S blades rotation speed,
- Sampling pots, placed on aqueous and organic outlets,
- Two on-line spectrophotometry measurements for plutonium monitoring in the aqueous phase using a "JOBIN-YVON" spectrophotometer with UV-visible and\or IR optical fibers 600 µm in diameter,
- Batch spectrophotometry monitoring using a CARY 50 scan spectrophotometer, equipped with IR optical fibers of 600 µm in diameter.

The experiment was carried out in mixer-settlers in conditions easy to extrapolate to industrial extractors like pulsed columns used in MFFF. 32 mixer-settler stages were used with a volume (mixer + settler) of about 25 mL per stage.

The several flows (feed, scrubbing and stripping aqueous phases and tri-butyl-phosphate / hydrogenated tetrapropylene -TBP/HPT organic phase-) were controlled using thermal effect mass flow meters and mass variation measurement. Except for the feed (manually recorded), these flows were automatically recorded throughout the experiment.



Picture 4 : Plutonium purification test: equipment setup in shielded cell.

The operating conditions were similar to the R4 facility ones [4, 8] and to the MFFF ones [7]. The reagents used are:

- Solvent : TBP (Tributyl Phosphate) 30% in HPT (hydrogenated tetrapropylene) 70%
- Washing solution : Nitric acid around 1.5 N
- Stripping solution : HAN (Hydroxylamine Nitrate) stabilized with N_2H_4 (Hydrazine nitrate)

The test duration was about 22 hours while it took 8 hours to reach steady state.

VI.B Extraction tests results

VI.B.1 Plutonium behavior

In the extraction zone, no plutonium trace was observed in the raffinates. The detection limit of on line measurement by spectrophotometry was between 10 and 20 mg/L. After the test, the raffinates were analyzed by X_L Ray Fluorescence and the plutonium content was found to be below the detection limit (< 0.5 mg/L) leading to a plutonium loss lower than 0.02 ‰ of the plutonium input.

In the stripping zone, Pu left the mixer-settler stripping zone quantitatively under Pu(III) form, and no trace was found in the solvent.

Finally, the Pu stream front could be seen visually in stages n°19 and 20 (blue color characteristic of Pu in oxidation state (III)). The stripped solvent was analyzed by alpha counting. The plutonium content was below $7x10^{-4}$ g/L.

VI.B.2 Impurities behavior

From data obtained from analysis by Induced Coupled Plasma Mass Spectrometry (ICP/MS) of the feed solution and of the stripped plutonium nitrate solution, it is possible to calculate a limiting lower value of the separation factors for the major contaminants :

- $Ga > 4.10^4$
- $Ag > 4.10^4$
- $Zr > 50$
- $Cr > 90$
- $Cu > 100$

The gallium concentration in the plutonium product was below the detection limit set for the analytical method used (50 $\mu g.L^{-1}$) i.e. 1.34 ppm. The decontamination factor (DF) achieved was thus higher than 4.10^4 i.e. close to the expected value of 10^5 [7].

VII. CONCLUSION

The feasibility of quantitatively dissolving, by electrogenerated silver(II) of plutonium powders obtained from molten chloride salts processing operations, milled and calcinated for two hours at 950°C under air, was demonstrated. For any of the tests performed more than 99.6 % of the plutonium has been dissolved in the nitric acid solution which had been previously dechlorinated with an efficiency better than 99%.

The kinetics of dechlorination and silver (II) plutonium oxide dissolution were determined. The electrochemical efficiency is lower than with pure PuO_2. It is adversely affected by phenomena (impurities, high gallium content ?) that could not be highlighted during the tests. The electrochemical efficiency of all the steps including electrolysis, was around 15 %. Since the electrolyzer had already been successfully tested during a dechlorination test with a $CaCl_2$ nitric acid solution, and with plutonium oxide from oxalic precipitation, the low electrochemical efficiency achieved was assumed to be due to the presence of impurities (Ga, Mn, etc) that could induce an electrolysis loop consuming electrons and thus decreasing the kinetic of plutonium dissolution. This cause seems confirmed by the additional tests showing that the kinetic is not affected by the thermal stabilization treatment at 950°C

Finally, it was possible to prepare for the extraction/purification tests about 3 liters of a nitric acid solution with a plutonium concentration higher than 30 g/L, as required, by mixing the two dissolution solutions prepared during the tests.

The liquid-liquid extraction test was successfully conducted leading to a Pu recovery close to 100 %, with an impurity content below the limits set for the process.

These tests confirm the process selection performed for the MFFF plant to polish low grade plutonium oxide from alternate feed: a silver(II) catalyzed electrolytic dissolution followed by a Plutonium purification by liquid-liquid extraction. They demonstrate that the

chosen process can be easily adapted to treat non standard materials.

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