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William S. Gilman

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ABSTRACT

The presently available dissolution data for plutonium dioxide have been compiled together with a bibliography on the subject. The ease of solubility in various media is strongly dependent upon the method of preparation and temperature to which the PuO_2 was subjected during ignition.

INTRODUCTION

Plutonium dioxide, one of the most stable compounds of plutonium, is of increasing importance as a nuclear fuel. Almost all compounds of plutonium are converted to the dioxide upon ignition in air at temperatures below 1,000°C. The dioxide is a dense, hard, corrosion resistant, refractory ceramic substance with high chemical inertness. This report is a compilation of the methods reported in the literature to dissolve plutonium dioxide.

DISSOLUTION IN MINERAL ACIDS

Plutonium dioxide prepared by ignition of a plutonium salt at temperatures less than 500°C can be dissolved slowly in boiling mineral acids.[1] The most common method involves refluxing the oxide in concentrated HNO_3 containing approximately 0.25 molar fluoride ion for an extended time.[2] The higher the initial HF concentration, the higher the dissolution rate. The following mechanism has been proposed[3] for the reaction of H_2O, HF, HNO_3 and PuO_2:

$$HNO_3 + HF + PuO_2 \rightarrow PuF_X \rightarrow H_{2-4}\,Pu\,(NO_3)_2 \rightarrow Pu(NO_3)_6^{=}$$

It has been reported[4] that moderately strong solutions of nitric acid attack plutonium metal only slightly, and since the dioxide dissolves in strong HNO_3 to form plutonyl nitrate, the metal can be cleansed of its oxide film. It has further been reported that after a few minutes immersion in warm 5 *N* HNO_3, the oxide coating is dissolved or removed, and the plutonium metal regains its metallic luster.

Mechanically mixed oxides of 10% PuO_2 - 90% UO_2 have been dissolved[5] in 8 *N* HNO_3. "Sol-Gel" prepared ThO_2 - 3% PuO_2 bodies have been dissolved in boiling 13 *M* HNO_3, catalyzed with HF and $Al(NO_3)_3$ mixtures.[6]

PuO_2 which has been sintered during reactor irradiation is difficult to dissolve by the conventional HNO_3 -HF technique.[7]

Wilson[8,9,10] has patented a method in which plutonium dioxide is dissolved in concentrated HNO_3 using cerous or ceric ions as the catalyst. This patent states that PuO_2 can be brought into aqueous solution more quickly than by the conventional use of fluoride ion catalysts and without the use of stoichiometric amounts of oxidizing agents.[11]

Plutonium dioxide can be converted to PuF_3 with a mixture of HF and H_2 at 400-600°C, and converted to PuF_4 with a mixture of HF and O_2 or H_2-free HF at the same temperatures.[12] Optimum conditions for hydrofluorination are calcination of the oxalate to the oxide below 480°C and hydrofluorination at 500°C. Under these conditions greater than 90% conversion was obtained. Calcination of the oxide at temperatures above 480°C results in much slower fluorination. The fluorination reaction proceeds in two phases; (1) the very fast reaction with the surface of the oxide; and (2) the slower reaction as HF diffuses into and reacts with the interior of the oxide particles.[13] Dawson, et al.,[14] reports that two products, $PuF_4 \cdot X\,H_2O$ and $Pu(OH)_3F_3$, HF, are formed when PuO_2 is fluorinated at 25°C.

The equilibrium constants for the reaction $PuO_2 + 4HF \rightarrow PuF_4 + 2H_2O$ were determined[15] both at 400°C and 600°C. The observed change in K with temperature required the heat of reaction to be -9000 cal/mole of heat evolved.

The PuO_2 prepared by igniting a plutonium salt at 870°C will react with hydrogen fluoride at 500°C to form either a blue trifluoride or the pink tetrafluoride.[1] Anslim, et. al.,[16] reported a blue violet color for PuF_3.

Bjorklund[17] reported that the rate of solution of PuO_2 in an HCl-KI solution:

$$PuO_2 + KI + 4\,HCl = PuCl_3 + \tfrac{1}{2}I_2 + KCl + 2H_2O$$

is greatest for samples prepared below 500°C and decreased markedly for oxides ignited at higher temperatures.

PuO_2 fired at temperatures less than 500°C dissolves slowly in 85-100% H_3PO_4 at 200°C, in 5 *M* HI and in boiling HBr.[18]

Although KI dissolved in HCl is partially effective for the dissolution of refractory plutonium dioxide at room temperature, the dissolution is slow. When the solution is heated, iodine is evolved. Similarly, commercial HI is stabilized with $H(H_2PO_2)$ and when the solution is heated, phosphine may spontaneously ignite in air. Plutonium dioxide prepared by burning plutonium in air was dissolved by refluxing in 9 *M* HBr. This method was far superior[2] to using either 12 *M* HCl or 16 *M* HNO_3. The effectiveness of this method is apparently due to the fact that HBr is both a strong acid and a reducing agent.[19]

When the dioxide is heated in excess of 500°C it is extremely difficult to dissolve. It can be dissolved[20] very slowly in hot concentrated H_2SO_4, HCl, HBr or warm 10 *M* HNO_3 containing 0.005 *M* HF. It has been reported[18] to dissolve in 12 *N* HCl under pressure at 300°C.

The dissolution rate of sintered PuO_2 pellets in boiling HNO_3 has been reported.[37] The rate was found to decrease exponentally with increase in pellet density over the range of from 8.86-10.38 g/cc. Studies also included a variety of additives to the HNO_3 including: HF, HF - $Al(NO_3)_3$, Ce(IV), O_3, H_2O_2, $Na_2Cr_2O_7$, $NaNO_3$ or $LiNO_3$, and HCl. Adding fluoride to the HNO_3 greatly increased the dissolution rate, whereas little or no additional increase over that with HNO_3 alone was noted with the other additives.

DISSOLUTION BY FUSION

Benedict and Lyon[21] have patented a method to dissolve uranium and plutonium oxides in a molten salt bath of sodium and potassium chlorides while passing anhydrous chlorine and hydrogen chloride through the bath in the presence of carbon.

A method has been described[22] to dissolve sintered compacts of heavy metal oxides such as PuO_2. The method involves immersion of the oxide in a molten alkali metal mixture, i.e., sodium-potassium or a sodium-potassium alloy at an elevated temperature until the molten metal has leached the oxide. The alkali metals are then removed and the oxide is treated with a mineral acid, for example, 12 *M* HNO_3, catalyzed with 0.001 *M* H_2SiF_6.

Occasionally, the oxide can be dissolved by fusion with sodium bisulfate, potassium pyrosulfate,[20] and ammonium bifluoride.[24] Material ignited to a bright red heat has been found to dissolve readily after fusion with $KHSO_4$ at a dull red heat.[23] Crocker[24] described an ammonium bifluoride fusion method for material ignited at 1000°C. The fusion mass is then taken up in an $Al(NO_3)_3$ solution.

DISSOLUTION BY HALOGENATION

Plutonium halides, except the tri-iodide, may be prepared by hydrohalogenation of the dioxide at approximately 700°C With HI the reaction product is PuOI and other oxihalides may be formed through the addition of appropriate quantities of water vapor to the hydrogen halide gas [25] Davidson and Katz[26] reported that plutonium tri-halides may be formed by reacting PuO_2 with halides of either phosphorus, carbon, or sulfur and a halogen.

The following reactions were reported by Abraham, et al,[27] for the preparation of $PuCl_3$:

a) $PuO_2 + H_2 + HCl \xrightarrow{600°C} PuCl_3$

b) $PuO_2 + CCl_4$ (vapor) $\xrightarrow{800°C} PuCl_3$ (sublimate)

c) $PuO_2 + S_2Cl_2$ (vapor) $\xrightarrow{800°C} PuCl_3$ (sublimate)

A method has been described[28] for the chlorination of PuO_2 ignited at elevated temperatures. The method involved extended reaction with dry H_2-HCl for approximately 100 hours at 500°C for less than one gram quantities. For preparing $PuBr_3$ from sintered PuO_2, the following reactions could be used:[29,30]

$PuO_2 + HBr \xrightarrow{600\text{-}800°C} PuBr_3$

$PuO_2 + S_2 + Br_2 \xrightarrow{800°C} PuBr_3$ (sublimate)

The action of hydrogen iodide on PuO_2 has also been investigated.[31]

$HI + PuO_2 \xrightarrow{750°C} PuOI$

Several attempts were made to form PuI_3 from PuO_2 but no evidence of reaction took place.

Chlorination of the plutonium dioxide to $PuCl_3$ using phosgene has been reported with 10-50 mg samples. With larger samples (5 grams) only partial chlorination was obtained due to the formation of a layer of molten plutonium trichloride which prevented the reaction from going to completion.[32] Chlorination at 700°C with carbon tetrachloride to form $PuCl_3$ was also investigated.[33]

Sorenson[34] found that PuO_2 particles less than 49 microns in diameter and calcined at 300°C for short times canbe chlorinated readily with phosgene. He also reported that PuO_2 prepared by direct calcination from nitrate solutions would be incompletely chlorinated with phosgene. It was assumed that this low reactivity is due, in part, to the relative impermeability of the particles, high degree of crystallinity, and lack of impurities in the PuO_2. Sorenson investigated further the effect of isotropic additives on the reactivity of directly calcinated oxides. It is postulated that these additives aid in the dissolution by causing an open or defective structure, whereby the attacking species gains less restricted access to the center of the particle. Both oxalic acid and $(NH_4)_2SO_4$ have been employed for this purpose. The latter produced the best results.

DISSOLUTION WITH COMPLEXING AGENTS

Five mg samples of PuO_2 have been found to dissolve in:

a) 0.25 *M* EDTA, 0.75 *M* NH_4OH, and 0.5 *M* N_2H_4 at 95-100°C after one hour, or

b) 2.3 g/l oxalic acid, 45 ml/l H_2O_2, 32 g/l sodium oxalate, and 11 ml/l peracetic acid at 95-100°C for one hour.

Visual examinations indicated successful dissolution in both media; however analytical results were inconclusive.[35]

CONCLUSIONS

The reactivity of plutonium dioxide is directly dependent on the method of preparation and the temperature to which it has been subjected. For example, ignition of crystalline $Pu(NO_3)_3$ or $PuO_2(NO_3)_2$ yields a porous fluffy, reactive PuO_2; ignition of $Pu(OH)_4$ forms a glassy, dense, non-reactive PuO_2; noncrystalline $Pu(NO_3)_3$ can be ignited to a crystalline, medium - dense product; and the oxalates produce porous, fine grained, reactive products after ignition. The rate of decomposition and the final temperature to which the oxalate was fired also determine the ultimate reactivity of the oxide product.[7,25,36] Plutonium dioxide prepared directly from the metal or any dioxide ignited to 1250°C was most resistant to attack.[1]

Bjorklund[17] concluded that ignition at higher temperatures causes a gradual perfection of the original highly distorted and impure plutonium dioxide crystal. This crystal perfection in turn decreases the reactivity of plutonium dioxide.

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