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EFFECTS OF IMPURITIES ON PuO_2 DISSOLUTION IN NITRIC-HYDROFLUORIC ACID SOLUTIONS*

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Nitric-hydrofluoric acid solutions are used in several areas of nuclear production and research to dissolve PuO_2.[1-4] In the present work, the results of an investigation into the effects of metal ion impurities on PuO_2 dissolution in 8.0 M HNO_3--0.1 M HF solutions are reported.

The experimental tests for this work were conducted by digesting 0.10 g of PuO_2 microspheres[5] in 5.0 ml of 8.0 M HNO_3--0.10 M HF with added 0.10 M metal ion impurity. The PuO_2 microspheres had a bulk density of 11.0 g/cm^3 and a surface area of 0.012 m^2/g. The digestions were made in 30-ml polyethylene sample bottles, with attached polyethylene air condensers, immersed directly in boiling (100°C) water. After digestion for 1 hr, the samples were allowed to stand at room temperature for 24 hr and were then filtered through Whatman No. 5 filter paper. The filtrates were analyzed for plutonium by gross alpha and alpha pulse-height analyses.

Table 1 lists the metal ion impurities investigated, along with the concentrations of plutonium dissolved in 1.0 hr and the first stability constants for the fluoride complexes[6] of the metal ion impurities. The data show that, in general, there is a trend toward lower concentrations of dissolved plutonium with increase in the magnitude of the first stability constants of the metal ion fluoride complexes present. Chromic and ferric ions, for reasons unexplained at this time, are exceptions to the trend in that these ions, which form fluoride complexes with relatively large stability constants, produced a negligible effect on the PuO_2 dissolution.

The logarithm of the molar concentration of the plutonium dissolved with separate 0.1 M concentrations of Cu^{2+}, Hg^{2+}, Zn^{2+}, La^{3+}, Ce^{3+}, Al^{3+}, Th^{4+}, or Zr^{4+} as metal ion impurities can be predicted with a 0.96 coefficient of determination by either of two empirical equations:

$$\log C_{Pu} = -0.32 \log K_F - 1.53 \quad (1)$$

or

$$\log C_{Pu} = -0.5\ Z^2/d - 1.11. \quad (2)$$

In the above equations C_{Pu}, K_F, Z, and d, respectively, denote molar concentration of dissolved plutonium at 1.0 hr, first stability constant for the impurity metal ion fluoride complex,[6] ionic charge for the impurity metal ion, and sum of impurity metal ion and fluoride ion ionic radii in angstroms. The Z^2/d values[6] for the metal ion impurities are listed in Table 1.

One interpretation of the effects of metal ion impurities on PuO_2 dissolution in HNO_3-HF-H_2O solutions which is consistent with the above findings is that the impurities serve to complex the free fluoride ions in solution and to decrease their effectiveness as dissolution catalyst. The results also tend to substantiate that individual effects of a number of metal ion impurities on PuO_2 dissolution in HNO_3-HF-H_2O solutions can be mathematically and systematically defined. However, the data obtained with Cr^{3+} and Fe^{3+} impurities show that caution should be exercised in applying such definitions to untested impurities.

Table I. Effects of metal ion impurities[a] on PuO_2 dissolution in $HNO-HF-H_2O$[b] solutions at 100°C

Metal ion impurity	Dissolved plutonium concentration at 1 hr (M)	Fluoride metal ion stability constant[c]	Z^2/d[d] (Å-1)
Cu^{2+}	8.7×10^{-3}	17	1.71
Hg^{2+}	8.7×10^{-3}	36	1.67
Zn^{2+}	5.7×10^{-3}	18	1.82
La^{3+}	3.0×10^{-3}	3.6×10^{3}	3.71
Ce^{3+}	1.7×10^{-3}	9.8×10^{3}	3.76
Al^{3+}	3.0×10^{-4}	1.0×10^{7}	4.71
Th^{4+}	5.0×10^{-5}	4.5×10^{8}	6.50
Zr^{4+}	8.3×10^{-6}	6.3×10^{9}	7.41
Cr^{3+}	7.3×10^{-3}	1.6×10^{5}	5.45
Fe^{3+}	1.2×10^{-2}	1.1×10^{6}	4.43
None	9.7×10^{-3}	–	–

[a]Initial metal ion impurity concentration in each sample was 0.10 M.
[b]Acid concentrations in each sample were 8.0 M HNO_3--0.1 M HF.
[c]Stability constant values from A. D. Paul report [Ref. 6].
[d]Z denotes ionic charge;d denotes sum of metal and fluoride ion radii in angstroms.

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