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ABSTRACT

The stoichiometry and the kinetics of the ambient temperature dissolution of alpha-phase plutonium in sulfamic acid has been determined. Hydrogen off-gas rates and plutonium concentrations were calculated as functions of time for a variety of dissolving conditions. Calculations show that nominal 2.2 kg Pu buttons (surface area, 171 cm^2) should yield solutions containing 60 ± 10 g Pu/L after a one-hour dissolving cycle. Hydrogen off-gas rates were calculated to vary from as high as 780 mL of gaseous hydrogen per minute (STP) at the beginning of a dissolving cycle to as low as 150 mL $H_2(g)$ per min near the end of a dissolving cycle.

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THE KINETICS OF THE AMBIENT TEMPERATURE DISSOLUTION OF PLUTONIUM METAL IN SULFAMIC ACID

INTRODUCTION

Plutonium metal that does not meet product purity specifications and aged plutonium metal into which the daughter product ^{241}Am has grown must be recycled through a recovery and purification process. At the Savannah River Plant (SRP), the initial step in this recycle is the conversion of the metal to an aqueous solution. Since about 1962, sulfamic acid has been the accepted dissolvent for plutonium metal in the SRP process.

The dissolution of plutonium in sulfamic acid is rapid and proceeds to depletion of the hydrogen ion. The dissolution is normally carried out at 20 to 35°C and in the absence of oxidizing agents. At temperatures above 40°C, and in the presence of oxidizing agents such as nitric acid, the sulfamic acid is decomposed by side reactions. When 1.7M sulfamic acid is used as the dissolvent at solution temperatures below 40°C, plutonium concentrations as high as 134 g/L are obtained with very little sludge formation.[1,2]

Although sulfamic acid has been used to dissolve plutonium metal at SRP for about 20 years,[3] no systematic study of the dissolving rates and hydrogen generation have previously been made. Therefore, a systematic study of the kinetics of plutonium dissolution in sulfamic acid was begun.

SUMMARY AND CONCLUSIONS

Plutonium metal dissolves readily in sulfamic acid (NH_2SO_3H) at ambient temperature according to the reaction

$$Pu + 3H^+ \longrightarrow Pu^{3+} + 3/2\ H_2(g)$$

Because heat liberated by this reaction is $\Delta H_{298} = -\ 141.9$ kcal/mol Pu,[4] adequate cooling is needed to maintain a low temperature during dissolution.

The rate of dissolution was found to depend on the hydrogen ion concentration and the surface area of the metal. A short induction period preceded the dissolution.

For calculational purposes, a typical dissolving cycle was: 1) charge a 2.25 kg plutonium button (171.2 cm^2 surface area) to 3.0 L of 1.67M sulfamic acid; 2) allow dissolution to proceed for 60.0 min; 3) displace 2.0 L of this solution with 2.0 L of fresh 1.67M sulfamic acid; 4) Steps 2 and 3 are repeated until the plutonium metal inventory decreases to 1300.0 g Pu; 5) charge another plutonium button; 6) repeat Steps 4 and 5 as long as necessary.

Dissolving rates obtained in the experiments were used to calculate the $H_2(g)$ off-gas rates and the expected plutonium concentration vs time for this assumed dissolving cycle. Under this procedure, the initial batches of solution from the dissolver would average about 50 ± 5 g Pu/L. After charging the second button, the plutonium concentration was calculated to increase to about 60 ± 10 g Pu/L for each batch displaced. These calculations agree very well with plutonium concentrations obtained from production-size dissolvers. The calculated off-gas rates varied from as high as about 780 mL $H_2(g)$/min at the beginning of a dissolving cycle to as low as about 150 mL $H_2(g)$/min near the end of a dissolving cycle.

To assure that the $H_2(g)$ concentration in the dissolver void space remained below the lower limit of inflammability, the dissolver should be purged at a rate of ∿20 L N_2/min at the beginning of a dissolving cycle. However, because the off-gas rate decreases with time, the purge rate could be dropped to about 3.8 L N_2/min at the end of the dissolving cycle.

EXPERIMENTAL PROCEDURE

The volume of hydrogen gas generated as a function of time was measured for all experiments by measuring the volume of water displaced from a gas-tight reservoir (Figure 1). The volume of water displaced was measured using a graduated cylinder; corrections were made for temperature and barometric pressure (STP). Plutonium metal turnings were used to determine the stoichiometry of the reaction. Reaction rates were determined on pieces of plutonium metal removed from the production dissolver. The surface area of these pieces was calculated from dimensions determined by calipers. Because these pieces were irregular in shape, the measurement of surface area was the least accurate of any of the measurements.

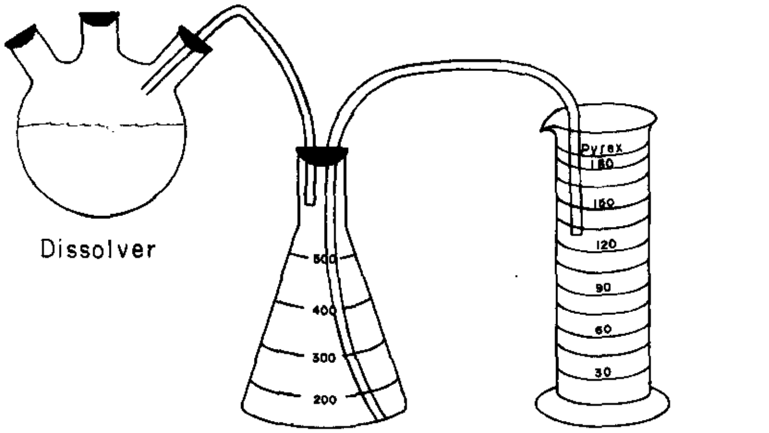

FIGURE 1. Experimental Apparatus

STOICHIOMETRY

Table 1 shows the dissolution rates and total gas evolved for varying weights of plutonium metal turnings. These data show an average of 98.04 ± 0.76% of the theoretical $H_2(g)$ was evolved, assuming the reaction is

$$Pu^{\circ} + 3H^{+} \longrightarrow Pu^{3+} + 3/2\ H_2(g) \tag{1}$$

In these cases, a residue of from 0.1 to 1% of the original mass of sample remained after dissolution. X-ray diffraction analysis of the residues indicated the major component to be PuO_2. Equation 1, therefore, is the correct stoichiometric relationship for the reaction.

CALCULATION OF BUTTON SURFACE AREA

Plutonium buttons are produced in the ceramic liner (Figure 2) of a bomb reduction furnace. A typical button is 0.75-in. thick, weighs about 2250 g, and has a density of 19.3 g/cm^3. To estimate the surface area, all surfaces were assumed to be smooth. For calculational purposes, the surface was divided into four segments: the first segment is a flat circle with a radius (r_1) of 4.763 cm; the second segment is the curved surface of the frustum of a right cone with a base radius (r_2) of 4.763 cm, a top radius (r_3) of 4.366 cm, and an altitude (h_1) of 1.1600 cm; the third segment is the curved surface of the frustum of a

TABLE 1

Dissolving Plutonium Metal Turnings

Pu, g	Plutonium Dissolution Rate, g/hr per g Pu charged	Hydrogen Evolution Rate, mL/sec per g Pu charged	Volume of Hydrogen Evolved, mL Measured Uncorr.	Measured At STP	Theoretical (STP)
5.6600	37.14	1.047	840	773	796
3.6846	30.20	0.8530	550	507	518
6.0020	30.43	0.8628	910	836	845
4.0021	-	-	600	552	562

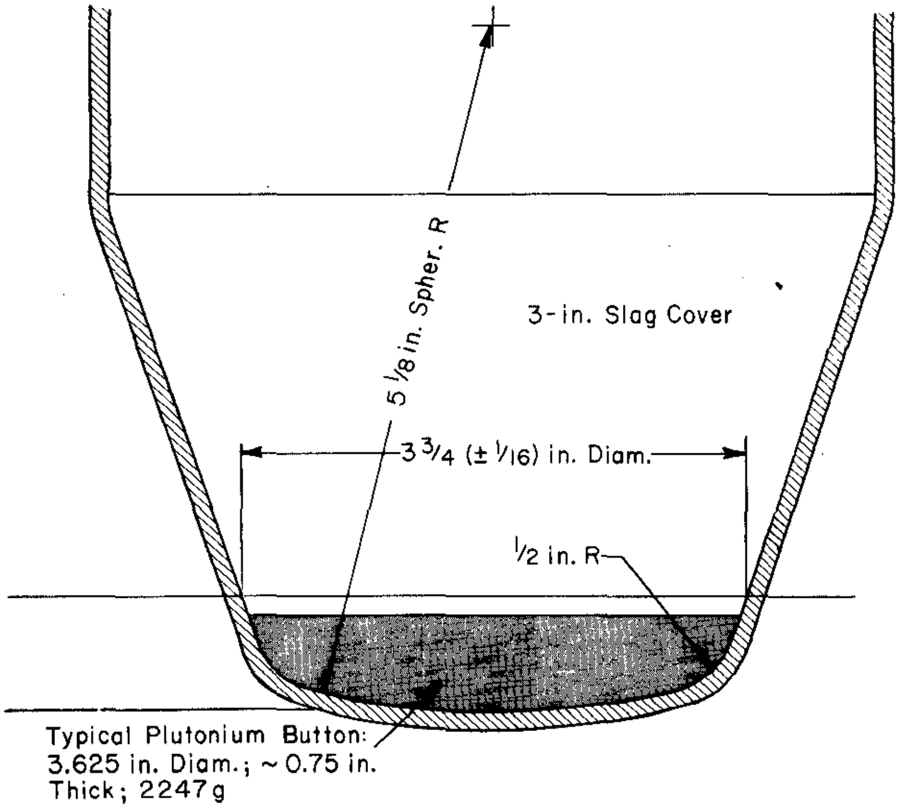

FIGURE 2. Ceramic Crucible for Preparing Plutonium Buttons

right cone with a base radius (r_2) of 4.3656 cm, a top radius (r_3) of 3.5719 cm, and an altitude (h_2) of 0.6250 cm; and the fourth segment is the curved surface of a spherical segment with a height (h_3) of 0.4800 cm, and the radius (r_4) of the sphere equal to 13.075 cm. The surface area of the button is then calculated with the equation.

$$A = \Pi \left\{ (r_1 + r_2) \sqrt{h_1^2 + (r_1 + r_2)^2} + (r_2 + r_3) \sqrt{h_2^2 + (r_2 - r_3)^2} + 2\, r_4\, h_3 + r_1^2 \right\}$$

The volume of the button is calculated with the equation

$$V = (\Pi/3) \left\{ h_3^2\, (2r_4 - h_3) + h_2\, (r_2^2 + r_2\, r_3 + r_3^2) + h_1 (r_1^2 + r_1\, r_2 + r_2^2) \right\}$$

Both the surface area and the volume of a typical button are shown (Figure 3) as a function of mass of plutonium remaining undissolved. The surface of a typical button is calculated to be 171.2 cm^2, and the volume is calculated to be 116.4 cm^3.

DISSOLVING RATES OF PLUTONIUM METAL

Hydrogen generation vs. time was determined for a series of plutonium metal pieces starting at varying concentrations of Pu(III) sulfamate in sulfamic acid solution. Typical curves for these dissolutions are shown in Figure 4. The rate of evolution (Figure 5) was determined from the tangent of the early portion of the curve for evolved hydrogen gas. This value was divided by the initial surface area of the plutonium metal piece being dissolved to determine the rate of hydrogen evolved in terms of surface area [mL H_2(g)/(sec-cm^2)].

Because the production process does not vary the sulfamic acid concentration fed to the dissolver, the sulfamic acid concentration is varied only by reaction with plutonium metal. For this reason, the H_2(g) evolution rate in mL H^2(g)/(sec-cm^2) of surface area vs initial plutonium concentration in g/L was determined as plotted in Figure 5.

The data obtained from these dissolving studies were then used to calculate both the dissolving rate of typical plutonium buttons (surface area ∿171 cm^2) for different cases and the volume of hydrogen gas evolved into the dissolver void space. The various cases are given in Table 2.

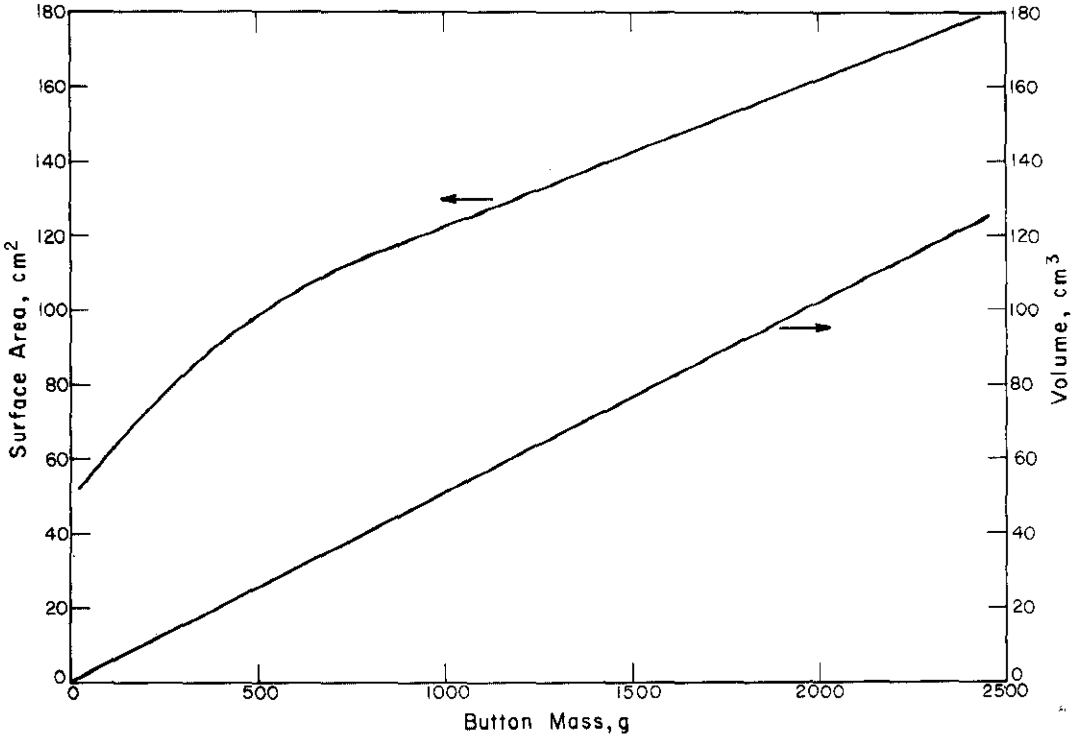

FIGURE 3. Calculated Surface Area and Volume of a Typical Plutonium Button During Dissolution

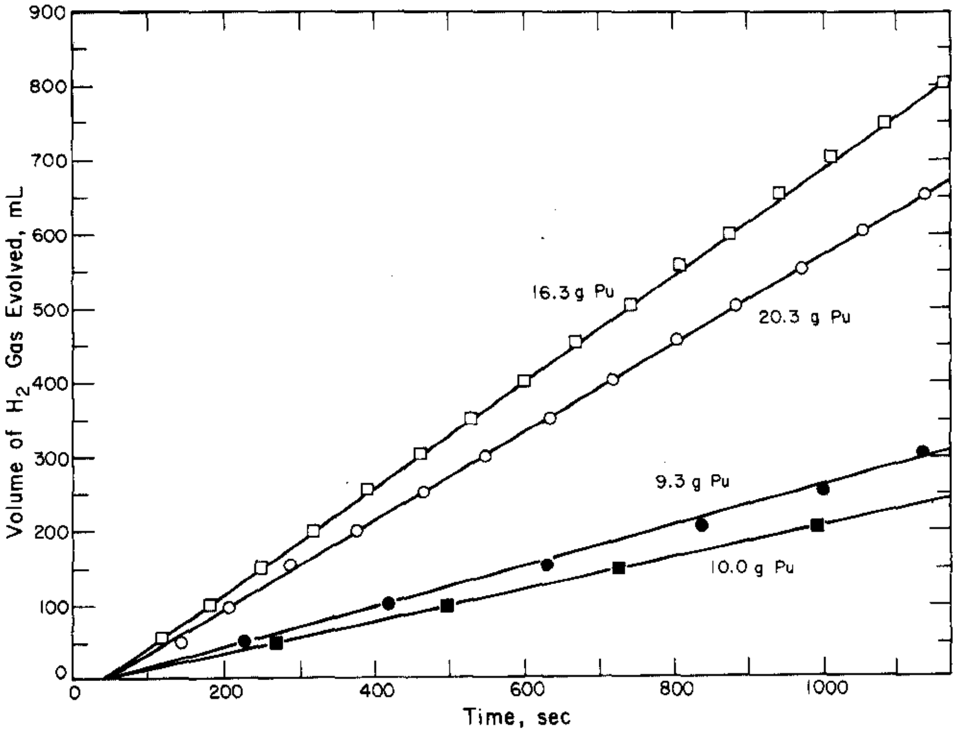

FIGURE 4. Volume of Hydrogen Evolved from Typical Tests of Dissolving Plutonium Metal in 1.67M Sulfamic Acid

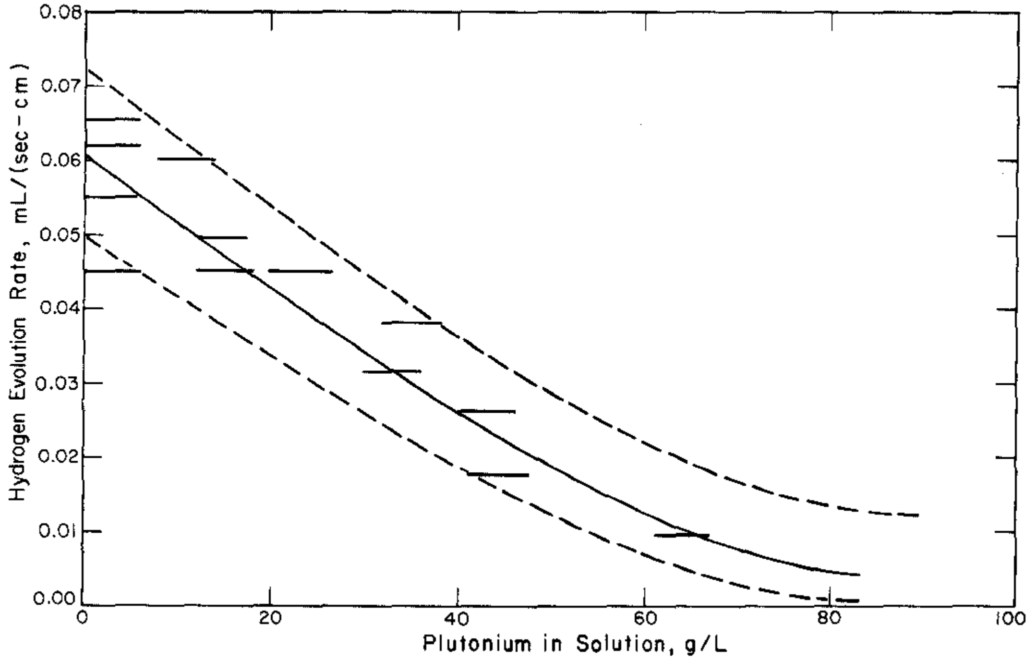

FIGURE 5. Rate of Hydrogen Evolution from Dissolution of Plutonium Metal in 1.67M Sulfamic Acid

TABLE 2

Calculations at Zero Time for Cases 1 through 4

Case No.	*Surface area, cm^2*	*Plutonium Metal, g*	*Plutonium in Solution, g/L*
1	171	2246.2	0.0
2	166	2095.9	16.7
3	161	1981.9	18.2
4	305	3546.2	20.0

Case 1: Dissolution of One Button in 1.67M Acid

The initial maximum rate of dissolution and of hydrogen evolution, at startup, would be predicted to occur if the initial button were charged to 1.67M sulfamic acid. Calculations show that this maximum hydrogen evolution rate would be about 625 mL $H_2(g)$ per min. After a one-hour dissolving time, the evolution rate is calculated to have decreased to about 190 mL $H_2(g)$/min (Figure 6), and the dissolved plutonium concentration to calculated to have increased to about 50 g Pu/L (Figure 7).

Case 2: The Second Dissolving Batch

The second dissolving batch is calculated to begin with a plutonium concentration of about 17 g/L with an off-gas of about 455 mL $H_2(g)$/min. After a one-hour dissolving time, the evolution rate is calculated to have decreased to about 150 mL $H_2(g)$/min (Figure 6), and the dissolved plutonium concentration is calculated to have increased to about 55 g Pu/L (Figure 7).

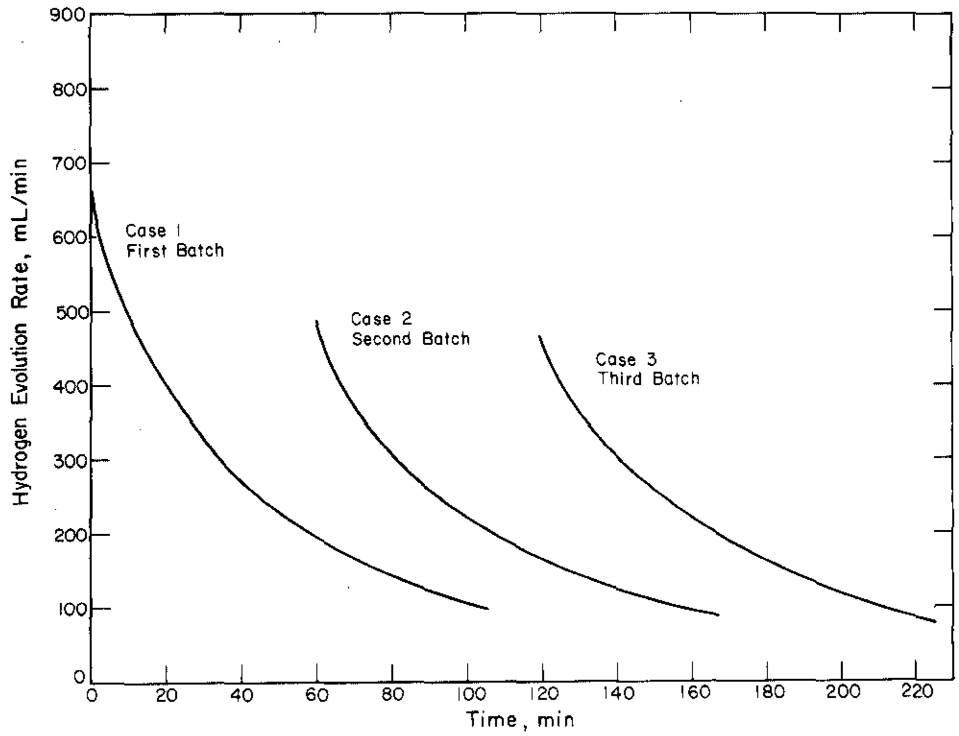

FIGURE 6. Rate of Hydrogen Evolution for Cases 1, 2, and 3

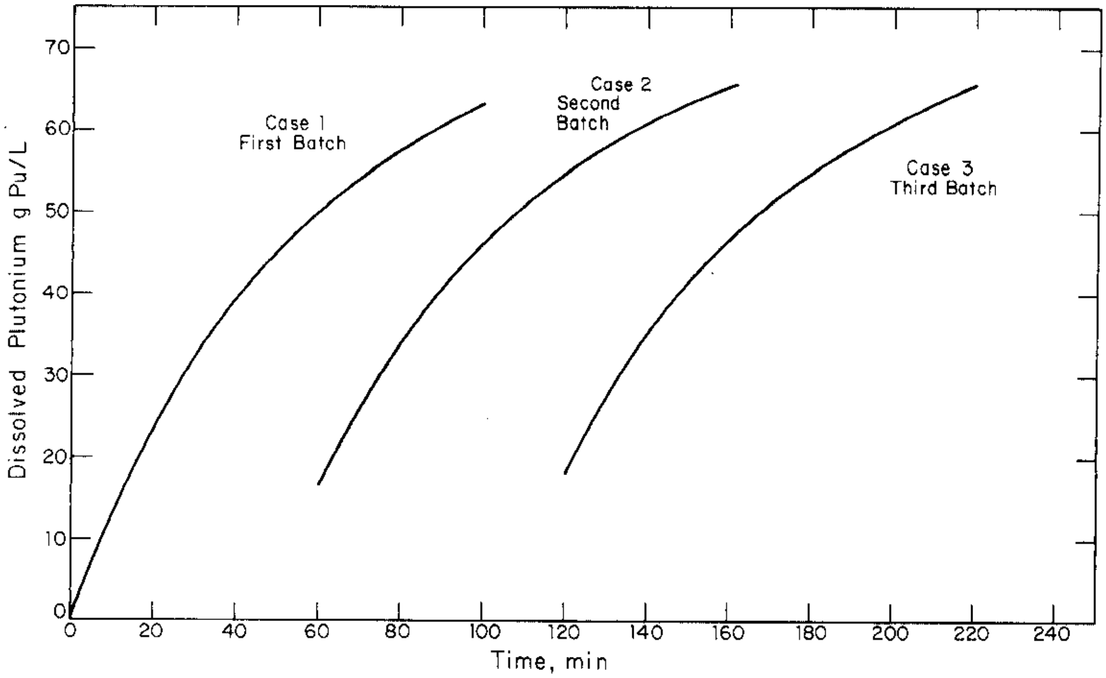

FIGURE 7. Rate of Plutonium Dissolution for Cases 1, 2, and 3

Case 3: The Third Dissolving Batch

The third dissolving is calculated to begin with a plutonium concentration of about 18 g Pu/L and increase to about 55 g Pu/L (Figure 7) at the end of a one-hour dissolving time. The off-gas rate is calculated to begin at about 430 mL $H_2(g)$/min and decrease to about 150 mL $H_2(g)$/min (Figure 6).

Subsequent batches from the dissolver would very slowly decrease in concentration as the surface area slowly decreases. This decrease in concentration would be slow because a half-dissolved button still has about 75% of the original surface area. Therefore, the concentration of the last sample aliquots before charging a second button to the heel of the first should have dropped to about 45 g Pu/L.

Case 4: Charging the Second Button

When about half the plutonium has been dissolved, a second button is charged to the dissolver. For calculational purposes, a residual inventory of 1300 g of plutonium metal was assumed. The total surface area is now about 305 cm^2; the $H_2(g)$ evolution rate is calculated to begin at about 780 mL/min and decreases to about 150 mL/min at 60 min after charging (Figure 8). In this same time, the plutonium concentration has increased from about 20 g Pu/L to about 70 g Pu/L (Figure 8). Subsequent batches will decrease in concentration as the surface area decreases.

NITROGEN PURGE RATES

As can be seen from the hydrogen off-gas rates, the evolution of hydrogen is calculated to be as high as 780 to 800 mL $H_2(g)$/min (STP) to as low as about 150 mL $H_2(g)$/min (STP). Therefore, to assure that the concentration of hydrogen in the dissolver void space will remain below the lower limit of flammability, the dissolver should be purged with nitrogen gas at a rate of 20 L/min (42.4 SCF/hr) at the beginning of a dissolving cycle, but could be dropped to about 3.8 L/min (8.05 SCF/hr) at the end of the dissolving cycle.

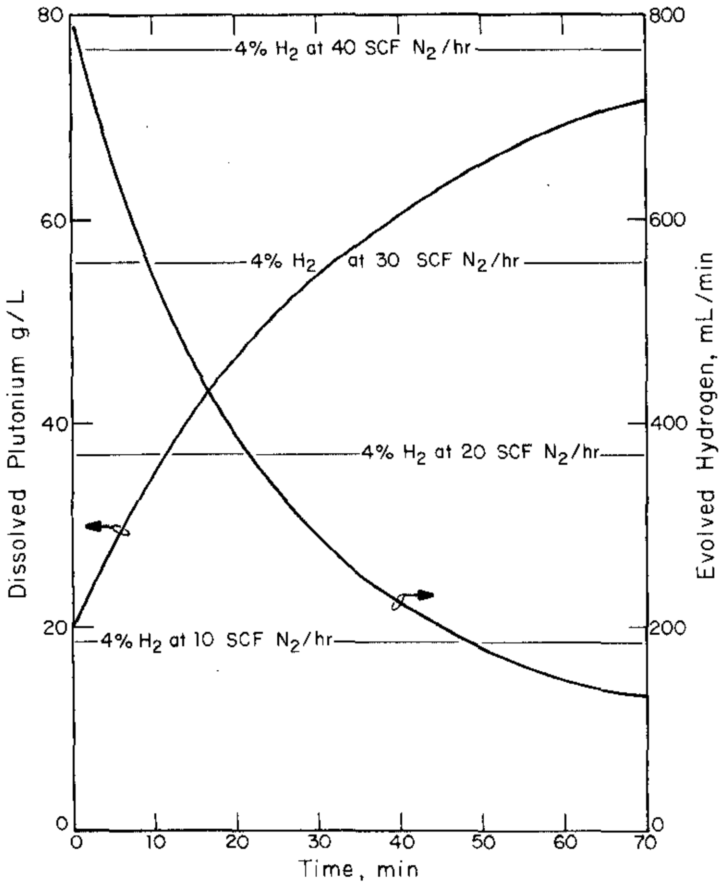

FIGURE 8. Rates of Hydrogen Evolution and Plutonium Dissolution for Case 4

REFERENCES

1. W. J. Jenkins. *Dissolving Plutonium Metal in Sulfamic Acid.* USAEC Report DP-737, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, S. C. (1962).

2. W. J. Jenkins. "Use of Sulfamic Acid for Dissolving Plutonium". *J. Inorg. Nucl. Chem.*, *25*, 463 (1963).

3. J. H. Radke. E. I. du Pont de Nemours & Co., Savannah River Plant, Aiken, S. C. Personal Communication.

4. L. Brewer, L. Bromley, P. W. Gilles, and N. L. Lofgren. "The Thermodynamic Properties and Equilibria at High Temperatures of the Compounds of Plutonium". Paper 6.40, *The Transuranium Elements*, National Nuclear Energy Series, IV-14B, Part II. McGraw-Hill, New York (1969).