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SUBJECT: Final Cycle Plutonium Recovery by Amine
Extraction
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ABSTRACT

The flowsheet visualized from development work thus far for final plutonium recovery and purification will accept as feed a Purex partition stream without feed adjustment beyond the usual reoxidation. Extraction with trilaurylamine at ~0.3 M appears suitable for 20-60 g Pu/liter product from 0.5-2 g Pu/liter feed. Scrubbing with either <<2 M or >>2 M HNO₃ is possible. Acetic acid is at present the first choice for stripping agent, with oil-soluble and aqueous-soluble organic reductants as alternates.

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Final Cycle Plutonium Recovery by Amine Extraction

The amine extraction of plutonium nitrate is being studied to develop flowsheets suitable for final cycle plutonium recovery and purification, after typical Purex extraction and partition from uranium. To compete successfully with tributylphosphate extraction-anion exchange cycles already designed, an amine extraction flowsheet must provide high decontamination and should provide reasonably high concentration in a single cycle, besides fulfilling its apparent promise of simplicity and much lower nitric acid consumption.

The flowsheet visualized from development work thus far is shown in Figure 1. It will take as feed a Purex partition cycle plutonium product stream in the range of 1 to 2 M HNO₃, carrying some sulfate from the ferrous sulfamate plutonium reductant. The expected nitric acid concentrations are close to that most favorable for plutonium extraction with tertiary amines, so that the only feed adjustment expected is reoxidation of the reduced plutonium to Pu(IV) with nitrite. An organic scrub to decrease TBP carry-over may be desirable.

Expected feed concentrations of 0.5 to 2 g Pu/liter (~0.002 to 0.01 M Pu) and desired product concentrations of 20 to 60 g Pu/liter suggested extraction at an amine concentration around 0.3 M. Work so far supports this as a good choice, although neither higher nor lower concentrations are ruled out. There are three different possible limitations to the plutonium loading that can be obtained in the extract, i.e., the effective extraction coefficient times the plutonium feed concentration, the stoichiometry of the extracted complex, and the phase stability of the loaded extract. In contrast to extracted uranyl sulfate, which is generally soluble in any amine-diluent combination that is also satisfactory with respect to solubility of the amine bisulfate, extracted Pu(IV) nitrate has a strong tendency to separate out of the extract. In the measurement of the plutonium extraction isotherms, organic phases were stable up to at least 15 g Pu/liter (sufficient for operation as indicated in Fig. 1) with 0.3 M trilaurylamine in Solvesso 100 or in diethylbenzene, and with 0.3 M Alamine 336 in the same diluents modified with ~10% tridecanol (Table 1). The extraction isotherm (Fig. 2) up to above 15 g Pu/liter loading were usefully well fitted by the empirical expression

$$E_a^O(\text{Pu}) \approx E_1 [\underline{M}_{\text{amine}} - 3 \underline{M}_{\text{Pu}}]^2.$$

E_1 was ~3300 in extraction from 1.5 M HNO₃ with both trilaurylamine and Alamine 336. This was decreased moderately by addition of sulfuric acid in the expected concentration range, and severely by higher concentrations (Table 2).

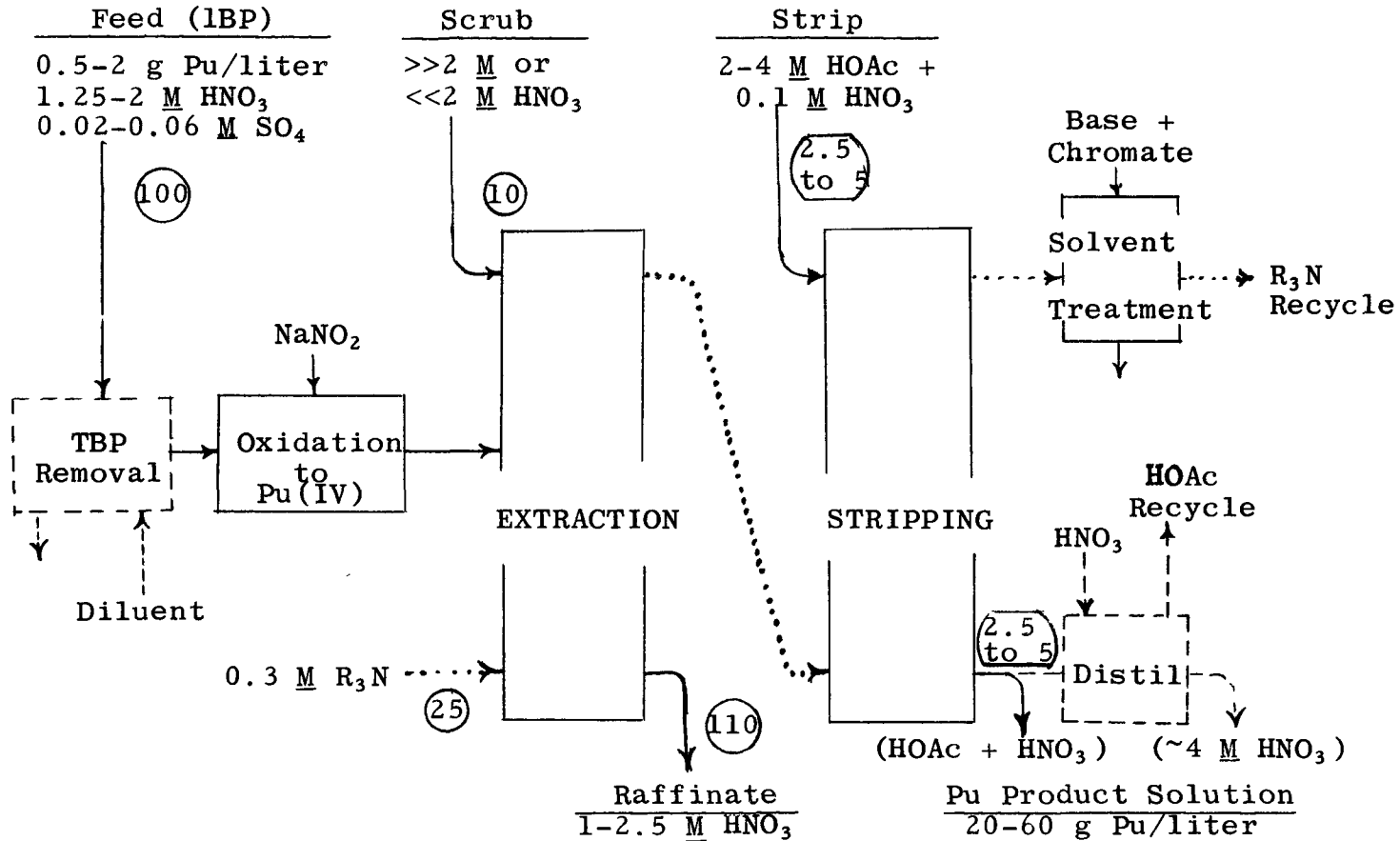


Fig. 1. Amine Extraction Cycle for Final Plutonium Recovery. (Circled numbers are tentative relative flow rates.)

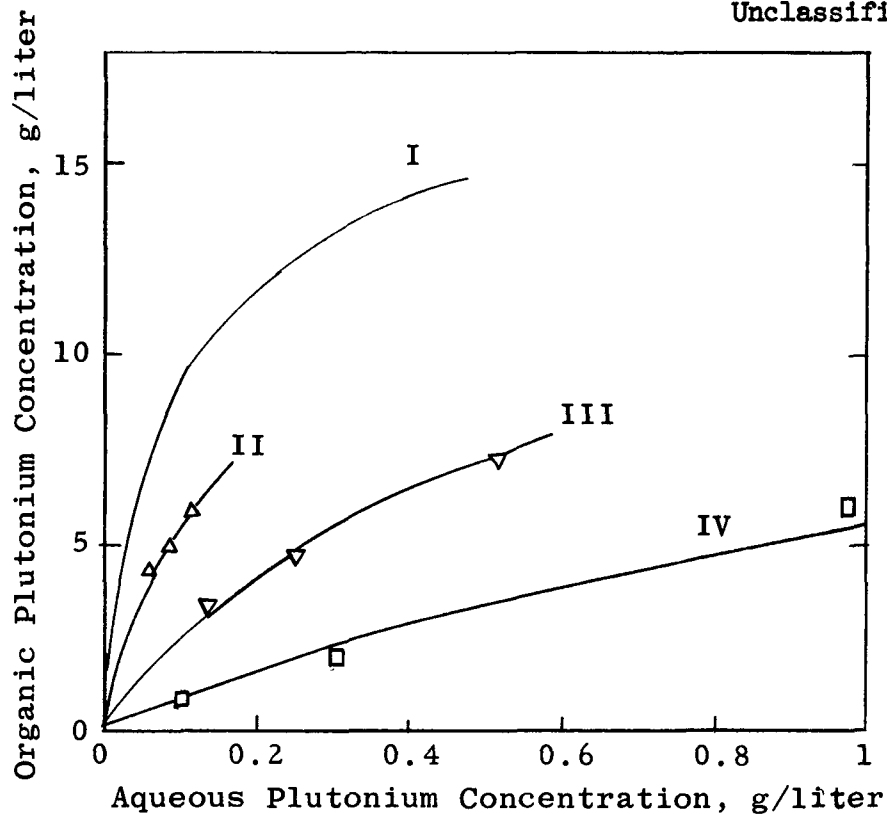


Fig. 2. Pu(IV) Extraction Isotherms. 0.28 M Trilaurylamine (EK) in Solvesso 100. Back extraction into 1.5 M HNO₃ with or without added H₂SO₄.

Curves: $E_a^0 = E_1 (0.28 - 3[\text{Pu}])^2$

- I No H₂SO₄, E₁ = 3300
- II 0.032 M H₂SO₄, E₁ = 1200
- III 0.113 M H₂SO₄, E₁ = 400
- IV 0.334 M H₂SO₄, E₁ = 120

Table 1. Organic Phase Stability

Amine and Diluent	Pu Loading, g/liter	
	1 Org. Phase	2 Org. Phases
<u>0.3 M Alamine 336 in--</u>		
Amsco 125-82	-	0
Amsco + 10% TDA	-	2
Solvesso 100	10	17
Solvesso + 10% TDA	15	-
Diethylbenzene	7	12
<u>0.3 M TLA(EK) in--</u>		
Amsco + 5% TDA	11	13
Solvesso 100	16	-
Diethylbenzene	16	-

Table 2. Pu(IV) Extraction Isotherms
Trilaurylamine or Alamine 336 near 0.3 M

$$E_a^O(\text{Pu}) \approx E_1 [\underline{M}_{\text{amine}} - 3 \underline{M}_{\text{Pu}}]^2$$

<u>M</u> HNO ₃	<u>M</u> NaNO ₃	<u>M</u> H ₂ SO ₄	E ₁
2	1	0	5000
1.5	0	0	3300
1.5	0	0.032	1200
1.5	0	0.113	400
1.5	0	0.334	120

With 0.3 M amine, extraction at flow ratios (Fig. 1) of A/O = 4/1 should be feasible with up to 0.015 M Pu in the feed, and A/O = 10/1 at lower plutonium concentrations.

The Pu(IV) extraction coefficients with tertiary amine remain high enough over a wide nitric acid concentration range (Fig. 3) to permit scrubbing at acidities either considerably higher or considerably lower than the feed acidity, as perhaps >>2 M HNO₃ for emphasis on eliminating ruthenium or <<2 M HNO₃ for emphasis on eliminating zirconium. Definition of the most useful scrub will be determined with actual feed solutions.

Although the plutonium extraction coefficients decrease rapidly with decrease of nitric acid concentration below 1 M (Fig. 3), they are not low enough for effective "water" stripping unless the tertiary amine concentration is considerably less than 0.1 M. Stripping by reduction with ferrous sulfamate and

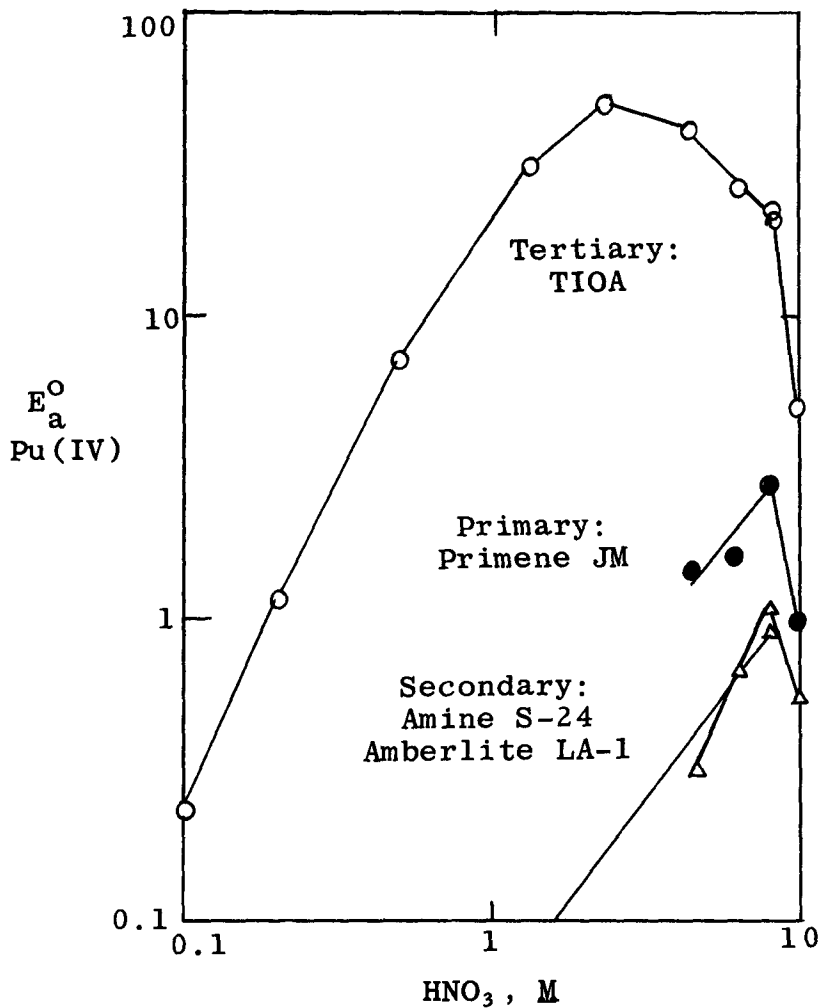


Fig. 3. Plutonium(IV) Extraction by 0.1 M Amines vs. Nitric Acid Concentration.

by complexing with sulfate are both effective. Since both would add major contaminants to the product stream, other possible stripping methods are being examined. Several water-soluble organic reductants are effective, notably hydroquinone, resorcinol, and ascorbic acid, but these may also be objectionable as residues in the product solution. The methods so far most promising for minimizing product contamination are stripping with organic-soluble reductants, e.g., di-tert-butylhydroquinone (Figs. 4 and 5), and stripping by complexing and displacement with acetic acid (Fig. 6).

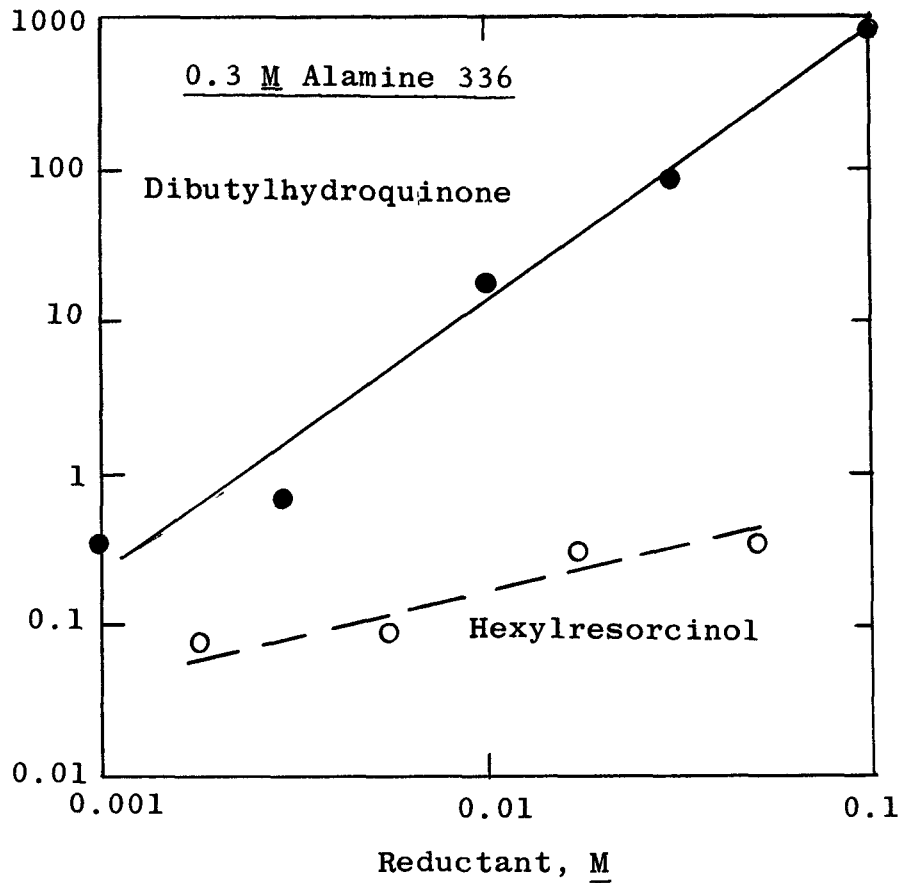


Fig. 4. Plutonium Stripping with Oil-Soluble Reductants. Solid reductant added in amount to give the indicated molarity in the organic phase; then plutonium stripped with 0.5 M HNO₃. Stripping coefficient in second of two equal-volume contacts.

~0.1 M Reductant
in 0.3 M Alamine 336

S_O^a (Pu)

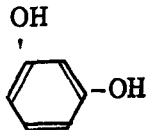
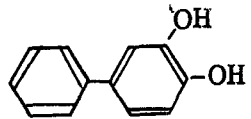
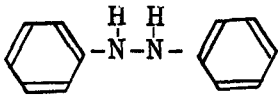
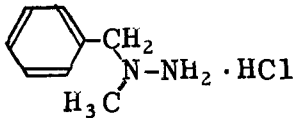
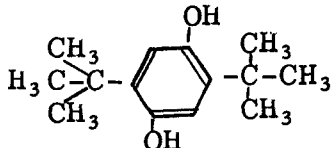
$\text{H}_3\text{C}-(\text{CH}_2)_5-$		Hexylresorcinol	0.6
		Phenylcatechol	35
		Hydrazobenzene	100
		Phenylmethylhydrazine hydrochloride	100
		Di- <u>tert</u> -butylhydroquinone	800

Fig. 5. Plutonium Stripping with Oil-Soluble Reductants. Solid reductant added in amount to give the indicated molarity in the organic phase; then plutonium stripped with 0.5 M HNO₃. Stripping coefficient in second of two equal-volume contacts.

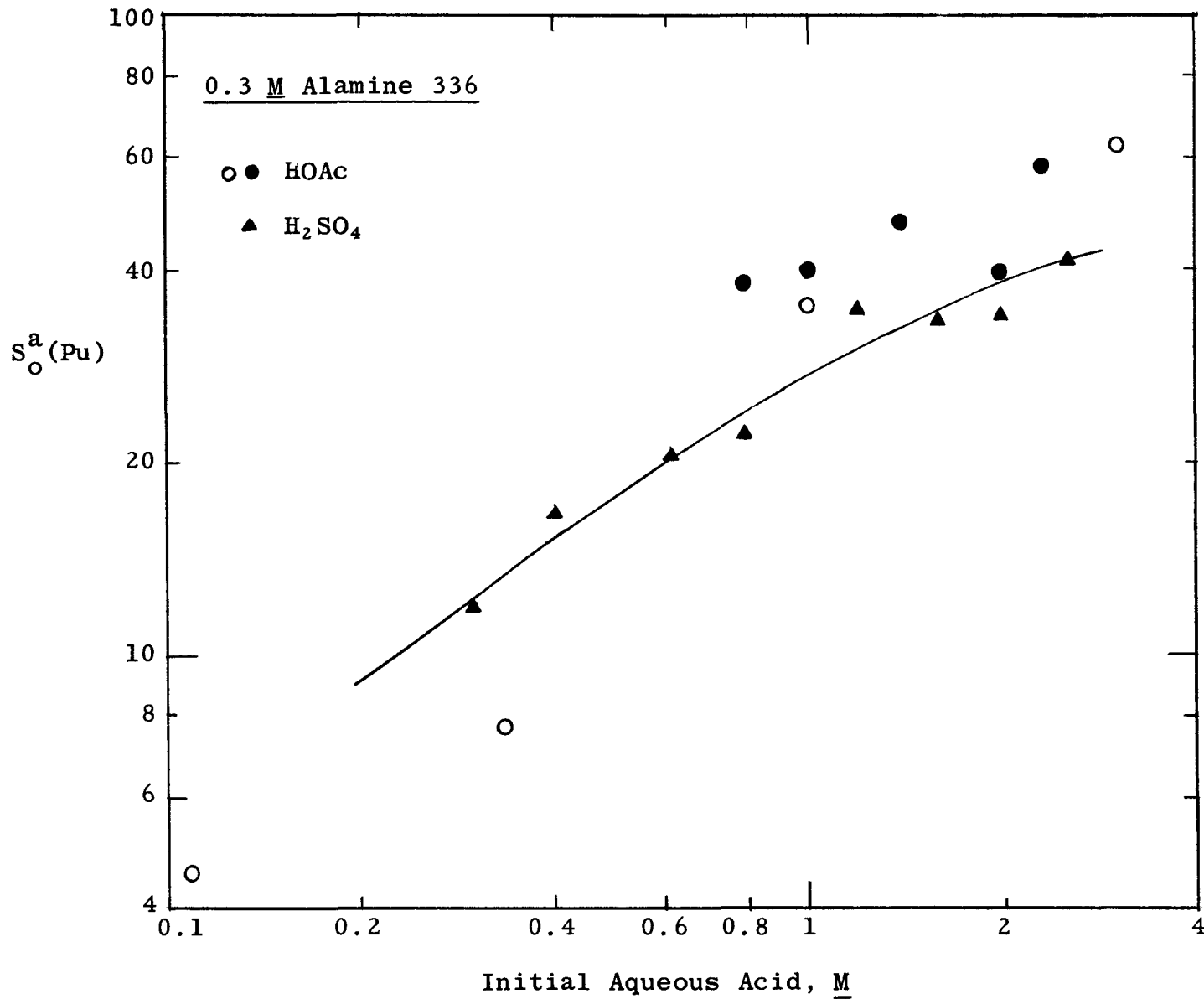


Fig. 6. Plutonium Stripping by Acetic and Sulfuric Acids. Geometric mean of stripping coefficients in two equal-volume contacts.

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