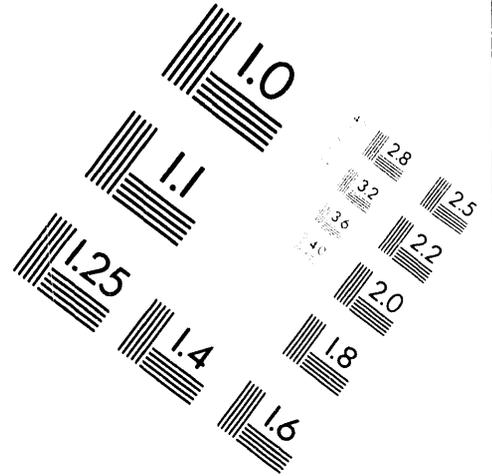
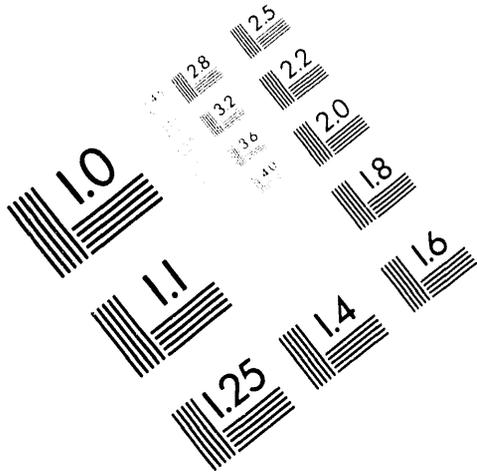




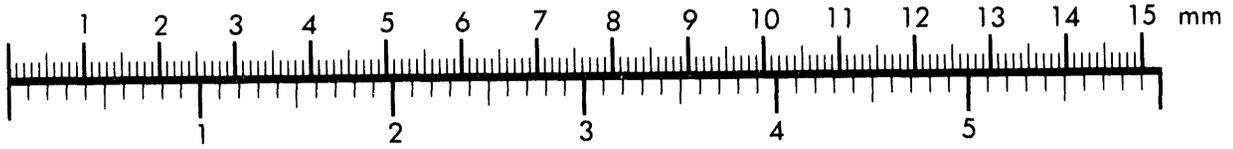
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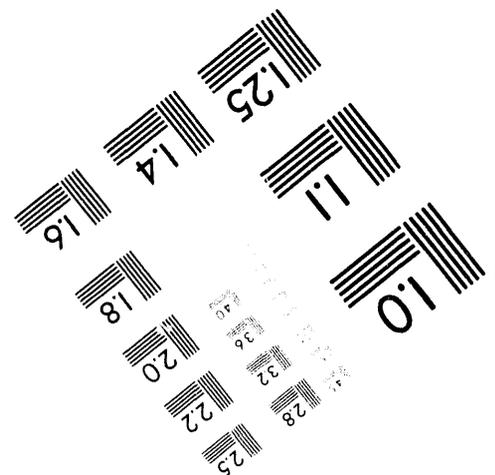
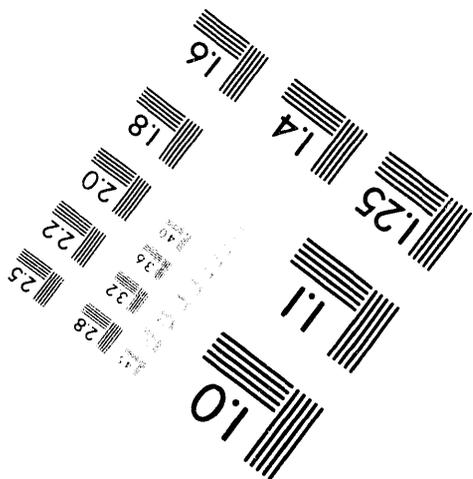
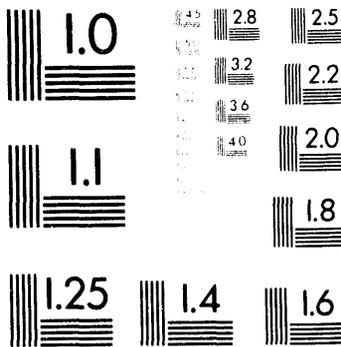
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SOLUBILITY OF PLUTONIUM AND WASTE EVAPORATION

by

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DOE Contract No. DE-AC09-89SR18035

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Keywords: Waste Supernate
Pu Solubility in Waste
Sludge Washing
Pu(IV) Oxidation

Retention : Permanent

Classification: U

Jama E. Saurin

Authorized Derivative Classifier

Solubility of Plutonium in Waste Evaporation

October 22, 1993

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Solubility of Plutonium in Waste Evaporation

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Issued: October 18, 1993

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1.0. Introduction

Chemical processing of irradiated reactor elements at the Savannah River Site separates uranium, plutonium and fission products; fission products and process-added chemicals are mixed with an excess of NaOH and discharged as a basic slurry into large underground tanks for temporary storage. The slurry is composed of base-insoluble solids that settle to the bottom of the tank; the liquid supernate contains a mixture of base-soluble chemicals--nitrates, nitrites aluminate, sulfate, etc. To conserve space in the waste tanks, the supernate is concentrated by evaporation. As the evaporation proceeds, the solubilities of some components are exceeded, and these species crystallize from solution. Normally, these components are soluble in the hot solution discharged from the waste tank evaporator and do not crystallize until the solution cools. However, concern was aroused at West Valley over the possibility that plutonium would precipitate and accumulate in the evaporator, conceivably to the point that a nuclear accident was possible.⁶ There is also a concern at SRS from evaporation of sludge washes, which arise from washing the base-insoluble solids ("sludge") with ca. 1M NaOH to reduce the Al and SO_4^{-2} content. The sludge washes of necessity extract a low level of Pu from the sludge and are evaporated to reduce their volume, presenting the possibility of precipitating Pu. Measurements of the solubility of Pu in synthetic solutions of similar composition to waste supernate and sludge washes are described in this report.

2.0 Summary

The solubility of Pu in synthetic waste supernate decreases from 5 ppm to 1 ppm as the waste is evaporated to ca. 2M NaOH, then increases to ca. 15 ppm at 5M NaOH. Synthetic waste supernate diluted 3:1, 10:1 and 100:1 with 1M NaOH to simulate sludge washes showed increased Pu solubility as the proportion of supernate increased. The Pu solubility was easily reversible. It is proposed that the increase in Pu solubility in high salt-NaOH solutions is due to partial oxidation of $\text{PuO}_2 \cdot x\text{H}_2\text{O}$ to the more soluble $\text{PuO}_2(\text{OH})_2$.

3.0 Data

Experimental Section

Synthetic Solutions

The synthetic waste supernate solutions were prepared from reagent-grade chemicals; the composition¹ of average waste supernate is shown in Table I. Since a clean separation of the waste supernate and the sludge wash solutions is not possible, the sludge wash solutions were considered to be mixtures of the 3M NaOH and waste supernate. The mixtures tested were 25, 10 and 1 volume % waste supernate in 1M NaOH.

Table I. Average Waste Tank Supernate

Compound	Concentration, M
NaOH	1.2
NaNO ₃	2.4
NaNO ₂	0.9
NaAlO ₂ *	0.5
Na ₂ CO ₃	0.2
Na ₂ SO ₄	0.2
NaCl	0.03
KF	0.02
Na ₂ C ₂ O ₄	0.02
Na ₃ PO ₄	

*Al added as Al(NO₃)₃•9H₂O; NaOH and NaNO₃ adjusted to compensate.

The solution is prepared in two portions--all chemicals except Al(NO₃)₃•9H₂O are dissolved in about 3/4 the final volume as one portion. The second portion dissolves Al(NO₃)₃•9H₂O and the Pu(IV) nitrate spike in water. The two solutions are mixed by pouring the Al-Pu solution into the basic solution with high agitation. Hydrated PuO₂ precipitates from the oversaturated solution after 1-2 hours as a fine green solid.

This oversaturation approach to solubility differs from the undersaturation method used by most investigators²⁻⁵ which adds the Pu spike as a small volume of concentrated solution. The undersaturation method has the disadvantage that Pu immediately precipitates, and the solution must be stirred and sampled until a steady-state composition is reached. The oversaturation method assures that the initial solution is saturated with Pu and the Pu solid phase is a fine material susceptible to re-dissolution. The Pu precipitate in the waste tanks should be similar to that produced from oversaturation.

To simulate sludge wash solutions, three solutions were mixed: two to make up the spiked synthetic waste supernate and a NaOH solution to represent the sludge washing solution. As described above, Pu precipitated within a few hours.

Experimental Procedure

The procedure in all experiments aimed to simulate evaporator operation. The solution was evaporated slowly and sampled at chosen levels of evaporation. Some solutions were diluted and mixed, then re-sampled to determine if the solubility determined during the evaporation could be reproduced for a solution of the same composition. The composition of the waste solutions changed during evaporation as different components crystallized out of the saturated solution. In general, NaOH and NaCl concentrations increased, NaNO₃ increased, then decreased, NaNO₂ and NaAlO₂ increased and Na₂SO₄, Na₂CO₃, Na₃PO₄, and NaC₂O₄ crystallized from solution as the evaporation continued. Figures 1 and 2 are graphs of the solution composition as the solution is evaporated⁶.

Analyses

Samples were filtered with 0.2 μ pore syringe filter cartridges, and Pu separated from the filtered solution by anion exchange. The sample was diluted with 4 volumes 9M HNO₃, and, after acidifying, treated with Fe(SO₃NH₂)₂ and NaNO₂ to assure a Pu(IV) valence. Column feed, 8M HNO₃ wash and 0.25M HNO₃ elutrient solutions were collected separately, and aliquots counted and pulse analyzed to determine the Pu concentration. Some analyses were repeated two weeks after the original determination with no significant difference in the result.

Speciation experiments with NaOH-NaNO₃ solutions omitted the valence adjustment before anion exchange. Under these conditions, Pu polymer, Pu(V) and Pu(VI) species are not absorbed by the anion column, and were removed in the column washing with 8M HNO₃. Pu absorbed on the column was eluted with 0.25M HNO₃; the ratio of the Pu found in the column feed and wash effluents to the total Pu was assigned as a measure of oxidized Pu. Attempts to perform similar experiments with the synthetic waste supernate found about 10% of the Pu in the combined feed and wash effluents, probably due to Pu(IV) polymer. The HNO₂ formed by acidifying the sample would reduce Pu(V) and Pu(VI) to Pu(IV).

Solutions were titrated for hydroxide, carbonate and aluminate with standard HCl. The procedure involved adding excess 1M BaCl₂ solution to precipitate BaCO₃ from one aliquot and titrating to pH 9.3-10.5 (thymolphthalein indicator) to determine hydroxide, then titrating to pH 5.2-6.8 (bromocresol purple indicator) to determine aluminate. Carbonate was estimated by titrating a separate aliquot to pH 5.5-6.8 and subtracting the titre of the first aliquot. Other species were determined by ion chromatography (NO₃⁻, NO₂⁻, Cl⁻, SO₄²⁻, C₂O₄²⁻, and PO₄³⁻) and inductive plasma chromatography (Al³⁺) on identical solutions that contained no plutonium. The composition of solid phases was determined by x-ray diffraction.

4.0 Results

The solubility of Pu as synthetic waste supernate evaporated is shown in Figure 3, a composite of two separate determinations. The minimum at ca. 2M NaOH suggests that there are at least two effects involved in Pu solubility; an attempt to explain this result will be made in this report. The solid phase in these experiments was identified as PuO₂·xH₂O by x-ray diffraction. The solubilities are in general agreement with those of Delegard³ and Hobbs, et al.^{4,5} on similar solutions. Differences from earlier studies might be expected from the oversaturation approach to solubility and the inclusion of minor components--NaCl, Na₂C₂O₄, Na₃PO₄, KF-- in these tests but not in those of Delegard or Hobbs, et al. However, these results and those of previous measurements are in reasonable accord.

The results of measurements of the solubility of Pu as initial mixtures 1, 10 and 25 vol % waste supernate-1M NaOH were evaporated are shown in Figure 4. In general, the Pu solubility increases as the mixtures are evaporated, and also increases as the proportion of waste supernate increases. The solid phase in these experiments was identified as PuO₂·xH₂O by x-ray diffraction. Equilibrium was evidently achieved in these experiments, as the solubilities found when concentrated solutions were diluted agreed with the solubilities found when dilute solutions were concentrated. From these data, both the salt and NaOH concentrations affect Pu solubility.

Two types of experiments attempted to identify a chemical component that was responsible for the increase in Pu solubility as the synthetic waste supernate was evaporated. The first experiment tested the effect of chloride ion on the solubility by evaporating a 1.5M NaOH-0.1M NaCl solution, and sampling during boil-down, as before. The results (Figure 5) show a lower solubility than was found for the synthetic waste solution, with about the same dependence on NaOH concentration that was found in the runs with supernate. This result could be best explained as a valence change of a fraction of the Pu as the solution became more concentrated. An increased solubility due to the increase in chloride ion would not show the minimum found at 3M NaOH.

A second series of experiments aimed at identifying the chemical component involved evaporating a NaOH solution 50%, measuring the solubility, then diluting back to the original volume, adding a component, evaporating this solution 50%, and repeating this procedure for the major components. The results of these experiments (Table II) actually showed no effect for any of the components tested.

Table II
Effect on Solution Components on Pu Solubility

Component	Pu, mg/L
2M NaOH	0.24
2M NaOH-4.8M NaNO ₃	0.43
2M NaOH-4.8 NaNO ₃ -1.8M NaNO ₂	0.34
2M NaOH-4.8M NaNO ₃ -1.8M NaNO ₂ -1M NaAlO ₂	0.46
plus 0.04M KF	0.40

The inference that Pu was oxidized by O₂ (air) in high salt-NaOH solutions was also investigated by speciation experiments on NaOH-NaNO₃ solutions. Pu(IV) might be oxidized to Pu(V) by



followed by the disproportionation



or directly, as



Anion exchange will absorb Pu⁺⁴ as the hexanitrate complex, but will not absorb Pu(IV) polymer, Pu(V) or Pu(VI). The column feed and wash effluents were assumed to be a mixture of Pu polymer, Pu(V) and Pu(VI); the ratio of non-absorbed Pu to total Pu during evaporation of a 0.35M NaOH-2M NaNO₃ is shown in Table III.

Table III
Non-Absorbing Pu to Absorbing Pu Ratio

NaOH, M	Pu, mg/L	[(Pu (V) + Pu(VI))/Pu Total]
0.35	0.71	0.18
0.64	1.1	0.38
1.13	1.4	0.42
Solution diluted to original volume with 1M NaOH added		
1.5	0.28	0.34
1.98	0.49	0.30
3.69	2.82	0.46
4.76	10.8	0.41

The correlation is rather imperfect, but the measurements that show higher solubilities also show a higher ratio of [Pu(V) + Pu(VI)]/ total Pu.

The Pu solubility was also measured in 20M NaOH, performed in a capped vial to prevent O₂ and CO₂ access to the solution. The Pu solubility found was 34 mg/L with a ratio of 0.6. The solution was then adjusted to 0.01M H₂O₂, stirred overnight, and then re-measured as 334 mg/L; ratio 0.4. A second 0.01M addition of H₂O₂ reduced the solubility to 98 mg/L after one week. An attempt to reduce the solution with Fe₃O₄ lowered the solubility to 66 mg/L, with a [Pu(V) + Pu(VI)]/Pu total ratio of 0.9. The effect of the Fe₃O₄ treatment is presumed to stabilize Pu(V); other solubilities are presumed to be Pu(IV)-Pu(VI) mixtures. These solutions are concentrated enough to show some color; sophisticated spectral measurements might positively identify the valence state of the Pu in solution.

5.0 DISCUSSION

The increase in Pu solubility with evaporation of the waste supernate indicates that Pu-bearing solids will not accumulate in the waste evaporator as long as the evaporation ratio is greater than 3 to 1. The Pu solubility was found to be reversible in these solutions, so should Pu be crystallized out of solution, a further evaporation of the solution would re-dissolve the precipitate. This agrees with experience at West Valley, where an evaporator clean-out found substantial uranium accumulation but no unusual Pu accumulation in the evaporator.⁶

The minimum in Pu solubility at ca. 2M NaOH indicates that two (or more) effects are involved in determining Pu solubility in strong base-high salt solutions. Air oxidation of some of the Pu(VI) to the more soluble Pu(V) or Pu(VI) is considered the most likely explanation. The high salt-NaOH solutions could affect the oxidation potentials

sufficiently to allow some oxidation to occur, with an accompanying increase in Pu solubility.

Although Pu(V) is a possible valence, the experiments with H_2O_2 and Fe_3O_4 suggest that Pu(VI) is the probable valence of the oxidized species. Pu(V) has been found as the predominate valence in 5M NaCl in neutral pH solution⁷ and carbonate ground waters⁸, but would be expected to disproportionate in strong base⁹.

The results reported here could be modified by the effects of oxidizing or reducing species produced by the radiation field in the SRS waste tanks. Previous studies⁷ have found that radiation produces ClO^- in chloride solutions, which then oxidizes Pu(IV) to Pu(V). The variety of components in SRS waste supernate raises the possibility that either oxidizing or reducing agents, or both, might be formed in the intense radiation field of the waste tanks.

Acknowledgements

The author is indebted to D. Walker and C. Parkman (Analytical Development Section) for experimental assistance.

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Figure 1.
Major Salt Concentrations in Evaporated Synthetic Waste Supernate

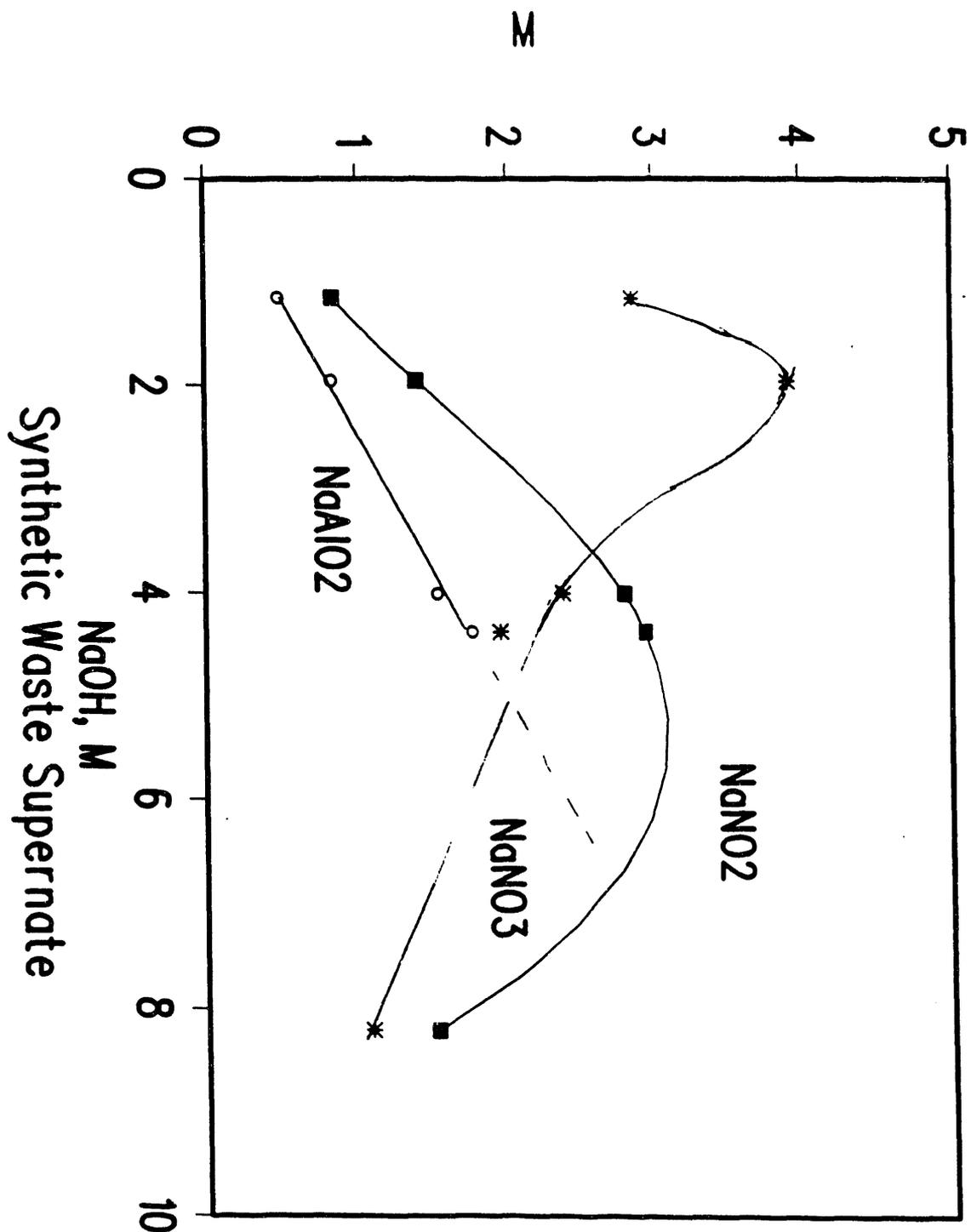


Figure 2.
Minor Salt Concentrations

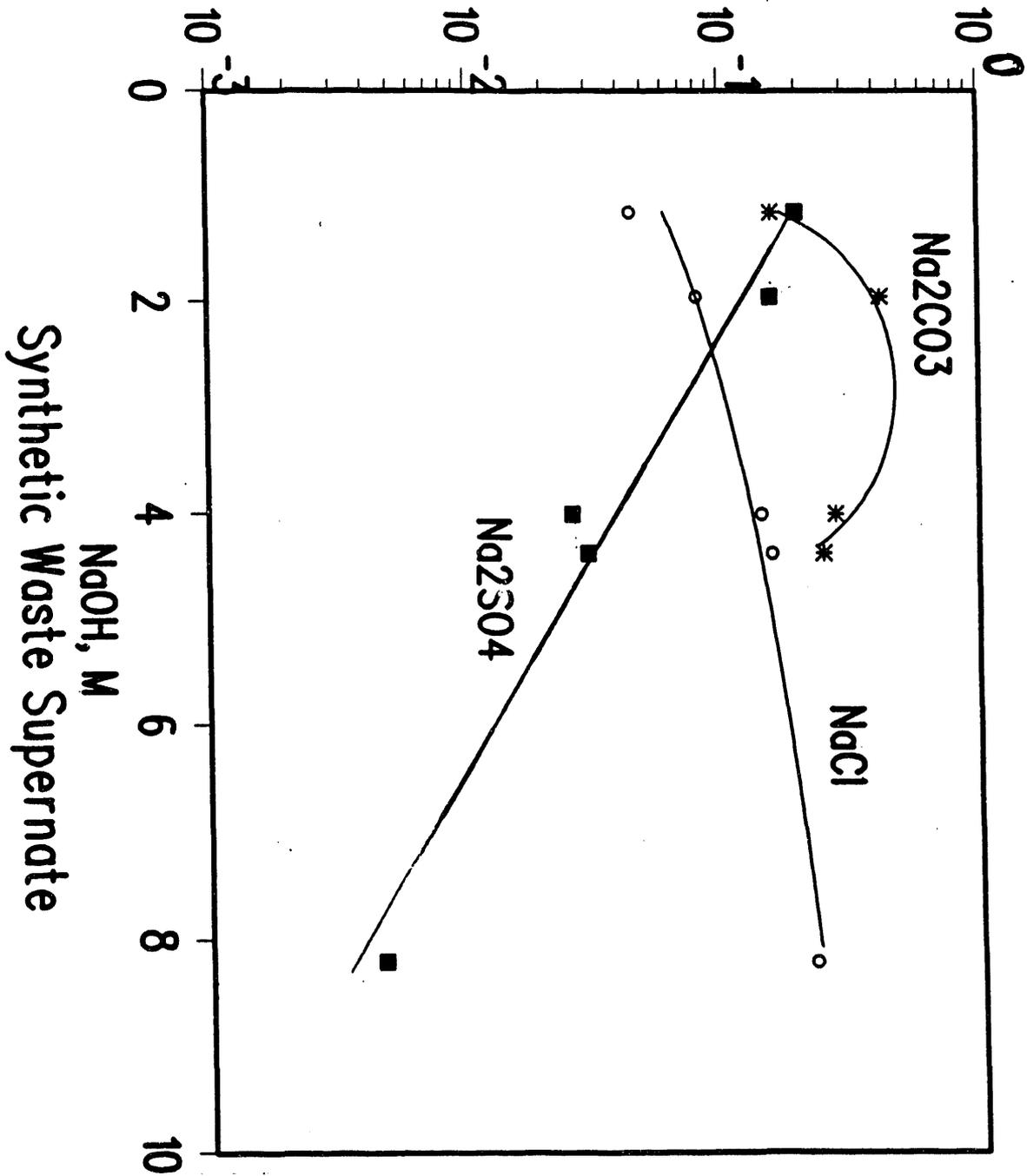


Figure 3.
Plutonium Solubility in Evaporated Waste Supernate

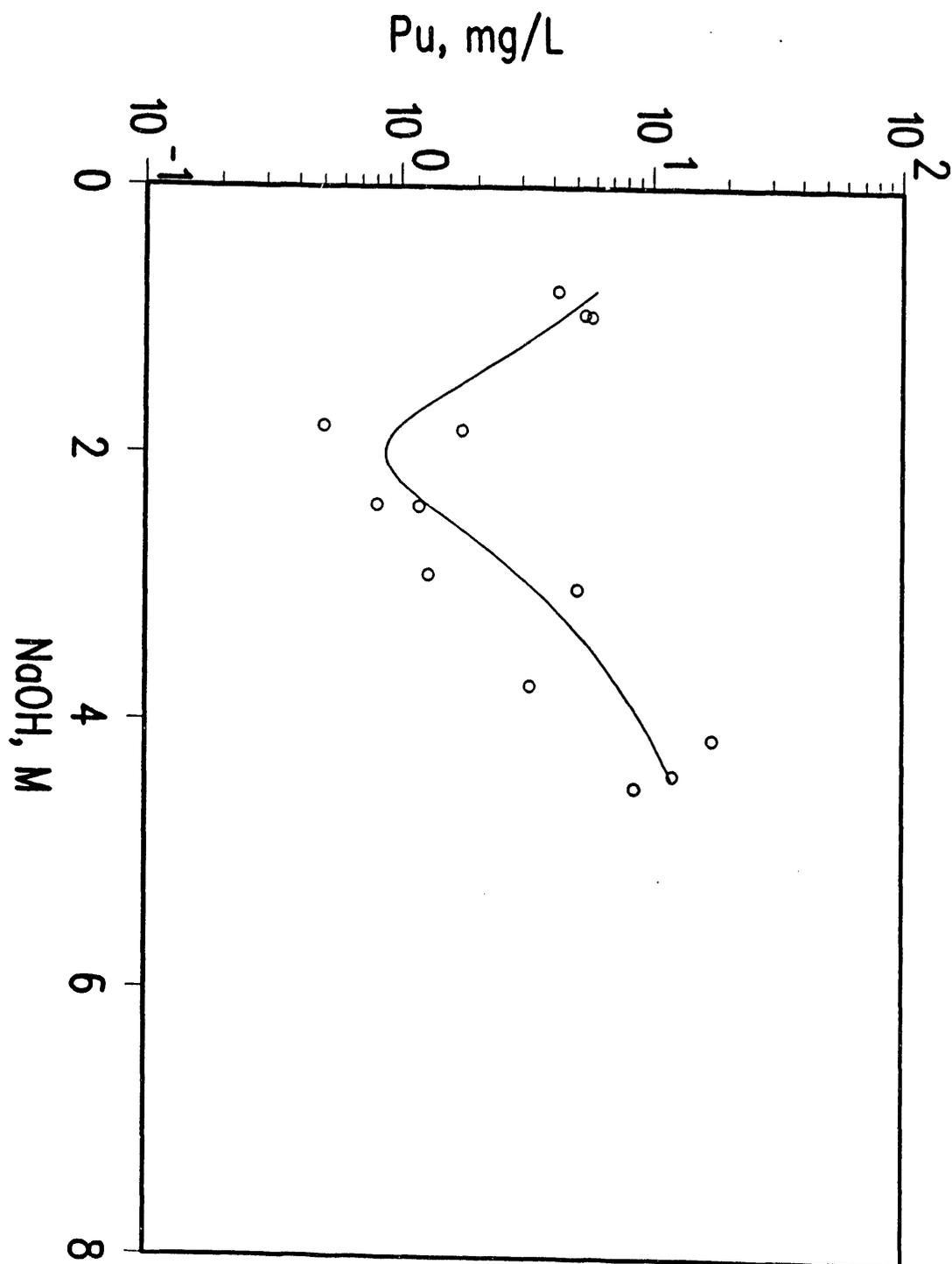


Figure 4.
Plutonium Solubility in Simulated Sludge Wash Solutions

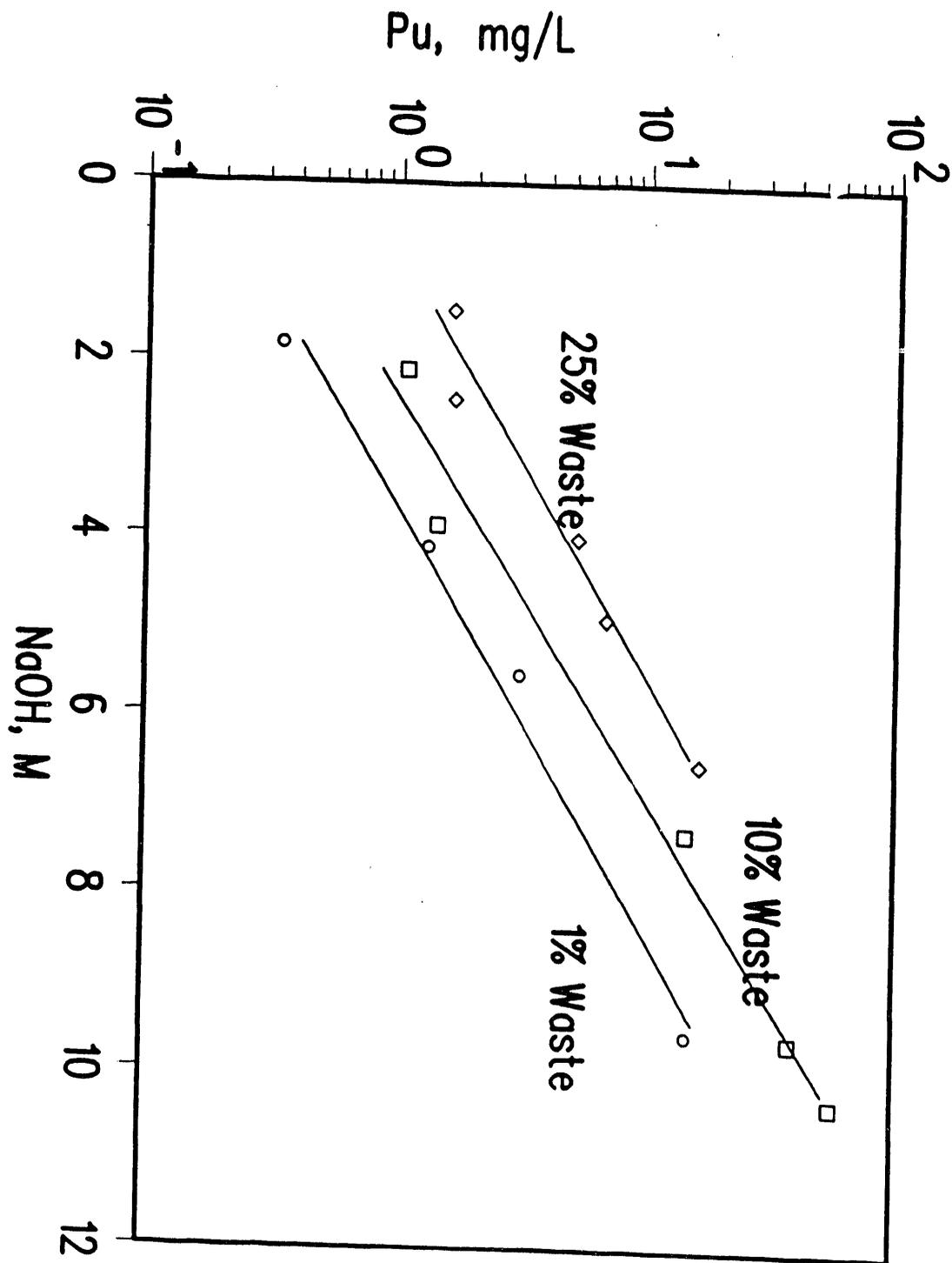
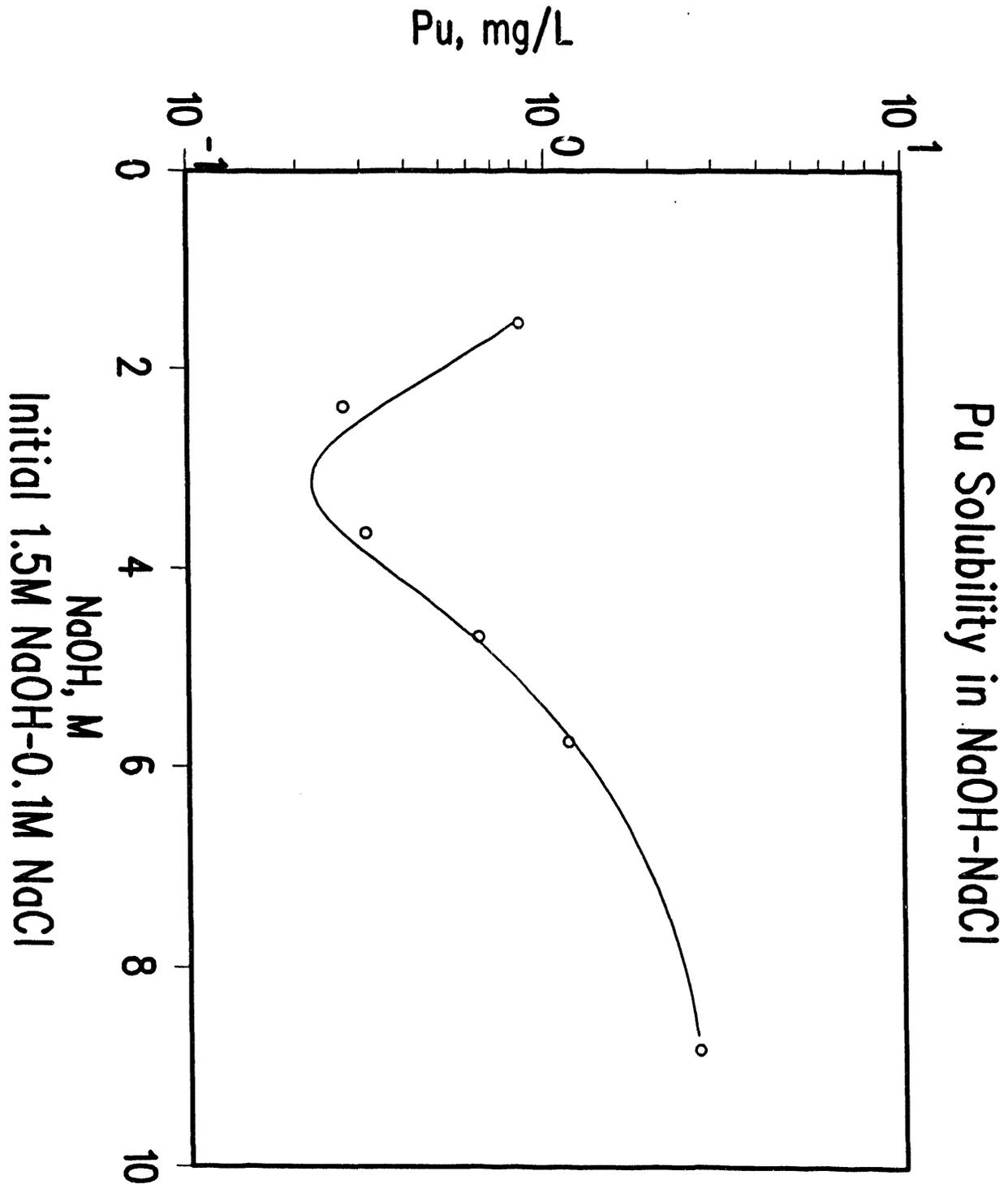


Figure 5.
Plutonium Solubility in NaOH-NaCl Solutions. Initial Concentrations, 1.5M
NaOH, 0.1M NaCl



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