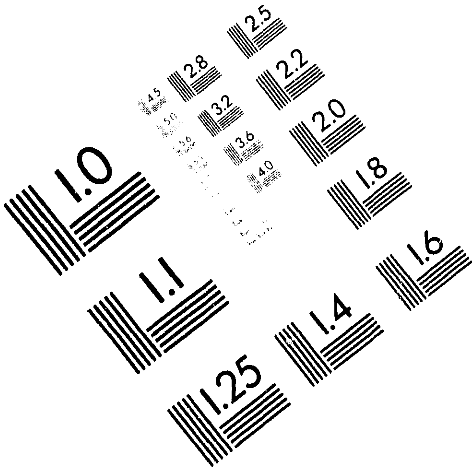

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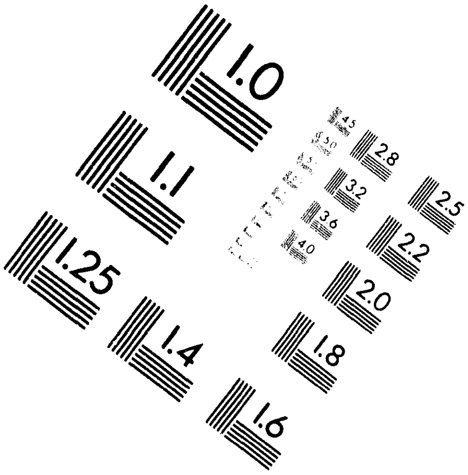

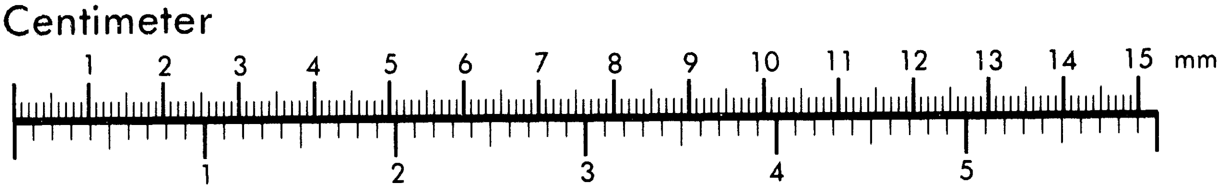

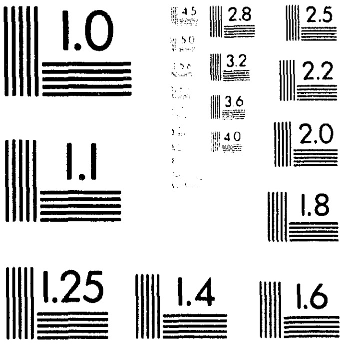

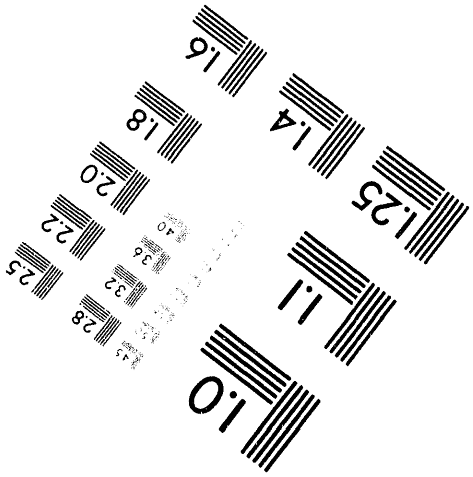

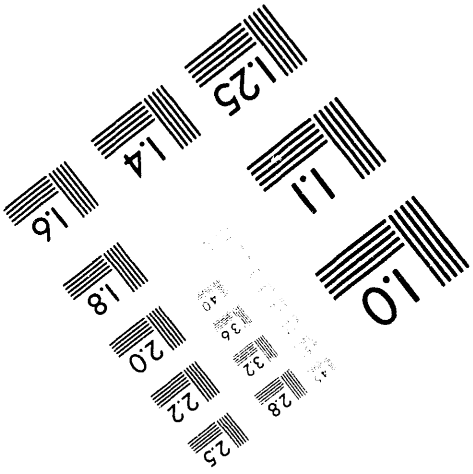

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WSRC-MS-94-061

RECENT RESULTS ON THE SOLUBILITY OF URANIUM AND PLUTONIUM IN SAVANNAH RIVER SITE WASTE SUPERNATE

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Keywords: SRS Waste Supernate, U solubility, Pu solubility, Waste Evaporation

RECENT RESULTS ON THE SOLUBILITY OF URANIUM AND PLUTONIUM IN SAVANNAH RIVER SITE WASTE SUPERNATE (U)

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INTRODUCTION

High-level waste (HLW) is stored at the Savannah River Site (SRS) in a highly alkaline condition to prevent corrosion of the carbon steel storage tanks. Major components in the liquid phase include nitrate, hydroxide, nitrite, aluminate, carbonate and sulfate. Minor components include chloride, fluoride, oxalate and phosphate. The low solubility of uranium and plutonium in the HLW becomes significant to nuclear safety analyses when the supernate is evaporated to solids to conserve waste storage space and then redissolved to process for permanent disposal. The study of uranium and plutonium solubility in synthetic waste tank solutions was initiated to define actinide behavior during waste removal operations.

BACKGROUND

Since startup of the site, HLW at the SRS has been processed and stored in underground tanks as shown in Figure 1. Waste, primarily from the Purex, HM and B-Line processes, was neutralized and discharged to the waste tank farm. The base-insoluble solids ("sludge"), which include the actinides and most of the fission products, settle to bottom of the tank; the supernatant liquid ("supernate") contains ^{137}Cs, ^{99}Tc in a 5M Na^+, 1.4M OH^- salt solution. After decay of the short-lived fission products, the supernate is decanted and evaporated (Tank Farm Evaporator) to reduce its volume. Upon cooling, salts crystallize from the concentrated supernate. Further evaporation of the concentrated supernate crystallizes more salts. This process is continued until the tank is filled. A layer of concentrated supernate is maintained above the crystallized salts.

For permanent disposal, the sludge will be mixed with a borosilicate frit and vitrified in the Defense Waste Processing Facility. To reduce the quantity of glass produced, the sludge is washed (Figure 2) with water to reduce the soluble salt content. Sludges high in aluminum will also be treated with ca. 3M NaOH and heated to 80° C. to dissolve the aluminum. These pretreatment steps will be performed in the waste tanks.

Criticality evaluation of the waste tank evaporation has conjured up two scenarios that caused this investigation of U and Pu solubility in the waste supernate. The first scenario involves tanks filled with salt cake, and presumes that during the redissolution of the salt the fissile isotopes do not dissolve, but settle to the bottom of the tank and could potentially form a critical mass. The second scenario considers that U and/or Pu would crystallize in the evaporator during supernate and sludge wash evaporations, and could lead to the accumulation of a critical mass in the evaporator. The study of the solubility of U and Pu in the waste supernate was initiated to evaluate these scenarios.

EXPERIMENTAL SECTION

Synthetic waste solution were prepared from chemically pure reagents; the composition of the average waste supernate is shown in Table 1. Measurements of the concentration of uranium in samples were performed by a kinetic fluorescence method ("Chemchek"), by x-ray fluorescence ("xrf") and/or inductively coupled plasma/mass spectrometry (ICP/MS). Comparison of the results of the three methods showed substantial agreement. Plutonium was assayed by alpha-counting, coupled with alpha pulse-height analysis to assure the rejection of other alpha-emitting radioactivity, and ICP/MS. Pu was separated from the mass of salts for analysis by anion exchange before counting. Most anions were analyzed by ion chromatography; Al was determined by ICP; carbonate and hydroxide by titration.

Table 1

Composition of Synthetic SRS Waste Supernate and Variable Range Explored in Statistical Design Tests

Component	Concentration	Range Explored in SD Experiment
NaOH	1.4M	0.5-2.0 M
$NaNO_3$	2.4M	1.0-4.0 M
$NaNO_2$	0.9M	0.1-2.0 M
$NaAlO_2$	0.5M	0.05-0.36 M
Na_2CO_3	0.2M	0.02-0.30 M
Na_2SO_4	0.2M	0.02-0.40 M
NaCl	0.03M	(a)
KF	0.02M	(a)
$Na_2C_2O_4$	0.02M	(a)
Na_3PO_4	0.01M	(a)
		Temp. 25°, 60° C

(a) Not included in statistical design tests

Uranium and plutonium were added to synthetic waste solutions by the "undersaturation" (addition of a concentrated solutions of U and Pu to the test solutions) in the SD tests, and by "oversaturation" (mixing a dilute acidic solution with a solution of the basic components) in the evaporation experiments. Test solutions were agitated betweeen sampling; samples were filtered through 0.45 or 0.2μ syringe filters before analyses. Particle sizes were determined with a Microtrack II laser scattering instrument.

Statistical design measurements were carried out over a 6-month period although the change from the first to the last sample of a particular solution was usually within a factor of two, and occasionally identical. Samples from evaporation and/redissolution experiments were usually analyzed within a week of sampling.

Results

The particle sizes of precipitated U was found to be considerably larger from the undersaturation than the oversaturation method of addition; after 16 hours stirring 10% of the solids were <3.3μ, 50% <18μ and 90% <60μ from undersaturated solutions. The comparable values for oversaturated solutions were 10% <2.3μ, 50% <3.8μ and 90% <13μ. Solids from a neutralized synthetic High Activity Waste Concentrate (HAWC) had approximately the same size distribution as the solids from oversaturated solutions.

Statistical Design Experiments

Solubilities from the statistical design tests were investigated to screen for significant factors and interactions among the components (Table 1) of the salt solutions. Over the range of hydroxide concentrations from 0.5 to 2.0 molar, the uranium solubility ranges from 2 to 10 mg/L (see Figure 3). The solubility of plutonium is lower, ranging from 0.01 to 1.0 mg/L. Note however, that at the bounding hydroxide concentrations, the plutonium and uranium concentration can vary by factors of between 3 and 30 depending on the concentrations of the other solution constituents.

Linear statistical models were developed from the results to allow prediction of solubilities within the range of variables investigated. Abbreviated equations are:

$$\mathrm{Pu(mg/L)} = 0.58[\mathrm{CO_3}] - 0.35[\mathrm{SO_4}] + 0.70\,[\mathrm{OH}][\mathrm{SO_4}] + 0.09[\mathrm{OH}][\mathrm{NO_2}] + 0.06[\mathrm{NO_3}][\mathrm{NO_2}] - 0.10[\mathrm{OH}][\mathrm{NO_3}][\mathrm{NO_2}]$$

$$\mathrm{U(mg/L)} = 3.02 + 0.48[\mathrm{NO_3}] - 0.90[\mathrm{NO_2}] + 3.91[\mathrm{OH}] - 4.81[\mathrm{CO_3}] - 0.92[\mathrm{OH}][\mathrm{NO_3}]$$

(Brackets [] denote molar units.)

Temperature was found to have an insignificant effect on the solubilities. For salt solutions within the range of the statistical design study, upper 95% tolerance limits for Pu and U are 1.7 mg/L and 17 mg/L, respectively.

Figure 4 shows a plot of plutonium solubility as a function of hydroxide concentration for the factorial design test and available literature data[6]. A quadratic model was fitted to the expression

$$\log[Pu] = -6.493 + 1.270\log[OH] + 0.505(\log[OH])^2$$

Because of the wide range of solution compositions, the solubility of plutonium can vary by as much as three orders of magnitude for any given hydroxide concentration and remain within the prediction interval. Additional tests are planned to determine the solubility of plutonium at lower hydroxide concentrations and also to determine the effects of coprecipitation with metal ions such as iron, manganese, nickel and aluminum.

Evaporation Studies

Simulated evaporator experiments involved evaporation of the a synthetic average waste supernate solution (Table 1), sampling the solution as the evaporation proceeded. During the course of the evaporation, salts crystallized from the solution, and thus the composition of the solution changed. Figures 5 and 6 show the composition of the solution as the salts crystallize. Concentration of sludge washing solutions was simulated by assuming that the decantation of supernate from sludge would leave a substantial heel of supernate to mix with the sludge washing solution. Succeeding sludge washes would then contain lesser amounts of supernate. Evaporation of sludge washes was simulated by evaporating mixtures of supernate and 1M NaOH.

The solubility of U during evaporation is summarized in Figures 7 and 8. In general, the solubility of U decreases to a value of 5-10 mg/L as the solution is concentrated above 5M NaOH. Figure 7 shows the data from two evaporations of synthetic supernate; Figure 8 shows the data from evaporation of both synthetic waste supernate and sludge wash-supernate mixtures. The solid phase from several evaporations was identified as "$Na_2U_2O_7$" by x-ray diffraction.

Redissolution of U with the crystallized salts found a distinctly lower solubility (2-4 mg/L) than when U was precipitated from solution. Typical data, including attempts to enhance the solubility with complexing agents, is shown in Table 2.

Table 2

Dissolving Tests on Salt Cake

Dissolving Solution	Mixing Time (days)	Final Solution Concentration NaOH, M	NaAlO$_2$,M	Na$_2$CO$_3$,M	U, mg/L
H_2O	1	1.65	1.44	0.26	3.8
H_2O	2	0.55	0.47	1.59	1.6
0.2M Na_2CO_3	1	0.32	0.73	0.79	1.5
0.2M Na_2CO_3	6	0.16	0.37	0.90	1.8
0.5M $NaHCO_3$	5	pH 9	0.58	0.85	34
0.01 M EDTA	1	3.16	1.40	0.23	3.2
0.001 M EDTA	7	2.38	1.39	0.67	2.7

The solubility of Pu during evaporation is shown in Figure 9, a double-valued curve that suggests that two or more factors influence Pu solubility. The solubility increases as the evaporation concentrates the solution to about 10 mg/L at 5M NaOH. The solubility in mixtures of synthetic supernate and sludge washes increases as the salt concentration increases (Figure 10). The solid phase in these tests was identified by x-ray diffraction as $PuO_2 \bullet xH_2O$. The solubility was normally reversible, i.e., dilution of an evaporated solution returned the Pu concentration to the same value it had before evaporation.

DISCUSSION

The major finding of these studies is that as supernate solutions are evaporated, U becomes less soluble, and Pu becomes more soluble. The presumption of accumulation is therefore more credible for U than for Pu, although the location of the accumulation--evaporator, sludge, or salt--will depend on physical factors, such as particle size, mixing, and equipment geometry. The solubility results conform with the results from an acid clean-out of the West Valley waste evaporator[1]. The acid washes removed 10.1 Kg U and 255 g Pu, indicating a substantial accumulation of U but an insignificant accumulation of Pu.

The difference between U solubility on precipitation and redissolution indicates that under the conditions of these experiments, U solubility is not an equilibrium process, and thus is influenced by manner of precipitation, particle size, etc. as well as by the composition of the solution. A possible explantaion might be found in the complex nature of the solid phase, which has been formulated as$_3$ $3Na_2O \bullet 7UO_3$ by Wamser, et.al.[2], and $Na_2O \bullet 6UO_3$ by Ricci and Loprest[3]. The latter propose that there are solid solutions of Na_2O in UO_3 with Na/U$_3$ratios from 8/11 to 1/3. The soluble species have been deduced[3] as polymeric species such as $U_2O_5^{2-}$, $U_3O_8^{2+}$ and $U_3O_8(OH)^+$. The kinetic path between the solution polymer and the solid polymer may depend on the transfer of U via species of low concentration, and thus might require a lengthy period to attain equilibrium.

Plutonium solubility appears to be readily reversible, indicating an equilibrium between the species in solution and the solid phase. The decreasing solubility as NaOH increases below 2M NaOH is consistent with a $Pu(OH)_4 \cdot xH_2O$ species, but the increase in solubility with increasing NaOH above 2M NaOH suggests that another factor has come into play. A conceivable explanation for this phenomenon is the air oxidation of some of the Pu from the IV valence to the more soluble V or VI state either by

$$4PuO_2 \cdot xH_2O + O_2 + 2H_2O \text{ ----> } 4PuO_2(OH) + (x-2)H_2O$$

possibly followed by

$$2PuO_2(OH) \text{ ----> } PuO_2 + PuO_2(OH)_2$$

or directly, as $PuO_2 \cdot xH_2O + O_2 + 2H_2O \text{ ----> } 2PuO_2(OH)_2$.

Evidence has been adduced for Pu(V) as a stable species in highly basic solutions. Pu(V) species have been produced by electrolytic reduction of Pu(VI) in 4M NaOH, and the absorption spectra of Pu(V) measured[5]. Delegard[6] has published absorption spectra for Pu in 15M NaOH that agrees with this spectra, and reports an experiment in a 10M NaOH Pu solution that can be interpreted as demonstating either a V-VI or a IV-VI mixture. Other studies, however, predict that Pu(V) would disproportionate in strong base to a mixture of Pu(IV) and Pu(VI) [7,8].

Assignment of a Pu(V) valence to the Pu in the supernate rests on the determination[5] of Pu(V) stability in strong (>2M) NaOH, and the assumption that the valence is the same in NaOH and NaOH-salt solutions. As Figure 7 shows, the solubility is strongly affected by the presence of the salts, and the possibility of a change in valence from the expected Pu(V) cannot be discounted.

Speciation of the Pu in these solutions could resolve question of Pu valence, but the presence of high levels of nitrite in the supernate prevents the use of simple chemical methods, such as solvent extraction or anion exchange from acidified solutions. On acidification, nitrite converts all Pu present to Pu(IV), and thus the identity of the valence in the basic solutions is lost.

One factor that has not been explored in this study is the effect of the 4×10^4 R/h radiation in the waste tanks. The free radicals generated by this radiation field could affect the valence of Pu in the actual waste supernate, and thus affect the solubility. Uranium solubilitywould not be expected to be affected by radiation, since the lower valences of uranium are oxidized to the uranyl valence by air alone in a basic system. A preliminary experiment indicates that the solubility of Pu is increased four-fold by exposure in a ^{60}Co source for 6 days. Further studies are in progress; in the meantime, Pu solubility in actual waste supernate remains in question.

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Storage and Concentration of High-Level Waste

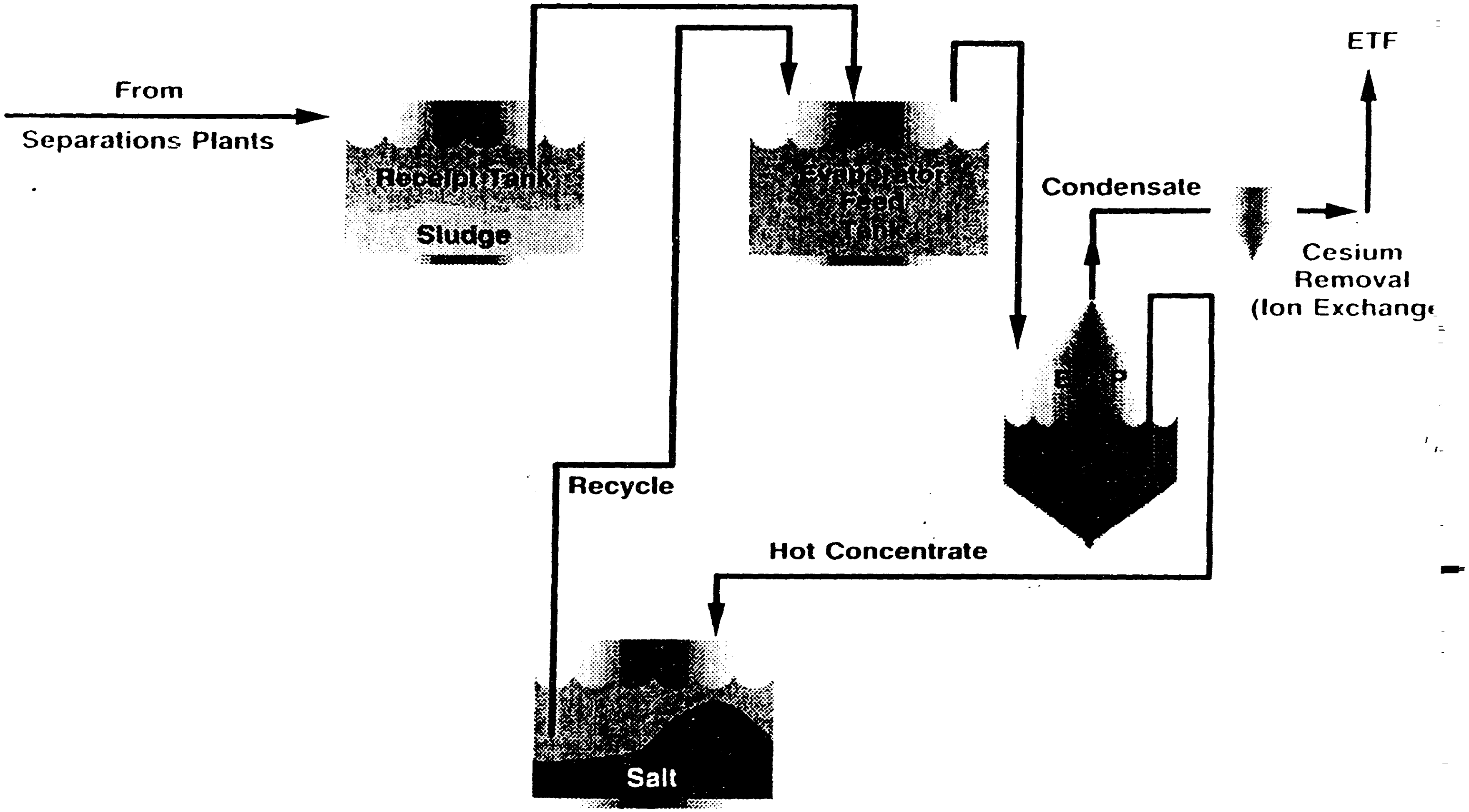

Figure 1.
Storage and Concentration of High-Level Waste at SRS

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Figure 2.
Sludge Washing and Al Dissolution at SRS

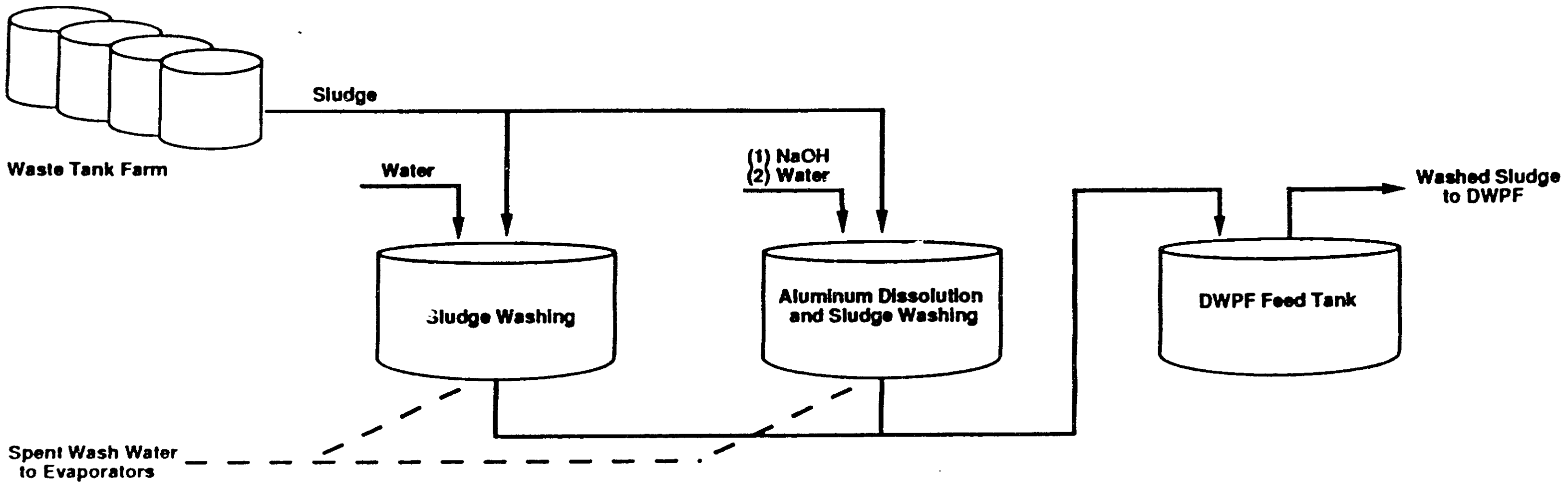


Figure 3.
Statistical Test Results on U and Pu Solubility

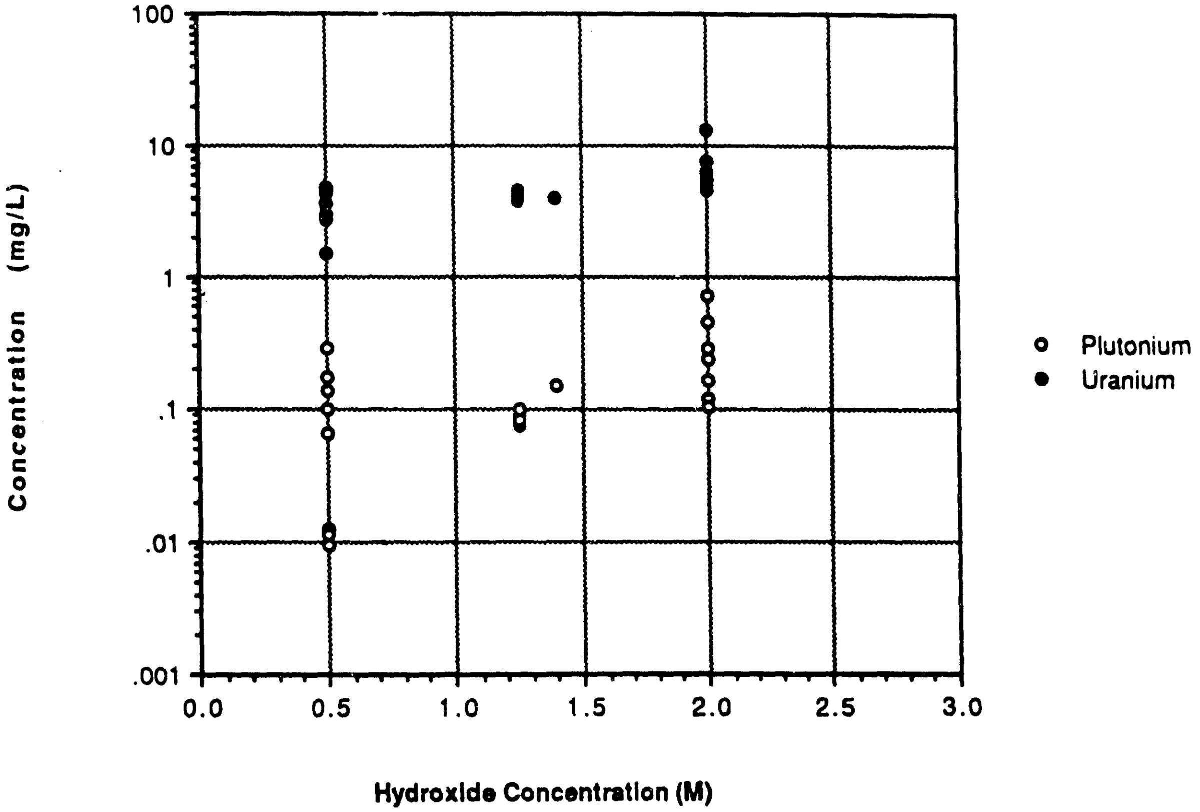


Figure 4.
Pu Solubility in Hydroxide Solutions

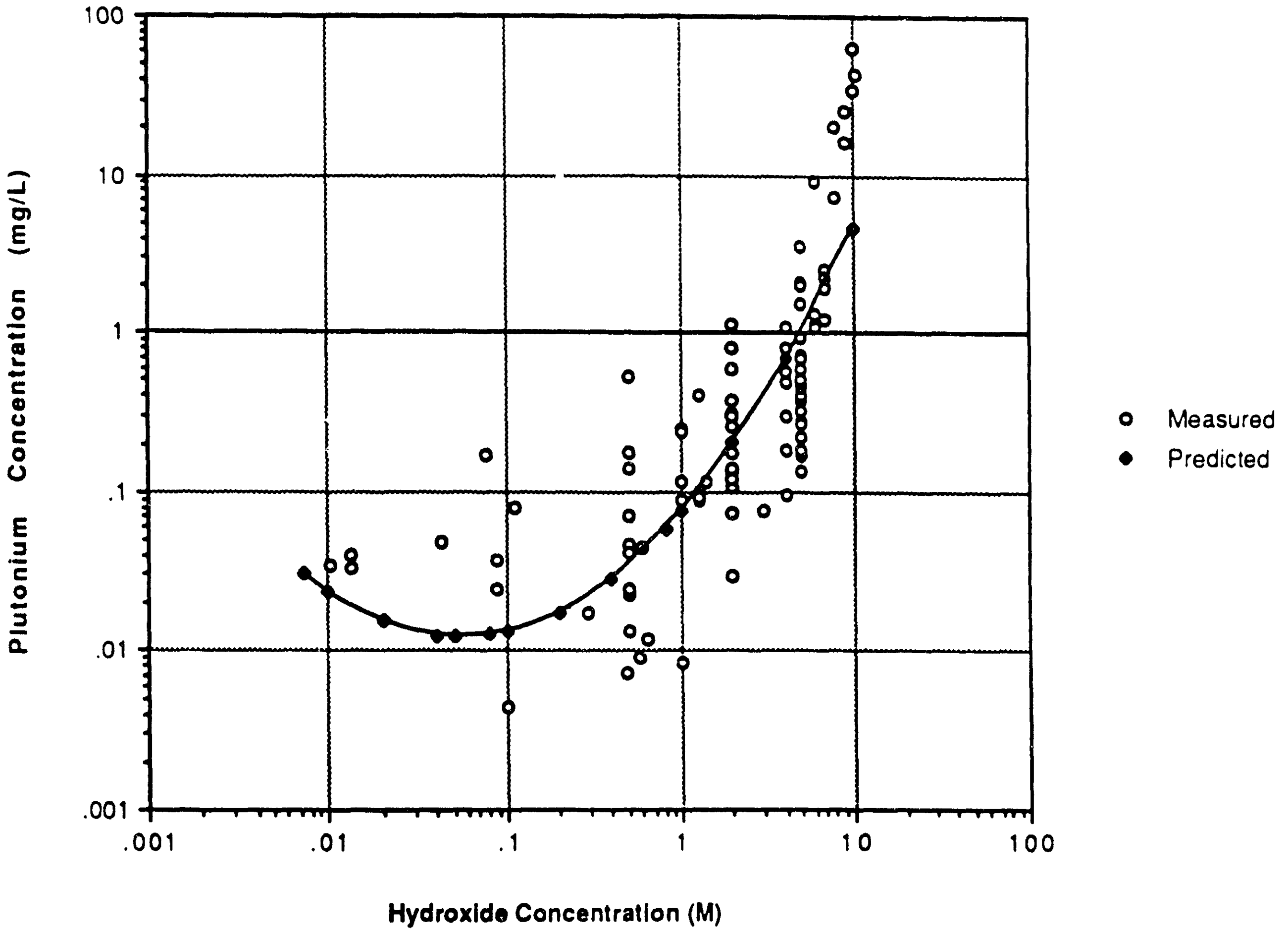


Figure 5
Synthetic Waste Supernate Major Species Concentration during Evaporation

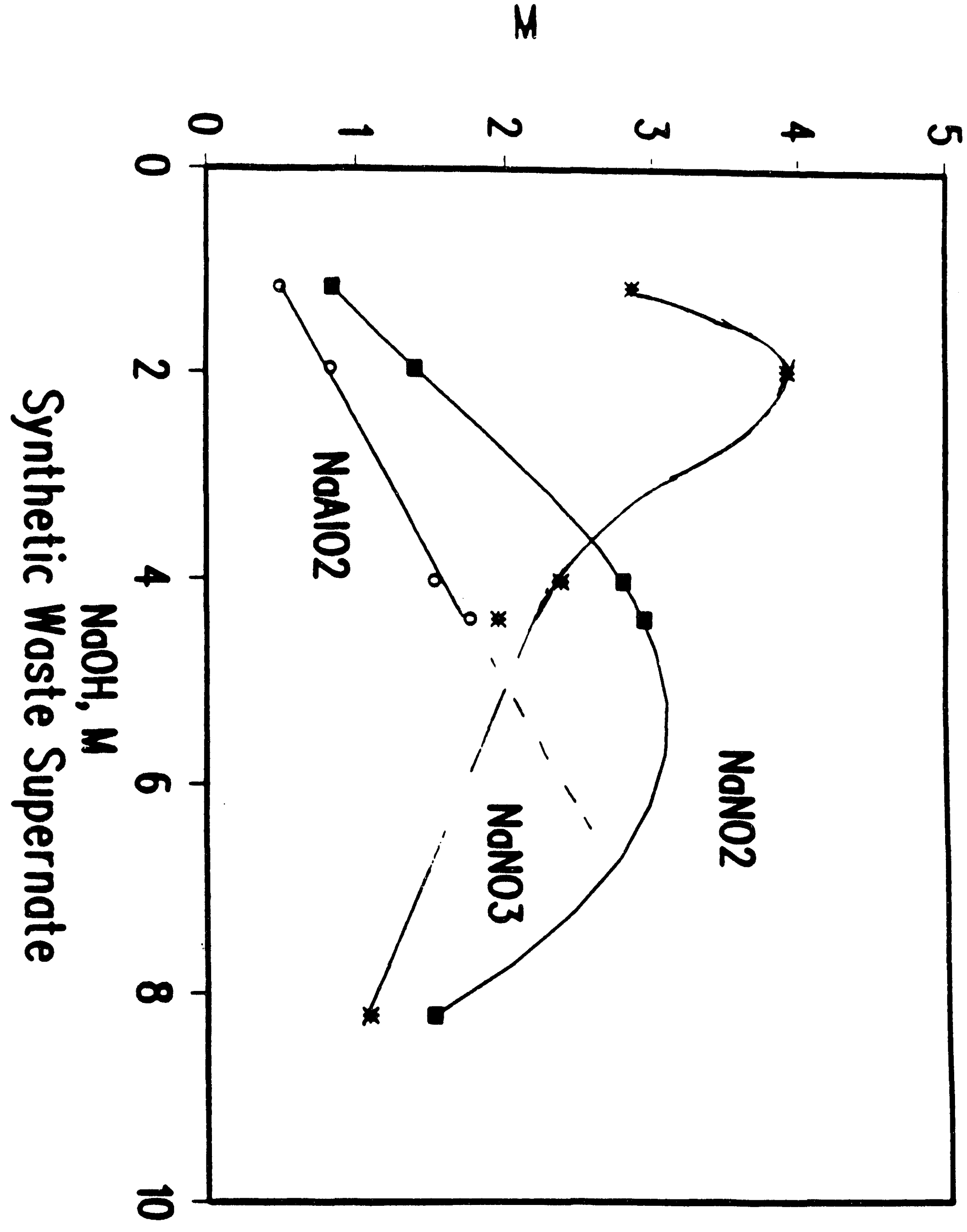


Figure 6.
Synthetic Waste Supernate Minor Species Concentration during Evaporation

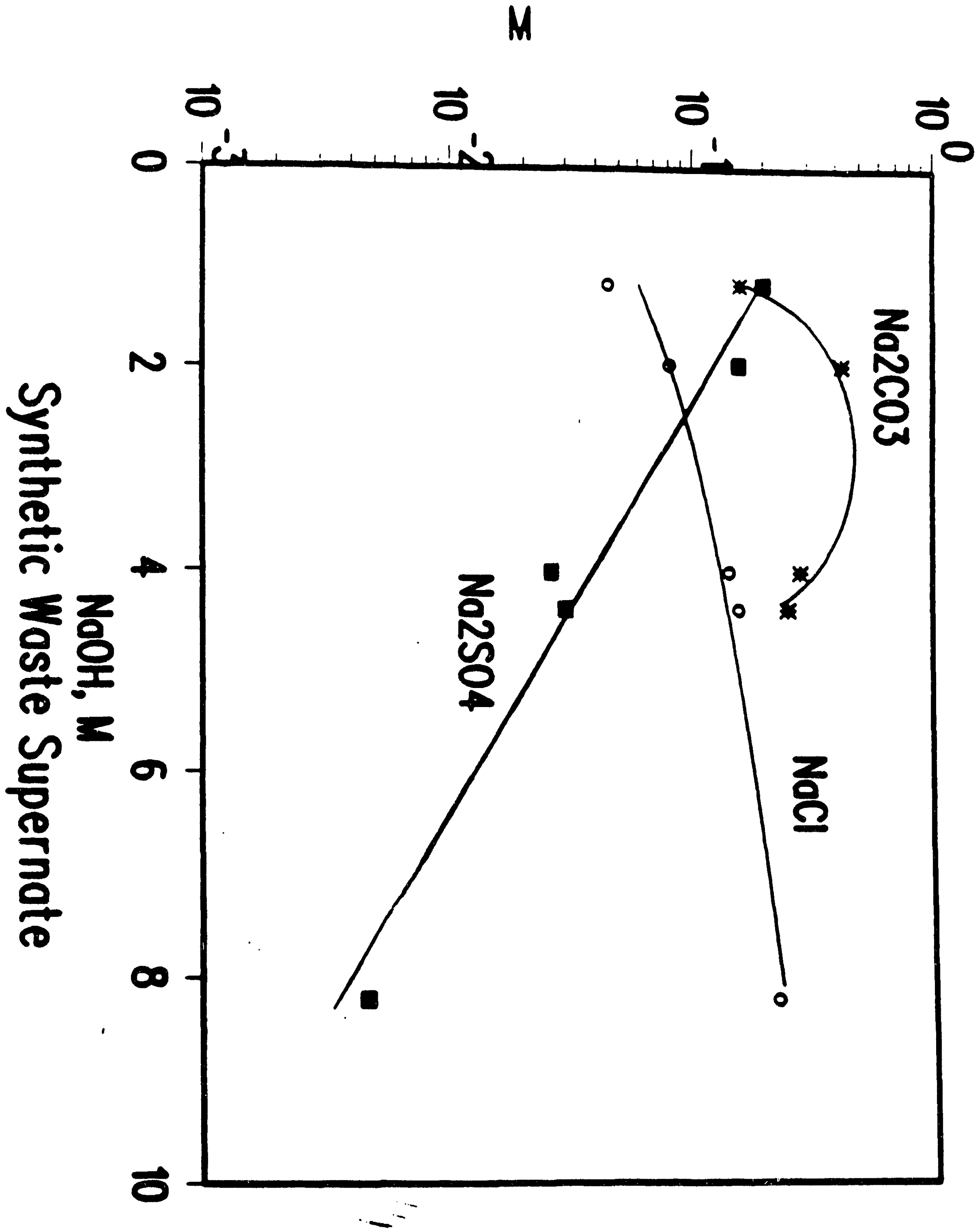
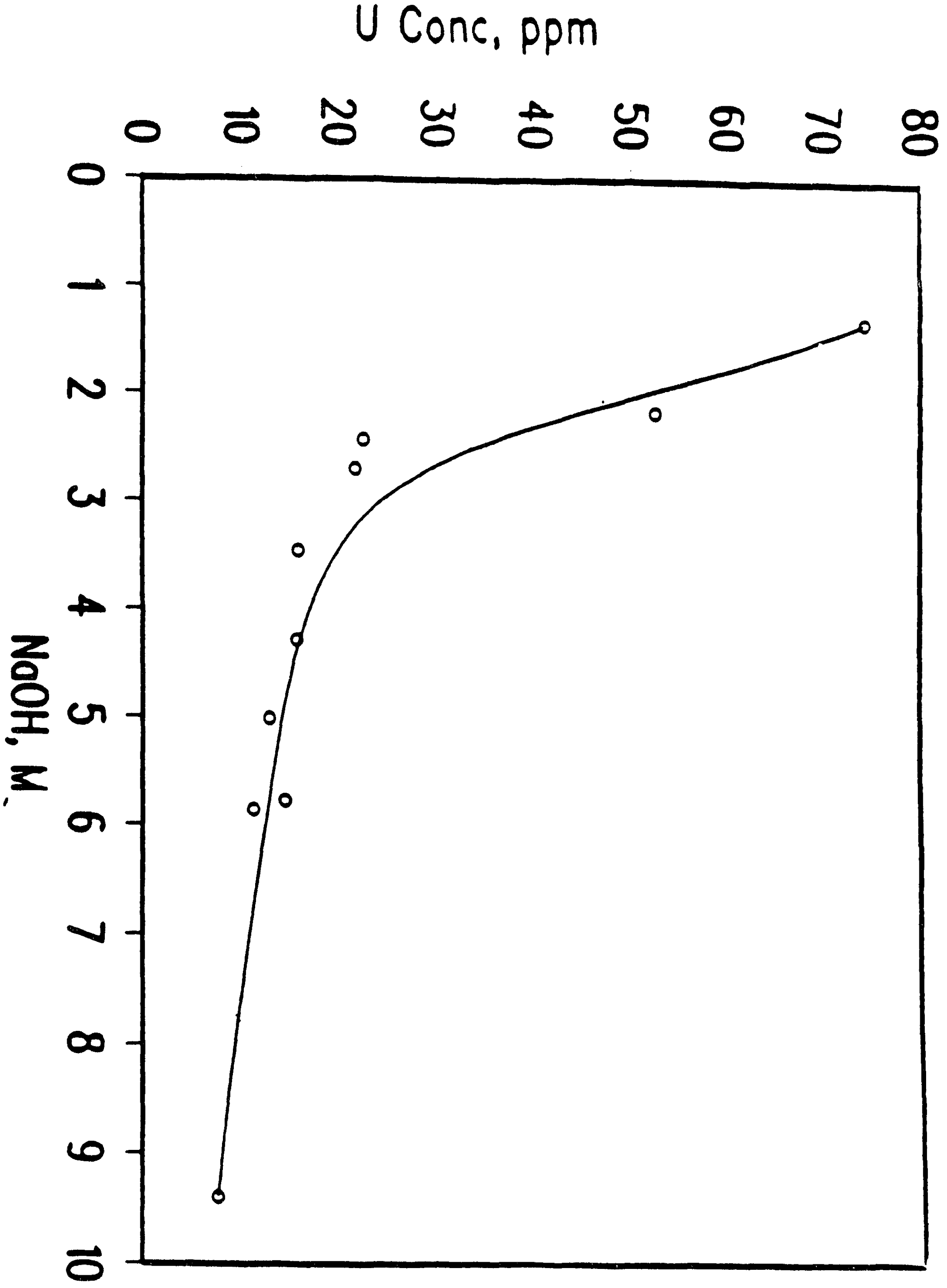


Figure 7.
U Solubility in Synthetic Waste Supernate



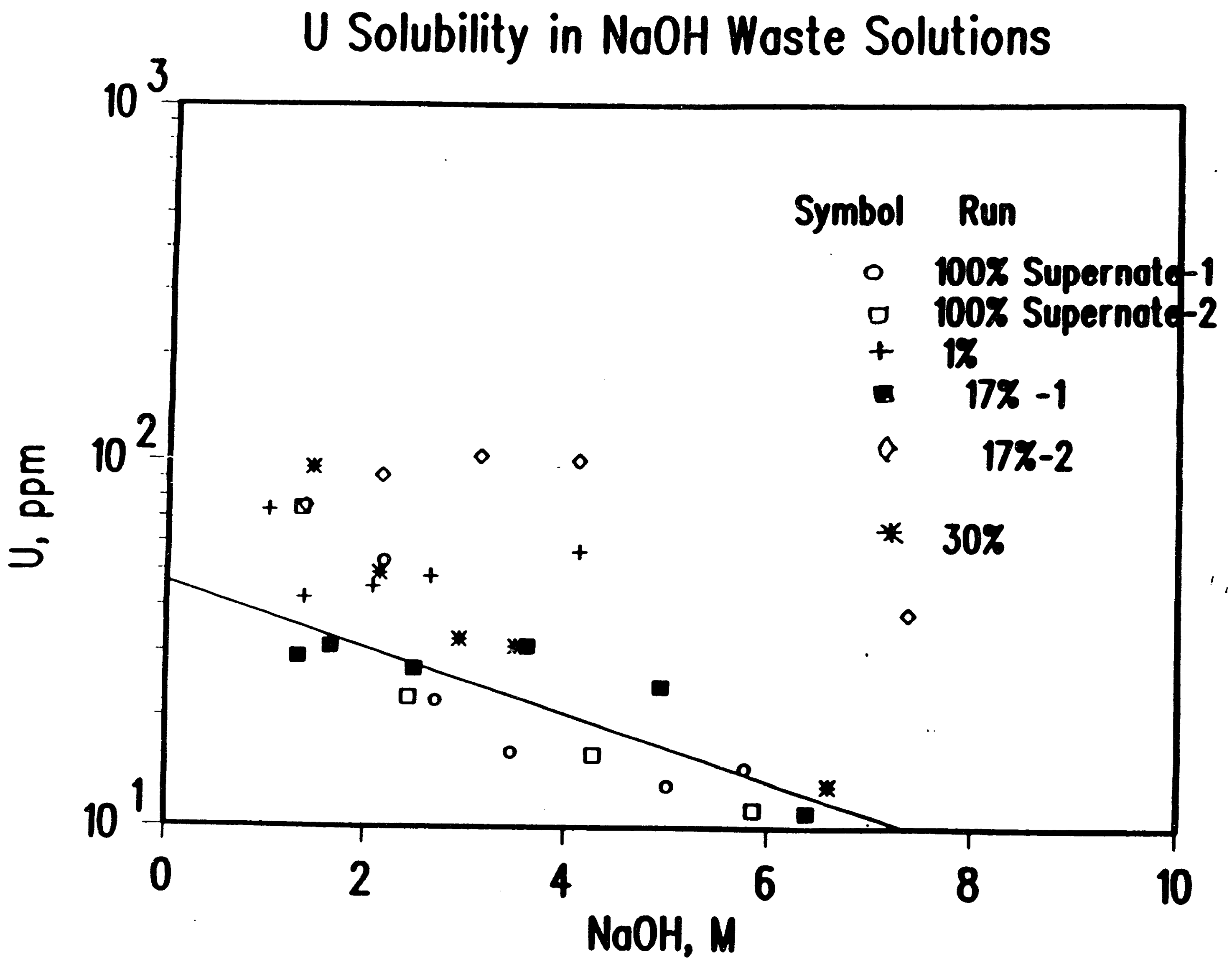


Figure 8.
U Solubility in NaOH Waste Solutions

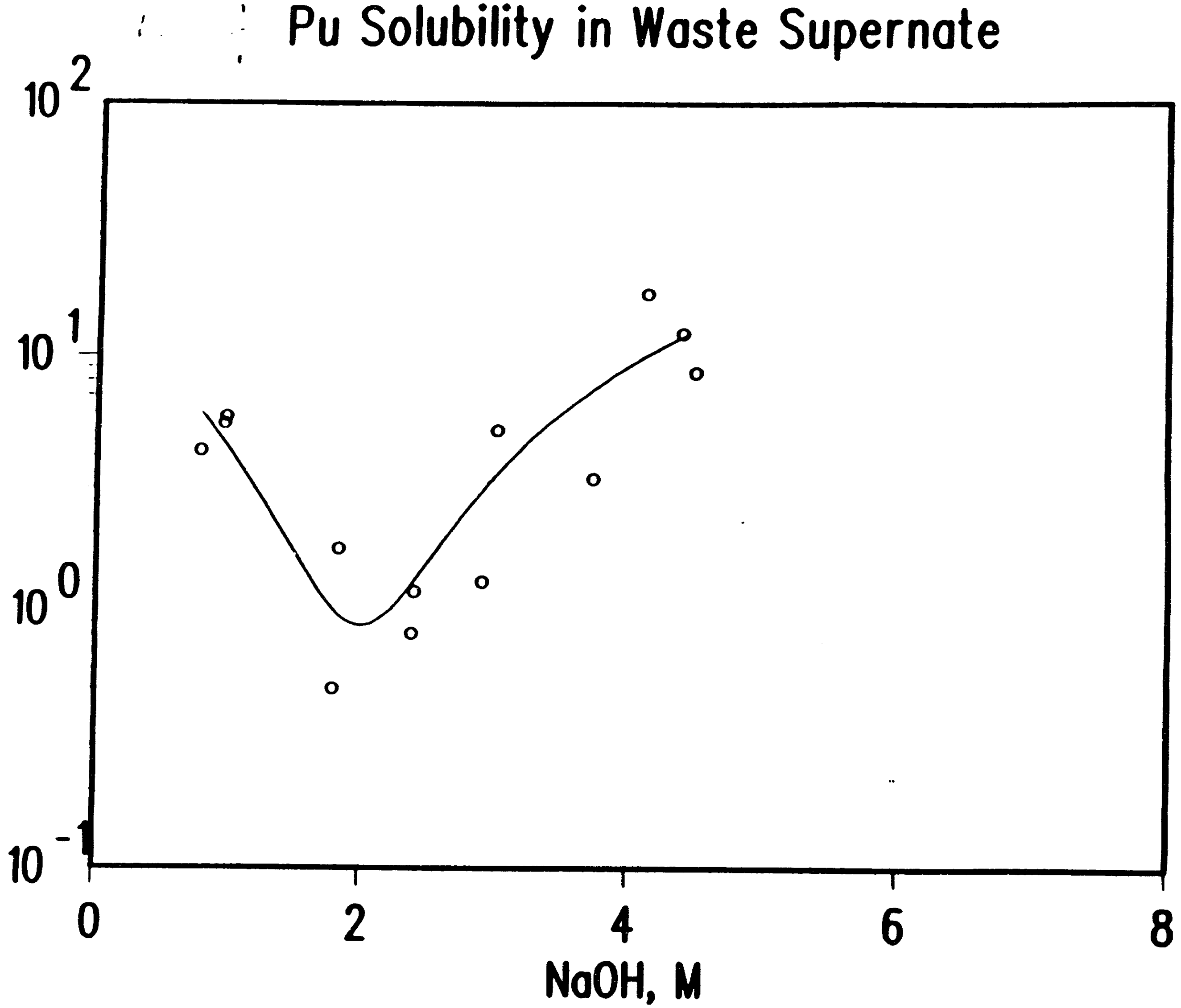


Figure 9.
Pu Solubility in Waste Supernate

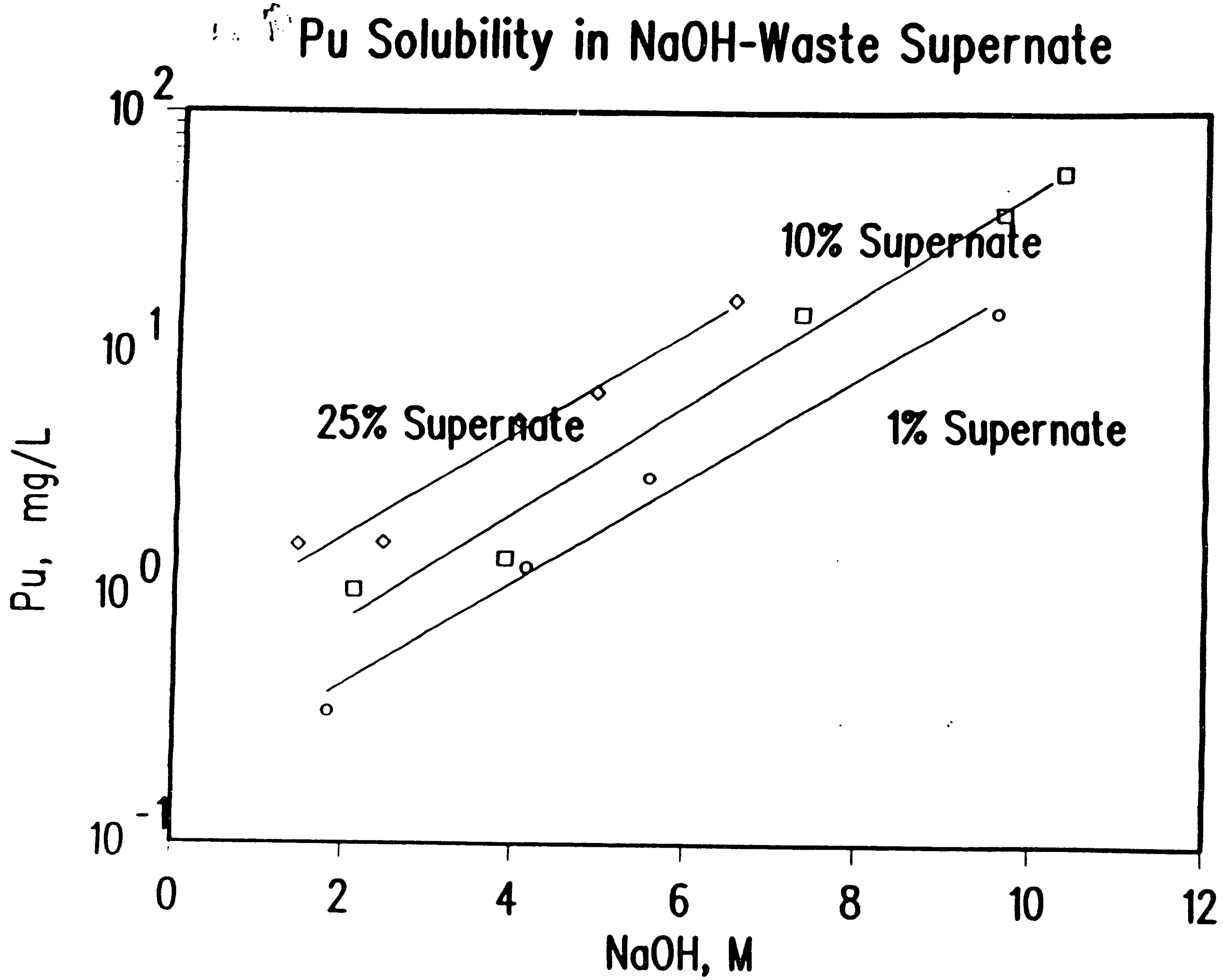


Figure 10.
Pu Solubility in NaOH-Waste Supernate

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