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CHEMICAL DEVELOPMENT SECTION TECHNICAL MEMORANDUM

SOLUBILITY RELATIONSHIPS OF ACIDIFIED STORED METAL WASTES

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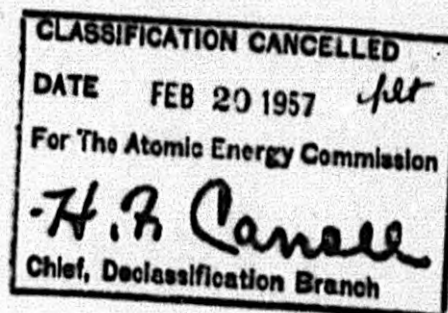
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FROM: M. H. Curtis

SOLUBILITY RELATIONSHIPS OF ACIDIFIED STORED METAL WASTES

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I. INTRODUCTION

The preparation of feed (RAF) solution for the TBP solvent extraction process from aged neutralized metal waste relies upon acid dissolution of the solid phases (sodium uranyl carbonates and sodium uranyl phosphates) which are present in the storage tanks. The process design demands that the acid concentration selected for the feed solution permit complete solution of all components, and that the acid concentration shall allow near maximum uranium concentrations in the solution. Further limiting restrictions with respect to acid concentrations may be found necessary to obtain the required performance in the solvent extraction system. Through experimental investigation it has been found possible to define the solubility relationships of the two solid phases (uranyl hydrogen phosphate and sodium nitrate) which occur in the acidified system, as a function of the acidity in a system containing the components (uranyl, sodium, hydrogen, phosphate, sulfate and nitrate ions) of the feed solution formed in the manner indicated.

The range of the acid concentrations studied is believed to embrace all those of interest in the preparation of the feed stream (RAF), and those of the aqueous phase at any point within the extractant (RA) column or its effluent aqueous (RAW) stream.

II. OBJECTIVE

The object of this investigation was to determine the solubility limitation of concentrations of uranium in the feed preparation step of the tributyl phosphate waste metal recovery process, and the subsequent solubilities in the RA column.

III. SUMMARY AND CONCLUSIONS

The solubility of uranyl phosphate governs the lower limit of the amount of acid that must be used in dissolving sludge. This solubility limit may be given by:

$$\log U = -1.078 + 1.321 \log H^+$$

where:

U = Moles of uranium present,
H⁺ = Moles of "titratable acid" present,
Uranium and phosphate are present in equal mole ratios,
Other ions, sulfate and sodium, are present in flowsheet ratios.

The uranyl phosphate precipitate (believed to be $UO_2HPO_4 \cdot 4H_2O$) is formed very slowly, and it is possible to obtain a high degree of supersaturation by approaching from the solution side. In actual sludge dissolution, the approach to equilibrium is from the solid side, and it should not be possible to exceed these solubilities. In these experiments the approach was from the solution side, but the data were checked against other data obtained by approach from the solid side.

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An upper limit on the amount of acid which may be used is the point of precipitation of sodium nitrate. The solubility of sodium nitrate in acidified waste metal solution is given by:

$$\log Na' = 1.571 - 1.521 \log H'$$

where: Na' = Moles of sodium ion present,
 H' = Moles of "titratable acid" present,
More nitrate than sodium is present, and other ions from waste metal recovery are present in flowsheet proportions.

The data in this report deal primarily with solubilities at 25°C. Freezing points were also obtained on a number of solutions, as the first step in obtaining temperature coefficients of the solubilities previously mentioned, and to see if any new solid phases would appear at other temperatures.

IV. DISCUSSION OF RESULTS

A. Uranyl Phosphate System.

Uranyl hydrogen phosphate precipitates very slowly from solution as has been discussed in many papers (1-6). Some unpublished data by M. K. Harmon have shown that attainment of equilibrium requires 20 to 30 days at 25°C. Hence, the solubility samples of Table I were made up by combining stock solutions, and though supersaturated with respect to uranyl phosphate precipitation, could be cooled to the point of precipitation of sodium nitrate. These solutions were also stable enough for analysis. After the freezing point of each solution with respect to sodium nitrate was determined, the samples were stored in a 25.0°C. bath for the period indicated. After this interval, the solids were removed and the solutions were analyzed.

The solutions of Table II were likewise prepared by combining stock solutions, but gave precipitates on mixing. For samples 15-19, the slurries were heated to 100°C., without attaining solution. These solutions of lower acidity are much more supersaturated than those of Table I, and hence might be expected to precipitate a uranyl phosphate at once. It is also possible (and consistent with the appearance of the slurries) that the material which precipitated under these conditions was $(UO_2)_3(PO_4)_2$ which was slowly converted to $UO_2HPO_4 \cdot 4H_2O$. Solution 26 probably also belongs in this class, but was not heated. Solution 32 also was not heated, but it is believed that the precipitate that formed immediately was sodium nitrate.

Table III presents the solutions from Tables I and II, in order of increasing acidity (solution 9 is not included because of excess phosphate). This table shows a direct relationship between acidity

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and uranium content, which is expressed by the equation, $\log U = -1.078 + 1.321 \log H^+$, as given in section III.

These data are plotted in Figure 1, along with data from CN 2195. The data from CN 2195 have been converted from the original basis of nitric acid to "titratable acid", which includes, based on present analytical methods, the hydrogen ions from the nitric acid, two hydrogen ions from the phosphoric acid, and one hydrogen from the sulfuric acid in those solutions containing sulfate. The difference between the two plots is to be expected since the solutions of the current investigation contain sulfate ions (increasing the uranium solubility) and sodium ions (which decrease uranium solubility), both lacking in the work of CN 2195.

The data of Table I and II were also correlated on a "nitric acid" basis, as was done in CN 2195, but the results were unsatisfactory, and this approach was abandoned.

B. Sodium Nitrate System.

1. Solubility at 25°C.

Table IV includes the 25°C. compositions of solutions with initial freezing points above 25°C. which did not fit the curve of Figure 1. It is presumed that sodium nitrate was the solid phase, as the solutions form a consistent set expressed by the equation:

$$\log Na^+ = -1.571 - 1.521 \log H^+$$

where: Na^+ = Moles of sodium ion present.
 H^+ = Moles of "titratable acid" present.

As H.W. #3 flowsheet (9) shows 15 moles of sodium per mole of uranium in the feed stream, hence we may substitute $15 UO_2^{++}$ for the Na^+ in the equation above. The plot of this new equation is shown together with the uranyl phosphate curve in Figure 2.

2. Freezing Points.

In this system are two potential solid phases in the region of interest. There are a great many solid phases and combinations of solid phases possible in the system, but in the region of interest (combinations which near room temperature could reasonably occur in the T.B.P. process) the solid phases are $NaNO_3$ and $UO_2HPO_4 \cdot 4H_2O$. The first solid phase comes out of solution rapidly, and equilibrium is attained within a few minutes. The second solid phase comes out slowly, and may not appear for as long as ten days. Hence, the solutions in Table V, though supersaturated with respect to

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$\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$, did not precipitate this phase at first, and in fact were cooled many degrees until solid NaNO_3 came out. The freezing point of Table V is thus a pseudo-equilibrium, as it is not in equilibrium with $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$, a phase which will eventually come out.

Thus it is possible to get into this metastable region by starting from the liquid side. If equilibrium were approached from the solid side (sludge) it would not likely be possible to get into this region.

V. APPLICATION

The optimum acidity in the TEP process will probably be that concentration which will allow the highest uranium content in the feed, the feed to be a single liquid phase. A very interesting process could be developed by using enough acid to get well into the region where sodium nitrate precipitates, thus permitting the removal of one of the major undesirable components of this aqueous feed. Such a process would yield a very concentrated feed, thereby insuring lower process stream volumes as well as a considerably decontaminated sodium nitrate, which might be cleaned up enough to crib. (7) But since such a process cannot immediately be developed, the feed concentration must necessarily be limited to that which will precipitate neither $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ nor NaNO_3 .

The limitations imposed by $\text{UO}_2\text{HPO}_4 \cdot 4\text{H}_2\text{O}$ are quite straightforward. The limitations imposed by the precipitation of NaNO_3 are more complex, in that they are governed by what is essentially the concentration of two extraneous ions, sodium and nitrate. The solubility of sodium nitrate is but little affected by the presence of uranium in the concentrations covered in this work. In order to recover the uranium from the waste, all ions must be taken as they occur, and since the sodium-uranium ratio is constant, the solubility of uranium in this region is determined by this sodium-uranium ratio as shown in Figure 3. The limit of uranyl phosphate solubility is also shown on this plot.

In Figure 2, are plotted three feed conditions, according to HW #1 (11), HW #2 (10) and HW #3 (9) flowsheets. On each flowsheet the expected sodium/uranium mole ratio is 15 and, since all the points are below the NaNO_3 line, they are all stable with respect to precipitation of sodium nitrate. However, since the HW #1 flowsheet point is above the uranyl phosphate line it is unstable with respect to uranyl phosphate precipitation. HW #2 is conditional, while HW #3 has a relatively wide margin of safety.

The above conditions control the concentrations in the feed tank. In the column however, only the sodium nitrate is critical, since the uranium concentration drops off so rapidly that uranyl phosphate precipitation is no problem. A very acid scrub (RAS) might precipitate sodium nitrate in extreme cases.

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VI. FUTURE WORK

The work presented in this report gives a good picture of the solubilities at 25°C. At lower temperatures the sodium nitrate solubility may be estimated from the freezing point data attached. However, it would seem unlikely that solutions with freezing points of 25°C. will make the optimum feed; a lower temperature might well be chosen. For this reason it is planned to repeat this work at a lower temperature (10°C). In addition to the solubility limitations which have been discussed above, a source of potential difficulty lies in the feed concentration step following sludge dissolving. Under the conditions which obtain in this operation, the compound $(\text{UO}_2)_3(\text{PO}_4)_2$ may be formed, and this material which exhibits retrograde solubility can conceivably be of critical importance. Additional work is planned to extend the present data to cover this phase of the proposed process flowsheet, with the inclusion of waste treatment (RAW) as an added possibility.

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TABLE I

URANYL PHOSPHATE SYSTEM - DELAYED PRECIPITATION

Initial Solution: Prepared by mixing stock solutions; analyses and freezing points are shown in first line for each solution.

Final Solutions: Analysis after residence time in constant temperature bath at 25.0°C. for indicated number of days, shown in second line for each solution.

Compositions: Results are expressed as moles per liter, based on analysis of liquid phase. H⁺ is "titratable acid."

No.	F.P. °C.	Days	Sp. Gr. (25.0°C.)	Compositions (M)				
				UO ₂ ²⁺	PO ₄ ³⁻	SO ₄ ²⁻	Na ⁺	H ⁺
1	0.5	0	1.3332	0.33	0.35	0.26	3.7	1.8
		47	1.3052	0.22	0.26	0.36	3.5	1.9
2	+2.0	0	1.3457	0.32	0.33	0.26	3.5	2.3
		47	1.3404	0.31	0.32	0.23	3.4	2.2
3	-2.5	0	1.3077	0.26	0.26	0.26	3.7	1.3
		47	1.2630	0.13	0.16	0.24	3.6	1.4
4	17	0	1.3913	0.32	0.34	0.26	5.5	1.3
		45	1.3536	0.13	0.14	0.26	5.1	1.5
5	13	0	1.4065	0.32	0.30	0.26	5.2	1.8
		45	1.3608	0.18	0.20	0.24	5.1	1.9
6	21	0	1.4115	0.32	0.32	0.28	4.8	2.2
		45	1.3762	0.23	0.25	0.24	4.8	2.1
7	12	0	1.4149	0.33	0.31	0.28	5.1	1.9
		45	1.3776	0.21	0.22	0.26	5.3	1.9
8	23.5	0	1.4325	0.32	0.29	0.33	4.9	2.7
		27	1.4232	0.33	0.34	0.32	4.6	2.9
9	2.0	0	1.4006	0.32	1.07	0.35	4.0	3.5
		60	1.3709	0.22	0.98	0.29	4.2	3.5

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TABLE IIURANYL PHOSPHATE SYSTEM - IMMEDIATE PRECIPITATION

Preparation: Prepared by mixing stock solutions; solid phase formed immediately.

Incubation: Seven days at 25.0°C.

Compositions: Results are expressed as moles per liter, based on analysis of liquid phase. H⁺ is "titratable acid."

No.	Sp. Gr. (25.0°C.)	Compositions (M)				
		UO ₂ ⁺⁺	PO ₄ ⁼	SO ₄ ⁼	Na ⁺	H ⁺
15	1.2850	0.031	0.036	0.39	1.82	0.47
16	1.2946	0.044	0.056	---	1.88	0.61
17	1.3003	0.055	0.058	0.40	1.88	0.76
18	1.3178	0.083	0.086	0.39	1.87	1.0
19	1.3587	0.130	0.132	0.44	1.98	1.33
26	1.1211	0.039	0.068	0.058	1.58	0.78
32	1.4407	0.39	0.41	0.38	3.7	3.4

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TABLE III

URANYL PHOSPHATE SYSTEM - ACID EFFECT AT 25.0°C.

Preparation: All solutions prepared by mixing stock solutions.
 Incubation: All solutions at least one week in contact with solid phase at 25.0°C.
 Compositions: Results are expressed as moles per liter, based on analysis of liquid phase. H⁺ is "titratable acid."

No.	Compositions (M)		$\frac{UO_2^{+}}{H^+}$
	H ⁺	UO ₂ ⁺	
15	0.47	0.031	15.16
16	0.61	0.044	13.86
17	0.76	0.055	13.82
18	1.0	0.083	12.05
19	1.33	0.130	10.23
3	1.4	0.130	10.77
4	1.5	0.130	11.54
5	1.9	0.18	10.55
7	1.9	0.21	9.05
1	1.9	0.22	8.64
6	2.1	0.23	9.13
8	2.8	0.33	8.48
32	3.4	0.39	8.72

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TABLE IV
SODIUM NITRATE SYSTEM AT 25.0°C.

Preparation: Prepared by mixing stock solutions. All freezing points above 25.0°C.

Incubation: Residence time in 25.0°C. bath for 10-40 days.

Compositions: Results are expressed as moles per liter, based on analysis of liquid phase. H⁺ is "titratable acid."

No.	Sp. Gr. (25.0°C.)	Compositions (M)				
		UO ₂ ⁺	PO ₄ ⁼	SO ₄ ⁻	Na ⁺	H ⁺
10	1.3636	0.19	0.20	0.18	2.1	6.8
11	1.3961	0.15	0.18	0.27	1.4	8.7
12	1.3795	0.19	0.21	0.37	2.6	6.2
13	1.3609	0.19	0.05	0.17	2.0	6.8
14	1.3658	0.15	0.04	0.14	1.3	8.6
27	1.4083	0.32	0.38	0.34	3.7	4.4
28	1.3993	0.30	0.36	0.35	3.0	5.2
29	1.3998	0.31	0.33	0.33	3.0	5.2
30	1.3927	0.29	0.33	0.31	2.2	6.6
31	1.3927	0.26	0.32	0.27	1.7	7.5

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TABLE V
SODIUM NITRATE SYSTEM
FREEZING POINTS OF SOLUTIONS

Preparation: Prepared by mixing stock solutions.

Freezing Points: Determined within 24 hours of solution preparation by slowly cooling with vigorous agitation to point of crystallization.

Compositions: Results are expressed as moles per liter, based on analysis of liquid phases. H^+ is "titratable acid." Total nitrates are based on synthesis.

No.	F.P. (°C.)	Sp.Gr. (25.0°C.)	Compositions (M)					
			UO_2^{++}	$PO_4^{=}$	$SO_4^{=}$	Na^+	H^+	NO_3^-
1	0.5	1.3332	0.33	0.35	0.26	3.7	1.8	5.3
2	+2.0	1.3457	0.32	0.33	0.26	3.5	2.3	5.7
3	-2.5	1.3077	0.26	0.26	0.26	3.7	1.3	4.8
4	17	1.3913	0.32	0.34	0.26	5.5	1.3	6.4
5	13	1.4065	0.32	0.30	0.26	5.2	1.8	6.9
6	21	1.4115	0.32	0.32	0.28	4.8	2.2	7.4
7	12	1.4149	0.33	0.31	0.28	5.1	1.9	7.7
8	23.5	1.4325	0.32	0.29	0.33	4.9	2.7	7.0
9	2.0	1.4006	0.32	1.07	0.35	4.0	3.5	5.7
10	38	1.4133	0.19	0.18	0.19	2.6	6.3	8.5
11	50	1.4347	0.15	0.15	0.15	2.2	8.5	8.5
12	35	1.3961	0.19	0.18	0.18	2.6	5.9	8.0
13	30	1.3973	0.19	0.05	0.22	2.4	6.8	8.5
14	39	1.3776	0.15	0.04	0.18	2.1	8.4	8.5
20	26	1.3776	0.19	0.05	0.20	2.4	6.3	8.0
21	8	1.4238	0.37	0.29	0.64	4.7	2.5	---
22	-3.0	1.3729	0.33	0.27	0.27	3.6	3.2	6.6
23	20	1.4082	0.33	0.32	0.26	3.5	4.4	7.8
24	17	1.4251	0.35	0.32	0.26	5.2	2.2	---
25	34	1.4731	0.32	0.32	0.25	5.2	3.5	6.9
33	16.7	1.3996	0.26	0.29	0.31	4.01	3.51	6.5
34	-7.8	1.3269	0.20	0.23	0.23	2.7	4.13	6.0

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FIGURE 1

URANYL PHOSPHATE SYSTEM

ACID EFFECTS

Comparison of data from CN-2195 with the data in this report. Uranium molarity of uranyl phosphate solutions in contact with the solid phase is plotted against the molarity of "titratable acid" in the liquid phase.

Titratable Acid: Hydrogen ion concentration as determined by titrating oxalate complexed solutions to their first break (pH 6.0 to 7.0). For purposes of this report it is assumed that titratable acid is the total of free nitric acid, plus one hydrogen ion from each sulphate and two hydrogen ions from each phosphate.

Conditions: The curves differ as shown:

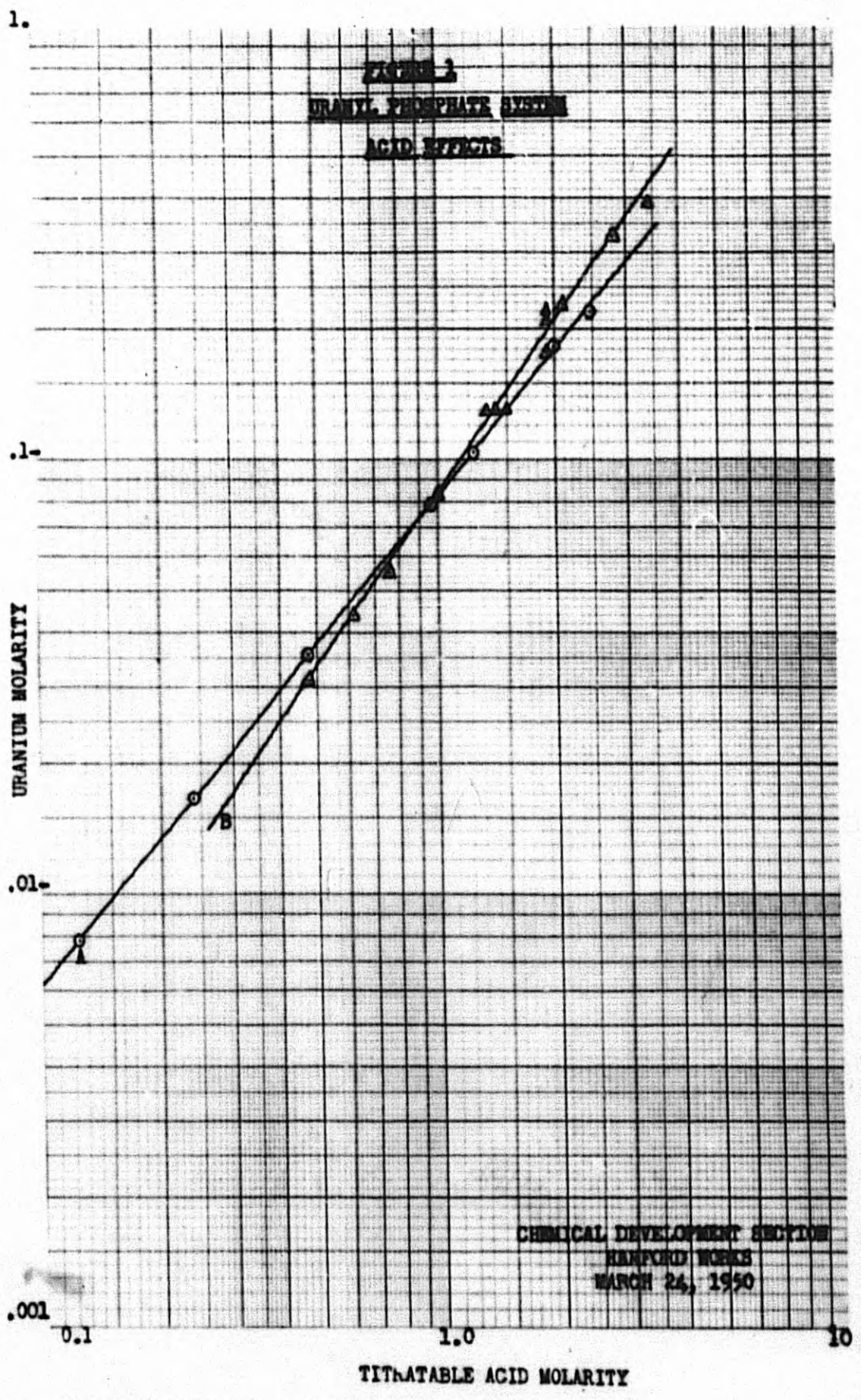
<u>Condition</u>	<u>Curve A</u>	<u>Curve B</u>
Source of Data	CN-2195	Table III, this report.
Temperature	27°C.	25.0°C.
Incubation	12 hours.	Seven days or more.
Acid Molarity	Corrected to titratable.	By analysis.
Equilibrium Compositions (M)	From solids.	From solutions.
UO ₂ ⁺⁺	As shown.	As shown.
PO ₄ ⁻	Equivalent to U.	Equivalent to U.
SO ₄ ⁻	0.0	0.23 to 0.40
Na ⁺	0.0	1.8 to 5.3

Equation: The curve determined statistically from the data of Table III, is given by: $\log U = -1.078 + 1.321 \log H^+$.

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FIGURE 2

URANYL PHOSPHATE - SODIUM NITRATE SYSTEMS

Curve B plots uranium molarity, and curve C plots one-fifteenth of the sodium molarity, against the "titratable acid" molarity, of solutions containing uranyl, sodium, phosphate, sulfate and nitrate ions. Shown also, are the three proposed flowsheet compositions.

Titratable Acid: Hydrogen ion concentration as determined by titrating oxalate complexed solutions to their first break (pH 6.0 to 7.0). For purposes of this report it is assumed that titratable acid is the total of free nitric acid, plus one hydrogen ion from each sulphate and two hydrogen ions from each phosphate.

Conditions: All solutions were incubated at 25.0°C. - those for Curve B, at least one week, and for Curve C, up to forty days.

Equilibrium: All solutions were prepared by mixing stock solutions, and were in contact with solid phases precipitated after make-up.

Compositions: All solutions contained the salts found in waste metal solutions, with uranium, phosphate and sulfate molar concentrations roughly equivalent. Sodium molar concentration was at least ten-fold greater than that of uranium, and nitrate concentration was at least twenty times the uranium molarity.

Feed Compositions: Three points are plotted to show the relative solubilities of three proposed TBP feed (RAF) solutions. As these solutions have a 1 to 15 mole ratio of uranium to sodium, the plot for sodium is the same as that for uranium.

<u>Flowsheet</u>	HW-1	HW-2	HW-3
<u>Document</u>	HW-15,186	HW-15,507	HW-15,987
<u>Composition</u>	M	M	M
UO ₂ ⁺⁺	0.33	0.33	0.27
PO ₄ ⁻⁻⁻	0.32	0.32	0.26
SO ₄ ⁻⁻⁻	0.32	0.32	0.26
Na ⁺	4.97	4.97	4.05
NO ₃ ⁻	5.00	6.50	6.50
H ⁺	1.63	3.13	3.76
Titratable Acid	1.31	2.81	3.50

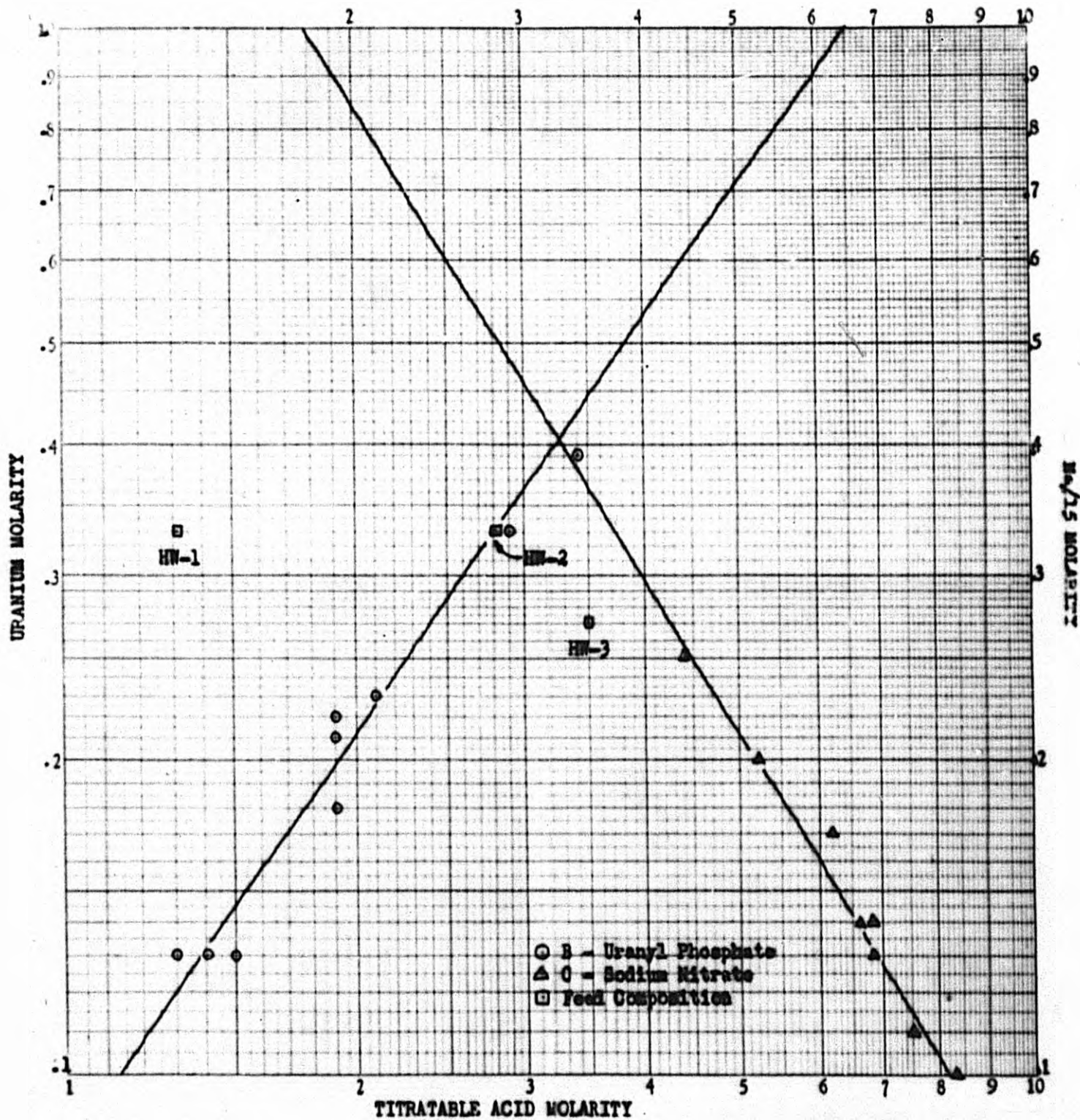
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FIGURE 2

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URANYL PHOSPHATE - SODIUM NITRATE SYSTEMS
ACID EFFECTS AT 25°C.

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FIGURE 3

SOLUBILITY AT 25°C.

EFFECT OF URANIUM-SODIUM RATIO

A data plot showing how the solubility of sodium nitrate limits the uranium content of acidified stored metal waste solutions at different uranium to sodium ratios.

Titrateable Acids:

Hydrogen ion concentration as determined by titrating oxalate complexed solutions to their first break (pH 6.0 to 7.0). For purposes of this report it is assumed that titrateable acid is the total of free nitric acid, plus one hydrogen ion from each sulphate and two hydrogen ions from each phosphate.

Conditions:

Data based on analysis of solutions which were incubated at 25.0°C. for extended periods of time.

Equilibrium:

Approached from the liquid side, with solutions prepared by mixing stock solutions. Supernates remained in contact with solid phases precipitated from the solutions after make-up.

Composition:

All solutions contained the salts found in acidified waste metal solutions, with uranium, phosphate and sulfate molar concentrations roughly equivalent. Sodium molar concentration was at least ten-fold greater than that of the uranium, and nitrate concentration was at least twenty times the uranium molarity.

Sodium Nitrate Curves:

All data for the NaNO_3 portion of the figure were based on sodium solubility of samples, as expressed by the equation: $\log \text{Na}^+ = 1.571 - 1.5209 \log \text{H}^+$. The family of lines was derived by assigning the different ratios shown, and applying this equation to them.

Uranyl Phosphate
Curves

$$\log U = -1.078 + 1.321 \log \text{H}^+$$

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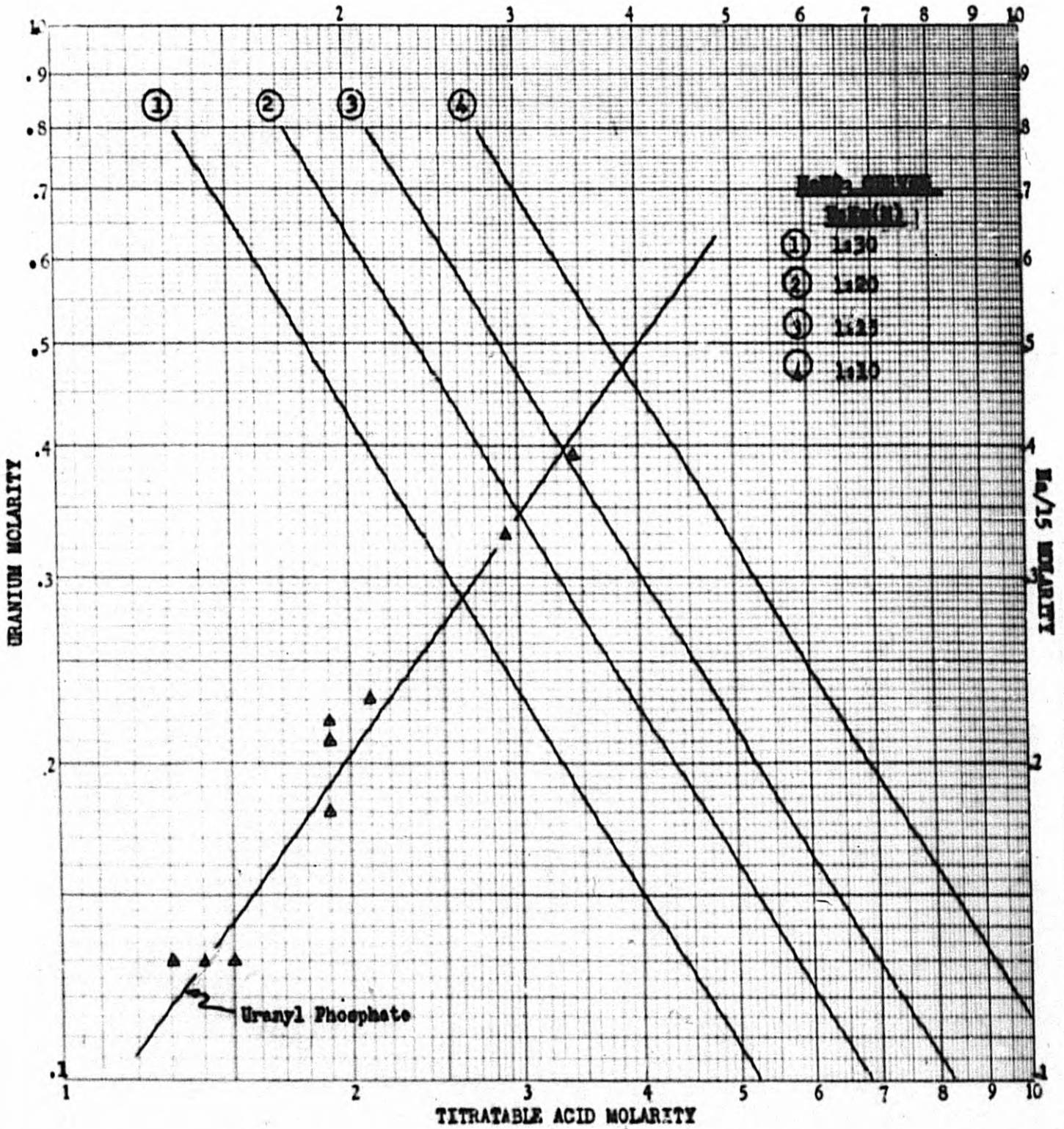
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FIGURE 3

SOLUBILITY AT 25°C.

EFFECT OF URANIUM-SODIUM RATIO



CHEMICAL DEVELOPMENT SECTION
HANFORD WORKS
MARCH 24, 1950

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