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RECOVERY OF URANIUM AS A SINGLE PRODUCT FROM THE FLORIDA LEACHED ZONE

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RECOVERY OF URANIUM AS A SINGLE PRODUCT FROM THE FLORIDA LEACHED ZONE

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Abstract

A wide variety of ore samples from the Florida Leached Zone were studied for extraction of uranium, and for recovery of uranium from the resulting pregnant liquor. Most but not all of the samples appeared amenable to a process using a minimum quantity of sulfuric acid to extract the most readily soluble fraction of the uranium from the classified ore fines, followed by anion exchange sorption of uranium from the clarified liquor. Variations of this process were also studied to a limited extent, including leaching of unclassified ore, recovery of uranium from the clarified liquor by precipitation or liquid-liquid extraction, and avoidance of filtration by means of slurry-liquid extraction or resin-in-pulp leaching.

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RECOVERY OF URANIUM AS A SINGLE PRODUCT FROM THE FLORIDA LEACHED ZONE

INTRODUCTION AND SUMMARY

The Leached Zone at the top of the Florida Bone Valley phosphate formation constitutes a part of the overburden now being stripped and discarded, ranging typically from zero to fifteen feet in thickness. It contains aluminum and calcium phosphates in varying proportions, diluted to varying degrees with silica and with clays. The uranium content also varies, but in general is higher than that of the unleached phosphate pebble formation beneath it, apparently having been increased both by residual concentration and by redeposition.[1] Uranium concentrations of 0.01 to 0.02% may be typical, but samples vary over a much wider range. Although the uranium concentration is low, the quantity in the Leached Zone is great enough to make it an important source of uranium if it can be recovered by an economical process.

Most of the phosphatic material is of very fine inherent grain size, while most of the silica is coarser, so that the ore can be upgraded by dispersion and classification. The uranium values concentrate in the fines with the phosphate minerals.[1,2,3,4] Clays, if present, accompany the phosphates and limit the upgrading obtainable.

In the past, private investigation has been made of processes for production of phosphate, alumina, or both from LZ ore. With the development of interest in the Leached Zone for its uranium content, a research project on AEC contract was established with at least one of the major Florida phosphate companies, The International Minerals and Chemical Corporation, with the objective of developing a process for production of uranium together with by-products.[3] Investigation of methods for utilizing the Leached Zone are currently being made by the Chemical Development Division of the TVA (Progress Reports starting December, 1951[4]), with emphasis on fertilizer production from the phosphate in the LZ ore.

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A sample of LZ ore (low calcium and fairly low clay; 0.03% uranium) was examined by the MIT Mineral Engineering Laboratory, Watertown Arsenal.[2] They reported best extraction with hot sulfuric acid, and suggested ion exchange recovery from the pulp to avoid filtration. They obtained only fair beneficiation by dispersion and classification, and pointed out that the reagent consumption was not decreased by the beneficiation.

Investigation of uranium recovery from LZ ores was begun in the Uranium Chemistry of Raw Materials Section of ORNL in May, 1951 (Quarterly Progress Reports starting June, 1951[5]). A principal objective of this investigation was to examine the recovery of uranium as a single product, independent of any potential by-products. A variety of attacks on the ore were tested; the one which appeared best suited for production of uranium alone consisted of leaching with a minimum amount of sulfuric acid to extract the most readily soluble fraction of the uranium. This attack on the ore, together with methods of recovering uranium from the resulting liquor, has been studied in terms of possible process flowsheets, in as much detail as seemed feasible on a beaker scale. In addition, briefer examination was made of other attacks which appeared promising for processes to produce uranium together with by-products; these will be reported separately.

Obviously, any process by which uranium might be obtained as a single product has the inherent disadvantage that all costs, including mining, transportation, equipment installation, etc., must be born by uranium alone. Thus the chance of producing uranium at a small cost is nearly eliminated at the outset. On the other hand, consideration of the possibilities of a single product seemed advisable as a starting point on the Leached Zone problem for several reasons. First, it offered a means of becoming generally acquainted with the properties of the Leached Zone material. Second, the analysis of subsequent work on other methods for treating the Leached Zone should be aided by having a presumably simple process established first for comparison Third, it might be expected that a single product process would be simpler than a multiproduct process and would require less capital investment and less time for installation, hence, an understanding of possible single-product flowsheets should be available in case of emergency. Also, it was considered that uranium produced alone would be independent of other markets, while uranium produced with by-products will depend on continuing markets for the by-products or on subsidy for stockpiling them if the markets should fail.

Exploratory and survey tests of attacks on the ore included direct leaching with acids and bases, leaching of the dry ore with complexing agents in organic solvents, and heat treatment in the presence of acids, acid salts, and

carbonates. Several of these methods showed some promise for production of uranium together with phosphate or aluminum as by-product, but so far leaching with sulfuric or nitric acid in dilute solution has appeared most feasible for production of uranium alone. Leaching with these acids was studied in detail over ranges of acid quantity and concentration, time, temperature, and variation in ore type. Results with these two acids were similar, so that sulfuric acid as the cheaper acid was indicated for use in a process to produce uranium alone.

A condensed flowsheet for a process using a limited amount of sulfuric acid ("Low Sulfate Process") is shown in Figure 1. Physical beneficiation of the ore, if sufficiently efficient in recovery and upgrading, will aid in obtaining a reasonable uranium concentration in the pregnant liquor. Countercurrent leaching, which if feasible would yield a higher concentration, may be ruled out by the difficulty of thickening and filtration. The flowsheet as shown requires one filtration after the one-stage leach, whereas a two-stage countercurrent leach would require three filtrations, since the ore could not be accepted as a dilute slurry but would be filtered before entering the first stage. For the flowsheet as shown the slurry of classified fines will require some thickening but not filtration before the leach.

The amount of acid required by the ores which are amenable to this process will depend more on the quantity of calcium in the ore than on the amount of uranium or the total weight of ore. The results with most of the ore samples tested have suggested that the calcium content of the ore may be a useful guide to the amount of acid to be used. Alternatively, the final pH may serve as a suitable guide.

Uranium will be recovered from the clarified liquor probably either by anion exchange sorption or by liquid-liquid extraction. Two alternatives are also indicated in Figure 1, slurry-liquid extraction and resin-in-pulp sorption, either of which would eliminate the filtration step. The possibility of a slurry-liquid extraction process might be especially attractive from the standpoint of process simplicity and operational costs, if engineering tests were to demonstrate its practicability.

Acid Leaching

The effects of acid quantity, temperature and time were studied chiefly with two of the minus 200 mesh ore samples (BC-1 and BC-3, Table 2), one high in calcium and the other low in calcium and high in clay minerals. Tests with both showed principally the calcium minerals attacked when the

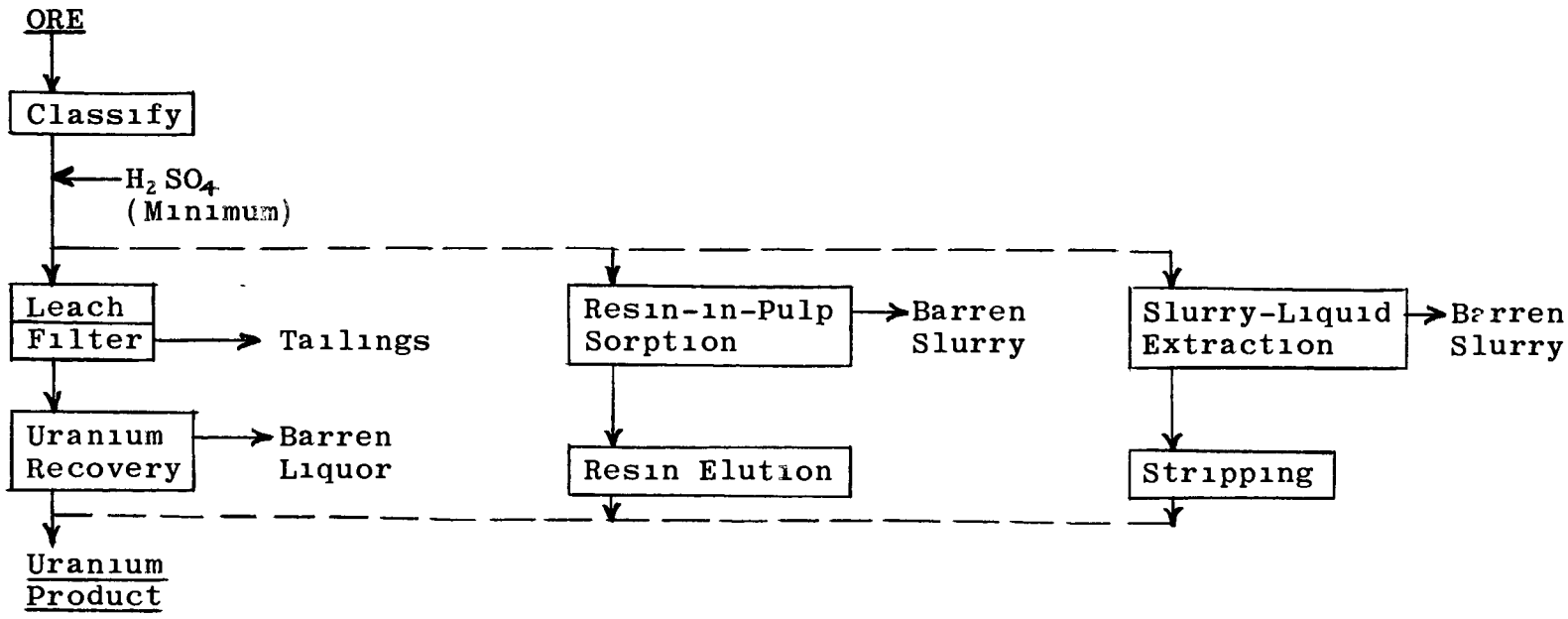

Figure 1

LOW SULFATE PROCESS FOR URANIUM ONLY

quantity of acid was sufficiently limited, followed by slower dissolution of aluminum phosphate minerals with more acid, and slow dissolution of at least a part of the clay minerals.

The amounts of uranium dissolved suggested that the uranium was associated with both the calcium and the aluminum phosphate minerals, and at a similar order of concentration in each. Thus, a selective leaching of uranium was obtained to the extent that it was associated with the selectively-leached calcium minerals, and this portion of the total uranium content was dissolved at a lower relative acid consumption than was required for dissolution of the remainder. The results did not suggest that any large portion of the uranium existed as discrete minerals, or in surface concentrations, which could be leached without extensive attack on the other minerals.

In nitric acid leaches, the percent dissolution of calcium was high and of aluminum was low, with phosphate intermediate. Uranium dissolution paralleled the calcium, usually falling between the calcium and the phosphate. The results with sulfuric acid were similar, except that calcium remained in the tailings.

In leaches at 80°C, uranium dissolution reached its maximum within six hours and nearly so within one hour. At room temperature, there was significant change between one and six hours, but little further dissolution between six and twenty-four hours. With sufficient time, there was little difference in results at 80°C and at room temperature.

Minus 200 mesh fractions from eight LZ ores (BC-0 to BC-7, Table 2) were leached with the quantities of sulfuric acid required to bring the final pH to 1.0, 1.5, and 2.0. For all except BC-7 and perhaps BC-3, the resulting acid consumption curves and uranium dissolution curves correlated fairly well with the calcium contents of the ores. The uranium extraction curves began to level off after the most readily available portion had been dissolved, at acid quantities usually close to equivalent to the calcium. This readily leached fraction varied from around 30% to around 80% of the total uranium, so that the amount of acid consumed by different ores (not including BC-7) varied from about 350 to over 1500 pounds of sulfuric acid (100%) per pound of uranium dissolved, while remaining fairly close to 2.5 pounds per pound of calcium in the ore concentrate.

Constant-pH leaches at 1.0, 1.5, and 2.0 did not show significantly different results from the leaches in which the same total quantity of acid was added all at one time. In some tests the presence of anion exchange resin during the acid attack appeared to improve the leaching, but the effect was not large and could not be definitely established.

Uranium Recovery from Solution

Recovery of uranium from the dilute sulfate-phosphate leach liquor by means of precipitation, anion exchange, and solvent extraction was examined. The greatest emphasis was placed on anion exchange, for which this type of liquor is particularly favorable because it is free from nitrate and chloride and its excess anion concentration is relatively low.

Single stage batch equilibrium tests of anion exchange sorption with strong-base resins from the low-sulfate liquor confirmed the favorable pickup which was expected on the basis of tests made with uranyl sulfate and phosphate solutions,[6] giving resin loadings of about 2 g. uranium per liter of resin. The loading increased as expected with increasing ratio of liquor to resin, and in column operation loadings of 15 to 20 g. uranium per liter of resin were obtained. Four column units in series at a retention time of about five minutes per unit were sufficient for saturation of the first unit before breakthrough from the fourth.

Satisfactory elution was obtained with acidified sodium chloride solution, giving eluate concentrations as high as 4 g. uranium per liter. Most of the sulfate and phosphate was eluted from the resin before much uranium was eluted, suggesting that most of the uranium could be collected in a liquor suitable for hydrolytic precipitation of product-grade uranium, and the rest in a liquor suitable for uranous phosphate precipitation. The eluted resin was readily regenerated from chloride to sulfate-phosphate form by means of a small fraction of the barren effluent which had been produced in the loading step.

Encouraging results were obtained in recovery of uranium from the low sulfate liquor by liquid-liquid extraction with some organophosphorus reagents which have recently been described.[5a,b,c] Percent uranium extraction, uranium loading in the organic phase, and the separation of the uranium from iron and aluminum were all favorable. The use of liquid-liquid extraction for processing the low sulfate liquor was not studied in as much detail as was the use of anion exchange, since the status of the extraction agents ha'ha' and their use was not yet so well established as that of the exchange resins.

Precipitation can be used to recover uranium from the low sulfate liquor, but it appeared less useful than either anion exchange or liquid-liquid extraction. The precipitates obtained by pH adjustment consisted principally of aluminum phosphate, with neither selective precipitation of uranium nor complete retention of uranium in solution at any pH in the precipitation

range. Best results were obtained from sulfate liquor which had been reduced. Nearly complete precipitation of the uranium was obtained only in very low grade cakes, typically 1% or less in uranium. Survey tests were made of upgrading of these cakes by various methods; some of these gave good uranium recovery, but none showed sufficient upgrading to give an acceptable uranium product in one step, and all indicated high reagent consumption.

Filtration

Aqueous slurries of the raw LZ ore, either total ore or concentrated fines, are difficult to thicken and very difficult to filter. The filtering characteristics can be improved by some pretreatments of the ore (as calcining,[4] or baking with acidic reagents), but by-products appear necessary to share the cost of such treatments; hence, they were not considered available for use in a process for production of uranium alone. Fortunately, a fairly dilute pulp can be used for the low-sulfate leach, so that filtration of the classified fines does not appear to be needed before the leaching step.

Filtration of the pregnant liquor from the tailings remains a serious problem. The test work to date has not been on large enough scale nor in suitable equipment for engineering measurement of filtration rates. Relative rate measurements in the laboratory filtrations at beaker scale indicated that the rates were improved little, if any, by the low acid leach at temperatures below 100°C. The temperature of the slurry during filtration showed some effect, with rates about twice as fast at 50-55°C as at 30°C. Slurries from different ore samples varied widely in rates, each showing some improvement at higher temperature.

Since the filtration is certain to be an important cost item and might even prove prohibitive, the possibility of avoiding filtration by means of resin-in-pulp sorption or slurry-liquid extraction was examined. In beaker-scale tests, extractions were accomplished by both methods. These tests were limited to measurement of uranium distribution, recovery, and loading, with no attempt to measure reagent losses or to obtain engineering design data. (Resin-in-pulp as a unit operation has been studied by the MIT Mineral Engineering Laboratory,[7] and special resins for this purpose have been studied by Rohm & Haas Company.[8]) Resin-in-pulp sorption could be used in a countercurrent process to build up the loading, but the number of stages practicable would probably be much smaller than can be obtained in column sorption from clarified liquors. Hence, the loading at a given recovery tolerance would be lower, and the inventory of resin and the size of the installation would be correspondingly greater.

Such factors and also engineering design data would have to be evaluated in larger scale tests of both resin-in-pulp sorption and slurry extraction before a clear choice between filtration and one of these alternatives could be made. If operable in these pulps, a slurry-liquid extraction process should offer distinct advantages over either resin-in-pulp handling or filtration for uranium recovery from clarified liquor.

Other Investigations

Besides the low sulfuric acid leach, several methods of attack on the LZ ore were tested in some detail before being rejected or suspended as appearing inferior to the low sulfuric acid leach. A few of the methods surveyed appeared promising provided that credit for by-products be allowed. The results of these tests will be reported separately.

Conclusions

Several samples of ore from the Florida Leached Zone were examined for the possible production of uranium as a single product. Some but not all of these samples were found amenable to a process which uses a minimum quantity of sulfuric acid to extract that fraction of the uranium which is most readily dissolved. The resulting leach liquor was favorable for uranium recovery by anion exchange, perhaps also by liquid-liquid extraction.

The ore can be accepted as a fairly dilute slurry, so that filtration before the leach will not be required. Filtration of the pregnant liquor from the tailings was difficult in laboratory equipment, and it might prove unfeasible in process equipment. Alternatives appeared to be possible in slurry-liquid extraction and in resin-in-pulp leaching. Further study might show one of these, especially slurry-liquid extraction, to be inherently better than the process requiring filtration.

Of eight ore samples tested, seven conformed to a pattern in which the fraction of the uranium readily leached varied approximately with the calcium content of the ore, and the quantity of acid required was nearly equivalent to the calcium. For these, the uranium extraction varied from about 30 to about 80%, with acid consumption of about 350 to over 1500 pounds sulfuric acid (100%) per pound of uranium dissolved. The eighth sample, although similar to some of the others in elemental composition, was not similarly amenable to low-acid leaching. Preliminary comparison tests of five additional

samples showed three amenable, two refractory. There is no reason to believe that the proportions of the two types in this set of samples represent the proportions of the quantities available; furthermore, there may be still other types of LZ ores which were not included in these samples.

ORE SAMPLES

A total of fifteen ore samples from the Florida Leached Zone were received during this investigation. Most of the tests were made with the first eight of these (BC-0 to BC-7), and briefer comparison checks have been made with those obtained more recently. The individual samples are described in the following list, with analytical data in Tables 1 to 4. Three of the samples received (BC-1, BC-2, and BC-3) were minus 200 mesh screen fractions. Minus 200 mesh fractions were cut from portions of most of the other samples, these samples of fines are identified by "B" added to the head sample number.

Mineralogical analyses of several of the samples were reported by the U.S.G.S.[9] The results are summarized in Table 6. Cuts of the more recent samples have been submitted to the U.S.G.S. for examination.

The original suggestion that the clay-like fine material of the Leached Zone was essentially uniform throughout, differing principally from place to place only in the degree of dilution with coarser sand, appeared to be confirmed by the first three samples received. The subsequent samples, however, demonstrated wide variations in mineral content and also wide variations in response to acid leaching. Correlation of leaching results with chemical composition allowed some of the samples to be grouped in a series ranging from high calcium phosphate to high aluminum phosphate, in which a fraction of the uranium approximately corresponding to the calcium was readily leached by dilute acid. Another group of samples (BC-7, BC-8, and perhaps BC-11 and BC-12), not dissimilar in major chemical composition to the foregoing, proved almost completely refractory to acid leaching under similar conditions. It may well be that there are ores of still other characteristics not included in these samples.

The range from high calcium (BC-0, BC-1, BC-2, TVA-I-1, and perhaps BC-13) to high aluminum is illustrated in Table 5, which includes ore analyses published by other laboratories as well as the analyses obtained here. The use of ratios for comparing these samples eliminates the variable effect of dilution by silica. The effect of dilution by clays is similarly eliminated from the ratios of U_3O_8 and CaO with P_2O_5, but not from the ratios involving alumina. If the gangue rejected by classification were pure silica, the ratios should stand the same for the unclassified ore samples and the corresponding fines. The corresponding pairs of ratios in Table 5 are not identical, but the differences are small compared with the general variation through the range of samples.

Table 1

MAJOR CONSTITUENTS OF UNCLASSIFIED ORES

Percent

ORNL NO.	U	U_3O_8	P_2O_5	CaO	Al_2O_3	Fe_2O_3	SiO_2	Loss at 1000°C
BC-0	0.020	0.024	15.1	17.4	8.8	1.9	49.8	6.6
BC-4	0.037	0.044	15.3	1.8	20.8	1.9	48.1	11.7
BC-5	0.026	0.031	12.2	4.9	18.0	2.6	51.8	9.4
BC-6	0.007	0.008	5.8	5.4	10.0	2.4	70.0	6.7
BC-8	0.030	0.035	18.4	4.6	17.2	4.5	42.8	10.3
BC-9	0.015	0.018	10.2	1.6	13.9	2.1	62.9	7.8
BC-10	0.033	0.039	15.5	4.5	18.1	2.0	47.3	9.6
BC-11	0.021	0.025	15.0	2.7	18.3	1.1	48.8	10.8
BC-12	0.021	0.025	9.4	1.8	16.1	2.2	56.8	8.6
BC-13	0.035	0.041	9.2	4.6	9.9	0.4	66.5	6.4
BC-14	0.035	0.041	15.3	6.0	18.6	2.2	47.0	9.4

Table 2

MAJOR CONSTITUENTS OF - 200 MESH FRACTIONS

Percent

ORNL No.	U	U_3O_8	P_2O_5	CaO	Al_2O_3	Fe_2O_3	SiO_2	Loss at 1000°C
BC-0B1	0.025	0.030	22.4	21.1	19.1	2.8	21.8	10.1
BC-0B2	.033	.038	20.4	21.2	20.5		21.1	12.0
BC-0B3	.031	.036	20.1	21.5	19.0		21.0	11.8
BC-1	.052	.061	26.6	16.3	24.2	2.8	12.2	12.5
BC-2	.036	.042	23.2	17.2	19.3	2.7	23.1	
BC-3	.034	.040	14.6	7.1	28.7	1.7	32.1	13.6
BC-4B	.053	.062	24.2	3.4	34.5		12.7	
BC-5B	.041	.048	16.1	5.9	30.9	2.2	25.6	15.4
BC-6B	.012	.014	8.0	3.5	20.9	6.8	46.3	10.3
BC-7	.039	.046	23.2	6.6	29.0	5.1	19.1	14.7
BC-8B	.040	.047	25.0	6.9	30.7	6.0	12.4	16.0
BC-9B	.037	.044	22.0	3.6	28.4		22.0	16.9
BC-10B	.052	.061	25.8	8.1	28.5		14.1	15.1
BC-11B	.039	.046	26.7	5.4	30.2		11.3	19.0
BC-12B	.031	.036	16.7	3.7	30.2		29.7	15.3

Table 3

CHEMICAL ANALYSIS OF ORE SAMPLES*

Percent

	BC-1	BC-2	BC-3
U	0.052	0.036	0.034
Ca	11.6	12.3	5.0
Al	12.8	10.2	15.2
Fe	2.0	1.88	1.20
Mg	.2	.33	
Na	.47	.6	.18
K	.34	.41	.33
Ti	.83	.69	.58
SiO_2	12.2	23.1	32.1
F	1.08	1.35	1.26
PO_4	35.6	31.0	18.9
CO_3	.93		.52
SO_4	.08		$<$.005

* Received as minus 200 mesh screen products.

Table 4

SPECTROGRAPHIC ANALYSES OF ORE SAMPLES*

Percent

	BC-1	BC-3	BC-9	BC-10
B	0.004	0.004	<0.03	<0.03
Ba	2	.08	.04	.08
Be	.0006	< .001	< .001	.001
Cd	< .04	< .04	< .04	
Co	< .04	< .04	< .04	< .08
Cr	.8	.04	.04	.08
Cu	< .04	.02	.04	< 04
K		.2		2
Li		.01		< .01
Mg		.2	< .04	.1
Mn	04	< .04	< 04	02
Mo	< 04	< 04	< 04	< .04
Na		.2		.6
Ni	< .08	< .08	< .08	< 08
Pb	< .08	< .04	< .04	< .08
Sn	< .04	< .02	< .04	< .02
Sr	1.0	.1	< .2	< .4
Ti		.3	.2	3
V	04	04	< .04	< .04
Zn	< .3	< .3	< .3	< 6
Zr	< .2	< .08	< .08	< .1

* "The spectrographic test results reported herein are semi-quantitative estimates which were obtained for use as a guide to chemical analysis and should not be interpreted or construed to be precise quantitative determinations."

Table 5

COMPARISON OF LZ ORE SAMPLES[a]

Sample No.[b]	Grade		Weight Ratio to P_2O_5			Weight Ratio to CaO		
	% U_3O_8	% P_2O_5	CaO	Al_2O_3	U_3O_8	P_2O_5	Al_2O_3	U_3O_8
BC-4[c]	0.044	15	0.12	1.36	0.0029	8.45	11.5	0.022
BC-4B	.062	24	.14	1.42	.0026	7.12	10.0	.018
MIT-E39[(2)]	.030	17	.17	1.41	.0017	5.74	8.10	.010
TVA-A[(4a)]	.032	14	.17	1.62	.0023	5.68	9.60	.013
TVA-A-2[(4a)]	.047	19	.18	1.63	.0025	5.53	9.00	.014
TVA-V-6[(4c)]	.016	11	.18	1.36	.0015	5.50	7.50	.0087
BC-9[f]	.018	10	.16	1.36	.0018	6.36	8.69	.011
BC-9B	.044	22	.16	1.29	.0020	6.11	7.80	.012
BC-11	.025	15	.18	1.22	.0017	5.56	6.78	.0093
BC-11B	.039	27	.20	1.13	.0015	4.95	5.60	.0072
BC-12	.025	9	.18	1.71	.0027	5.23	8.95	.014
BC-12B	.031	17	.22	1.81	.0019	4.52	8.16	.0084
BC-8[d]	.034	18	.25	.94	.0018	4.00	3.75	.0075
BC-8B	.047	25	.28	1.24	.0019	3.63	4.45	.0068
BC-7[d]	.046	23	.29	1.25	.0020	3.50	4.38	.0070

Table 5 (Cont'd.)

COMPARISON OF LZ ORE SAMPLES[a]

Sample No.[b]	Grade		Weight Ratio to P_2O_5			Weight Ratio to CaO		
	% U_3O_8	% P_2O_5	CaO	Al_2O_3	U_3O_8	P_2O_5	Al_2O_3	U_3O_8
BC-10	0.039	16	0.29	1.17	0.0025	3.44	4.02	0.0087
BC-10B	.052	26	.31	1.10	.0020	3.18	3.52	.0064
BC-14	.041	15	.39	1.22	.0027	2.55	3.10	.0068
BC-5[c]	.031	12	.43	1.46	.0025	2.31	3.38	.0058
BC-5B	.045	16	.37	1.87	.0025	2.67	5.00	.0067
BC-3	.040	15	.47	1.89	.0026	2.14	4.04	.0056
BC-13	.041	9	.50	1.08	.0045	2.00	2.16	.0089
BC-1	.061	27	.61	.91	.0023	1.63	1.48	.0037
BC-2	.042	23	.74	.83	.0018	1.35	1.12	.0024
BC-6[e]	.008	6	.93	1.73	.0014	1.08	1.86	.0015
BC-6B	.014	8	.43	2.60	.0017	2.30	6.00	.0040
TVA-I-1[(4b)]	.025	19	1.02	1.11	.0013	.98	1.09	.0013
BC-0	.024	15	1.15	.58	.0016	.87	.50	.0014
BC-0B1	.030	22	.94	.85	.0013	1.06	.91	.0014
BC-0B3	.036	20	1.07	.95	.0018	.94	.88	.0017

a) Data for unclassified ore samples are underlined.
b) Superscripts in parentheses refer to List of References.
c) Sample picked for high wavellite content.
d) Sample reported to contain principally millisite.
e) Sample from TVA Batch C.[(4a)]
f) Sample from TVA Batch V-6.

Table 6

MINERAL COMPOSITION OF LZ ORES*

Percent

Mineral	Ore Sample, ORNL No.:						
	BC-OB1	BC-1	BC-2	BC-3 (Estimated)	BC-5	BC-5B (Estimated)	BC-6
Apatite	38	12	25	10	6	10	4
Wavellite	18			25	20	25	8
Pseudowavellite		66	50	10	10	15	2
Quartz		12	11	10	40		45
Kaolinite	20			40	20	40	
Montmorillonite	18				4	8	40
Hydromica	—	—	—	5	—	—	—
	94	90	86	100	100	98	99

* Reported by the U.S.G.S. (9)

Altschuler and Boudreau[1] have demonstrated correlation of the uranium content with calcium rather than with aluminum or with total phosphate in vertical sections of the Leached Zone. However, for the samples described in Table 5, originating from different areas, the variation in the ratio U_3O_8 : P_2O_5 was much smaller than the variation in the ratio U_3O_8 : CaO.

Description of Ore Samples

BC-0. Sample as dug, received from International Minerals and Chemical Corporation. Nearly white, containing hard lumps, a small amount of hard rock, and also particles superficially resembling phosphate pebble.* The batch was stage crushed through 1/8 inch (most of the material also passed through 20 mesh). Three portions were separately dispersed in water and wet-screened: Plus 200: BC-0A1, BC-0A2, BC-0A3. Minus 200: BC-0B1, BC-0B2, BC-0B3.

BC-1. Sample of classified concentrate (screen product) obtained from I.M.C.C. Nearly white. Nominal minus 200 mesh, but contained a small amount (<1%) of plus 100 mesh sand.

BC-2. Sample of classified concentrate (screen product) obtained from I.M.C.C. Nearly white. Nominal minus 200 mesh, but contained about 4.5% of plus 100 mesh sand.

BC-3. Sample of classified concentrate (screen product) obtained from I.M.C.C. Light tan. Nominal minus 200 mesh, containing less than 0.1% of plus 100 mesh sand.

BC-4. Special sample hand-picked from the upper part of the Leached Zone to contain a high proportion of wavellite, obtained from Mr. John Ruch. Nearly white. Dispersed in water and wet-screened: BC-4A: plus 200 mesh. BC-4B: minus 200 mesh.

BC-5 Special sample supplied by the U.S.G.S., hand-picked (but on a larger scale than BC-4) from the I.M.C.C. Borrow Pit; material from the upper part of the Leached Zone, intended to represent typical well-leached wavellitic sand. Tan colored.

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* A petrographic examination (made by Dr. T. N. McVay) showed the following heavy minerals present in the fine fraction: Collophane, tourmaline, sillimanite, staurolite, epidote, zircon, rutile, kyanite, garnet, and titanite. Monazite and xenotime were absent. The wavellite seemed to be present as extremely tiny crystals, too small for positive identification by microscopic examination.

Stage crushed through 1/8 inch (most of the material also passed through 20 mesh). The minus 1/8 plus 20 fraction contained an appreciable quantity of hard but friable lumps. A portion was dispersed in water and wet-screened: BC-5A: plus 200 mesh. BC-5B. minus 200 mesh.

BC-6.* Sample as dug, essential minus 1/4 inch, obtained from the TVA Laboratory at Wilson Dam (from TVA Batch C(4a)). Light brown color. Contained a fairly large amount of hard rock. The batch was stage-crushed through 1/8 inch. A portion was dispersed in water and wet-screened. BC-6A: plus 200 mesh. BC-6B: minus 200 mesh.

BC-7. Special sample prepared and furnished by the U.S.G.S. from an ore sample (cf. BC-8) expected to contain pseudowavellite and phosphosiderite. This sample was expected to be a concentrate of pseudowavellite. It was subsequently reported to contain principally millisite.** Light tan. Minus 200 mesh. Most of the material in this sample was of uniform size, not much smaller than 200 mesh, in contrast to much very fine material present in other samples.

BC-8. Special sample picked to contain a mineral at first thought to be pseudowavellite, later identified as millisite,** obtained from the U.S.G.S. Light tan. A portion was dispersed in water and wet-screened. BC-8A: plus 200 mesh. BC-8B: minus 200 mesh.

BC-9. Sample as dug, obtained from the TVA Laboratory at Wilson Dam (from TVA Batch V-6(4c)). Light tan. Stage-crushed through 1/8 inch. A portion was dispersed in water and wet-screened. BC-9A: plus 200 mesh. BC-9B. minus 200 mesh.

BC-10. Sample as dug, supplied by the U.S.G.S., obtained from Clear Springs. Almost white.*** Stage-crushed through 1/8 inch. A portion was dispersed in water and wet-screened: BC-10A: plus 200 mesh. BC-10B: minus 200 mesh.

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* This sample was much lower grade in both uranium and phosphorus than were the other LZ samples, and appeared more earthy. It may not be a valid LZ sample, but it was included in the comparative leaching tests because of the possibility that inclusion of a portion of such material might be unavoidable in large-scale mining.

** Z. S. Altschuler, personal communication.

*** One bag of sample BC-10 contained grey material. Grab samples were taken of the grey and the lighter material, before the entire sample was crushed and mixed.

BC-11. Sample as dug, supplied by the U.S.G.S., obtained from the I.M.C.C. Borrow Pit. Almost white. Stage-crushed through 1/8 inch. A portion was dispersed in water and wet-screened: BC-11A: plus 200 mesh. BC-11B: minus 200 mesh.

BC-12. Sample as dug, supplied by the U.S.G.S., obtained from the Plant City Dump. Light tan. Stage-crushed through 1/8 inch. A portion was dispersed in water and wet-screened: BC-12A: plus 200 mesh. BC-12B: minus 200 mesh.

BC-13. Sample as dug, supplied by the U.S.G.S., obtained from Achan. Light grey. Stage-crushed through 1/8 inch.

BC-14. Sample as dug, supplied by the U.S.G.S., obtained from Homeland. Almost white. Stage-crushed through 1/8 inch.

Fine Ore Fractions

Upgrading of LZ ores by attrition grinding and classification to separate the phosphatic fines from the coarser sand has been studied in other laboratories.[3,4] Physical beneficiation was not studied in this laboratory. Minus 200 mesh fractions were separated from portions of most of the ore samples for comparative leaching tests, but these fines can be considered not more than a first approximation to the process ore concentrates which may be available from these ores. This is because simple dispersal by prolonged stirring was used instead of any form of an attrition grind. The primary purpose was to obtain a sample of the fines, and the possibility of failing to disperse and collect some inherently fine material was considered less objectionable than the possibility of grinding and collecting minerals which were actually coarse at the start. Failure to separate and collect some of the fine material should have a relatively small effect on the composition of the fine sample, although the effect could be important on the percent uranium recovery and on the composition of the oversize fraction. Uranium and phosphate grades in the separated fine fractions are shown in Table 7.

Table 7

RESULTS OF ORE CLASSIFICATION

Head Ore			-200 Mesh Fraction				
ORNL No.	Grade		ORNL No.	Grade		Recovery	
	% U	% P_2O_5		% U	% P_2O_5	% of U	% of P_2O_5
BC-0	0.020	15.1	BC-0-B1	0.025	22.4	44	44
			BC-0-B2	0.033	20.4	51	40
			BC-0-B3	0.031	20.1	68	53
BC-4	0.037	15.3	BC-4B	0.053	24.2	50	31
BC-5	.026	12.2	BC-5B	.041	16.1	69	54
BC-6	.007	5.8	BC-6B	.012	8.0	46	38
BC-8	.030	18.4	BC-8B	.040	25.0	32	31
BC-9	.015	10.2	BC-9B	.037	22.0		
BC-10	.033	15.5	BC-10B	.052	25.8		
BC-11	.021	15.0	BC-11B	.039	26.7		
BC-12	.021	9.4	BC-12B	.031	16.7		

ACID LEACHING

Tests to establish conditions for acid leaching of the LZ ores were made principally with the three minus 200 mesh samples, BC-1, BC-2, and BC-3. BC-1 and BC-3 were used for most of the small scale leaching series to determine the effects of acid quantity, pulp density, temperature, and time. BC-2 (which appeared quite similar to BC-1) and BC-3 were used in several large scale leaches, made primarily to furnish liquor for uranium recovery tests.

Other ore samples as they became available were tested for amenability to the leaching conditions established for the first ores. Most of them showed a similar type of response to leaching by sulfuric or nitric acid at low levels, although quantitatively the uranium dissolutions varied over a considerable range. A few ores proved almost completely refractory to leaching at low levels of either acid, and even at high acid levels in the cold. The mineralogical information available to date indicates that two of these ores consisted principally of millisite, which was not reported in the preceding samples. This suggests that the millisite may be the material that is resistant to attack by dilute acid. Mineral analyses of the more recent ore samples should aid in clarifying the significance of the millisite.

Acid Requirements

The acid consumption by ores BC-1, BC-2, and BC-3 over a range of leaching conditions is shown in Figures 2 to 10, which give the final pH, the dissolution of total solids, and the dissolution of uranium for increasing quantities of sulfuric or nitric acid.

The leaches of ore BC-1 were made at 10% and 20% pulp density, and those of ores BC-2 and BC-3 at 15% pulp density (original weight of ore, calculated to oven-dry basis, over the total weight of slurry). Hence, the acid concentrations represented by a given quantity of acid in different leach tests varied over a range, e.g., 1.1%, 1.8%, and 2.5% acid when 200 lb acid per ton was used, or 5.6%, 8.8% and 12.5% acid when 1000 lb acid per ton was used, at pulp densities of 10%, 15%, and 20%, respectively. The leaching results with ore BC-1 were found to be generally similar at 10% and 20% pulp density, as shown in Figures 11 and 12. Hence, the different pulp densities are not distinguished in the foregoing figures.

The results obtained with sulfuric acid and with nitric acid were generally similar. With the data plotted against weight of each acid, the leach curves would be expected to fall

[redacted]

DWG. 18128

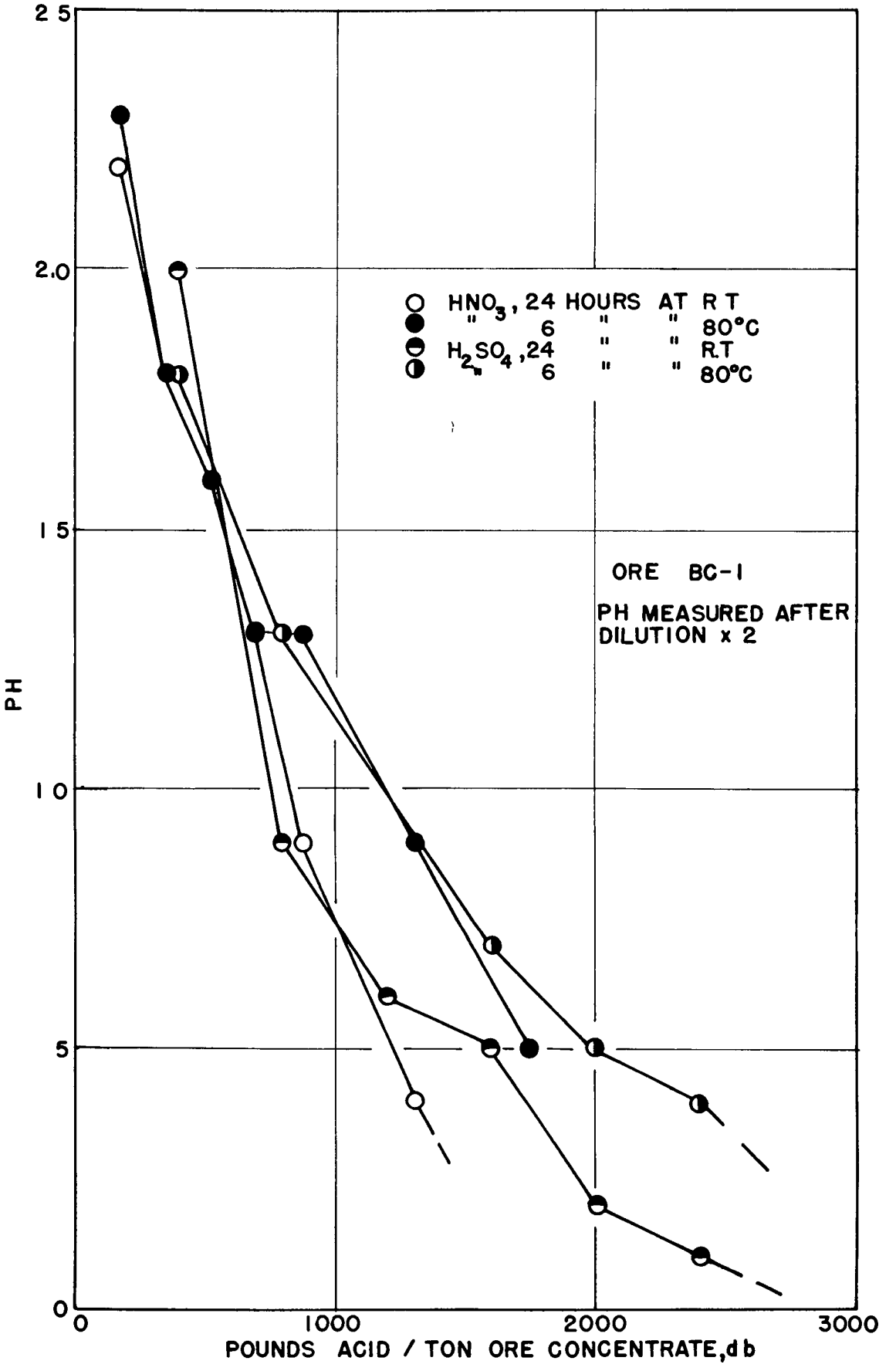
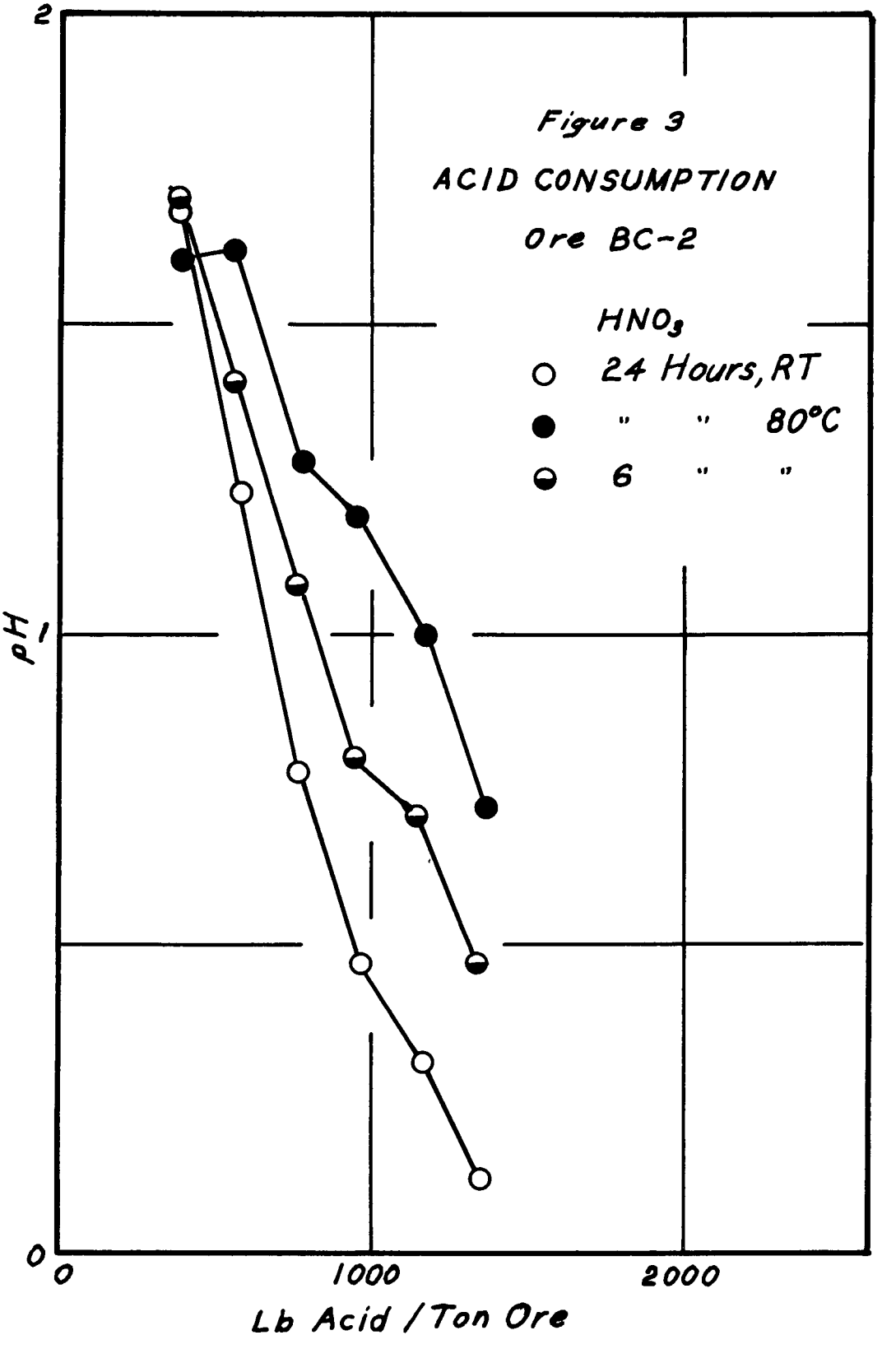


FIGURE 2 ACID CONSUMPTION

[redacted]

DWG. 18129



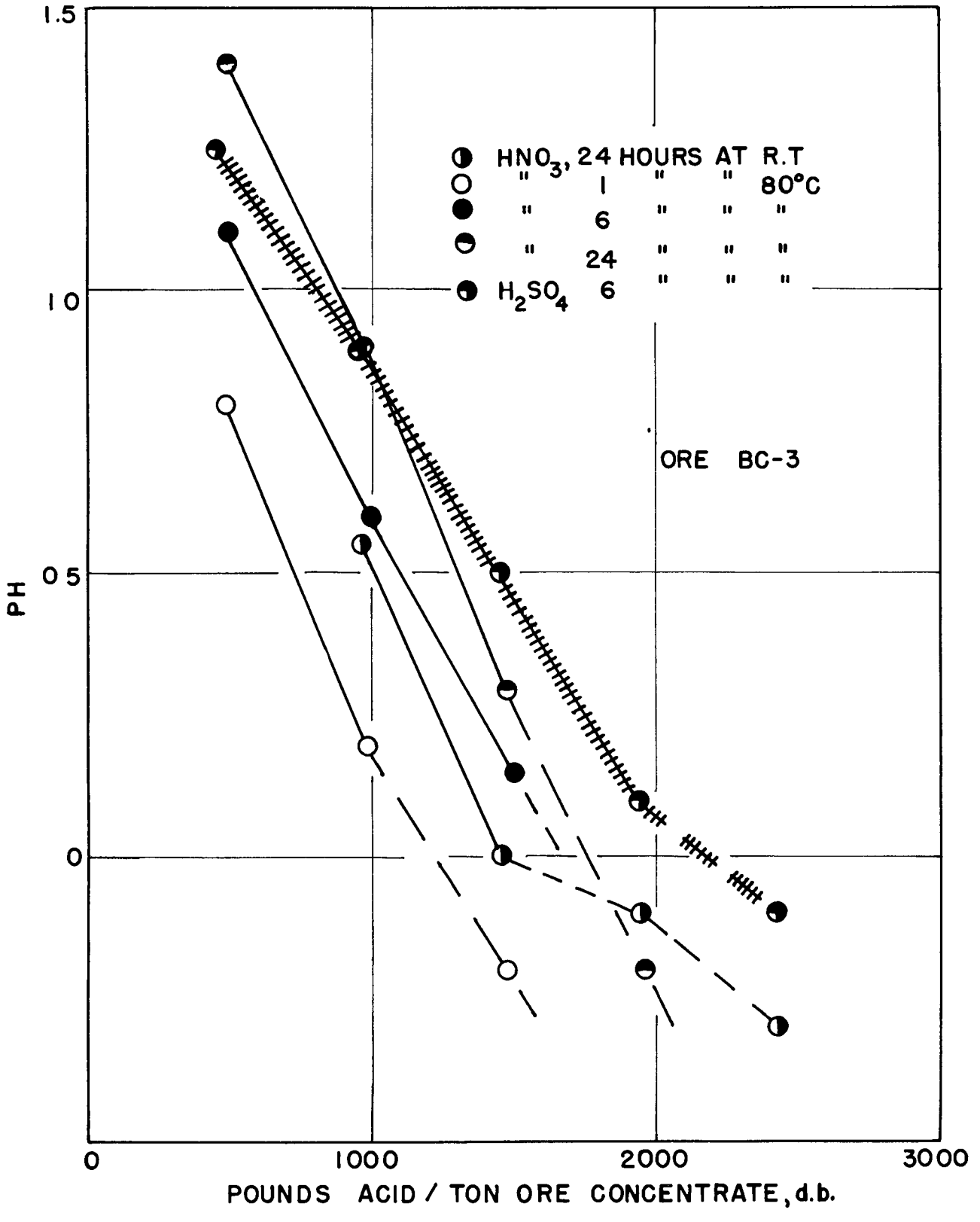


FIGURE 4 ACID CONSUMPTION

[redacted]

DWG. 18131 30

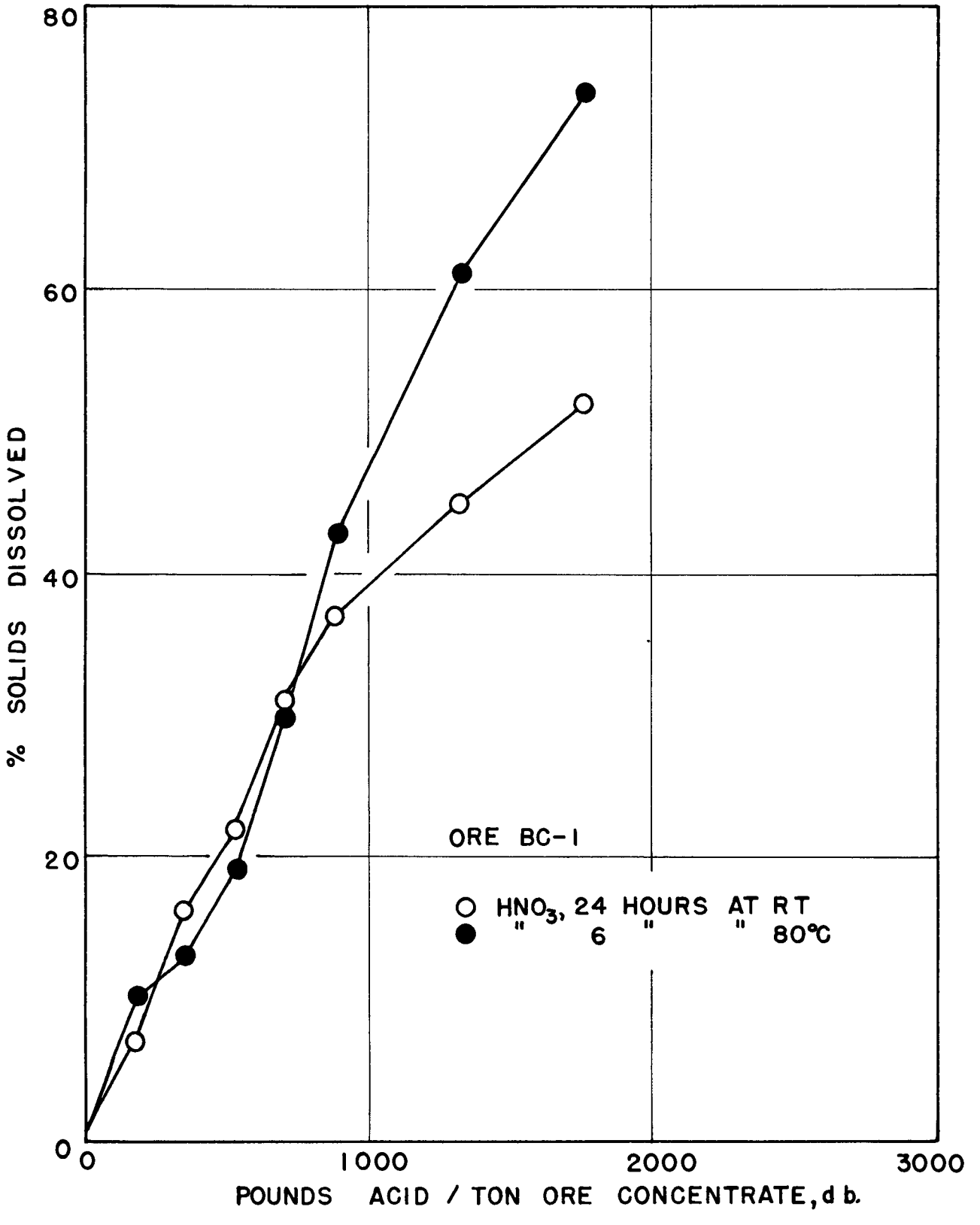


FIGURE 5 PERCENT DISSOLUTION OF SOLIDS

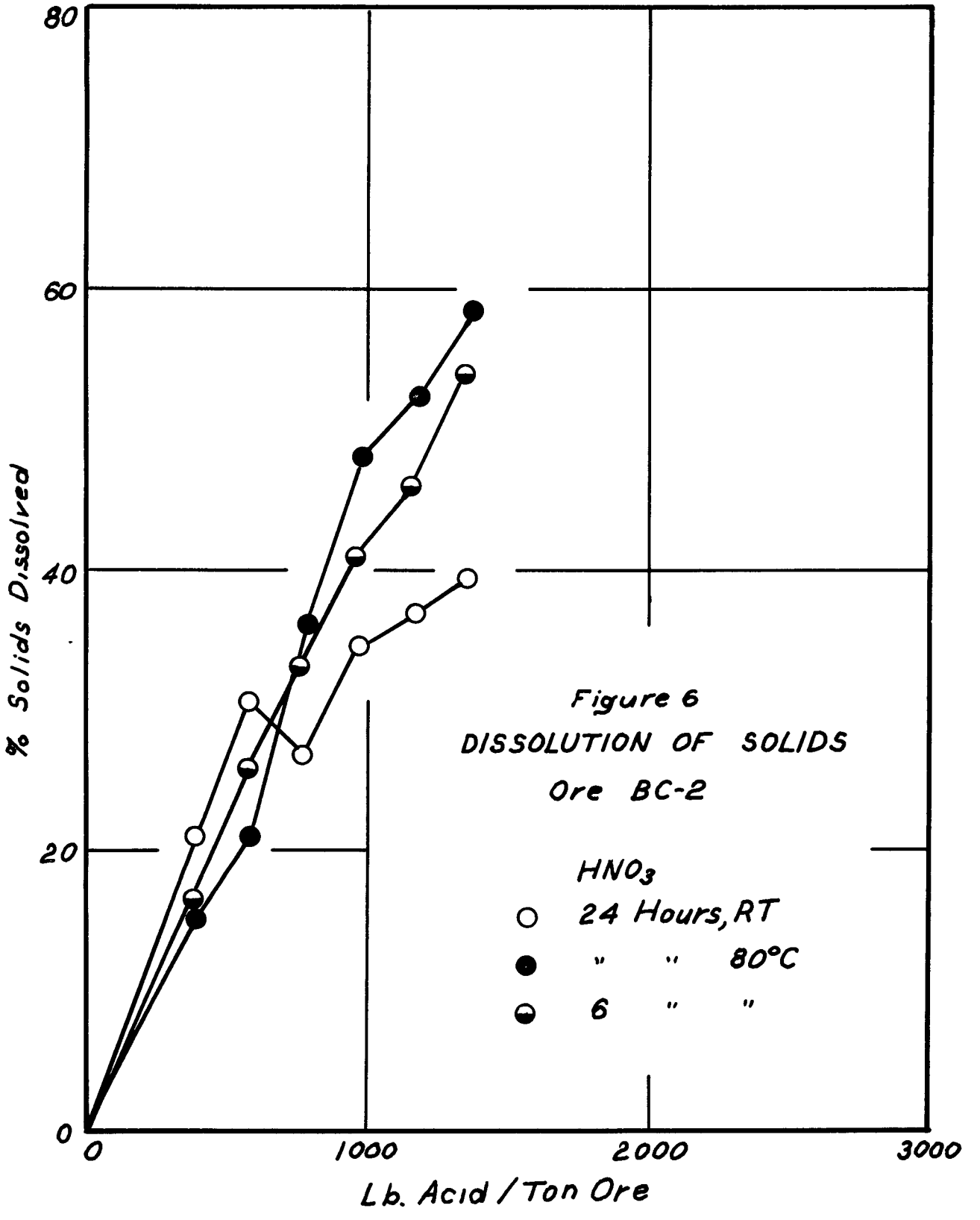


Figure 6
DISSOLUTION OF SOLIDS
Ore BC-2

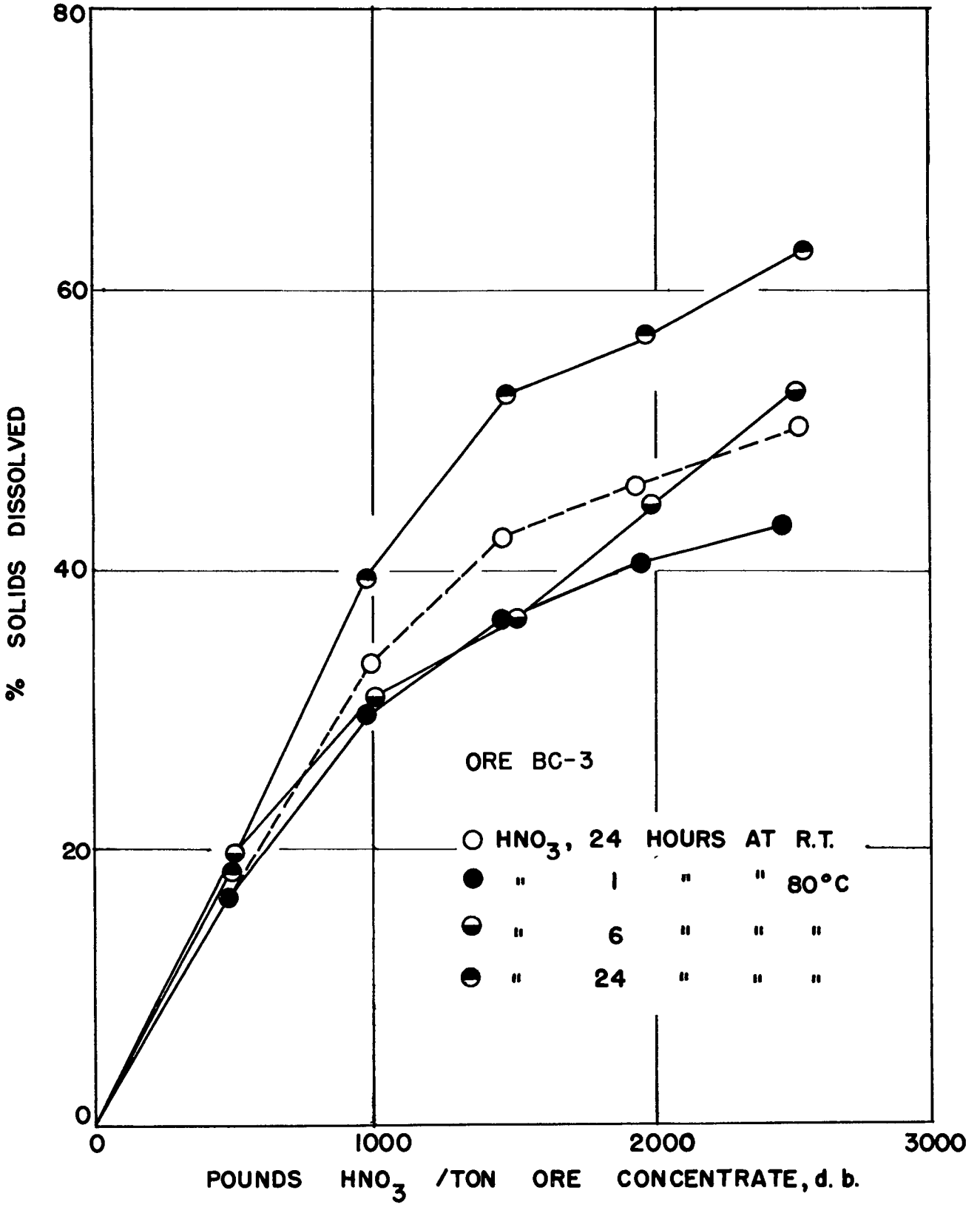


FIGURE 7. PERCENT DISSOLUTION OF SOLIDS

DWG. 18134

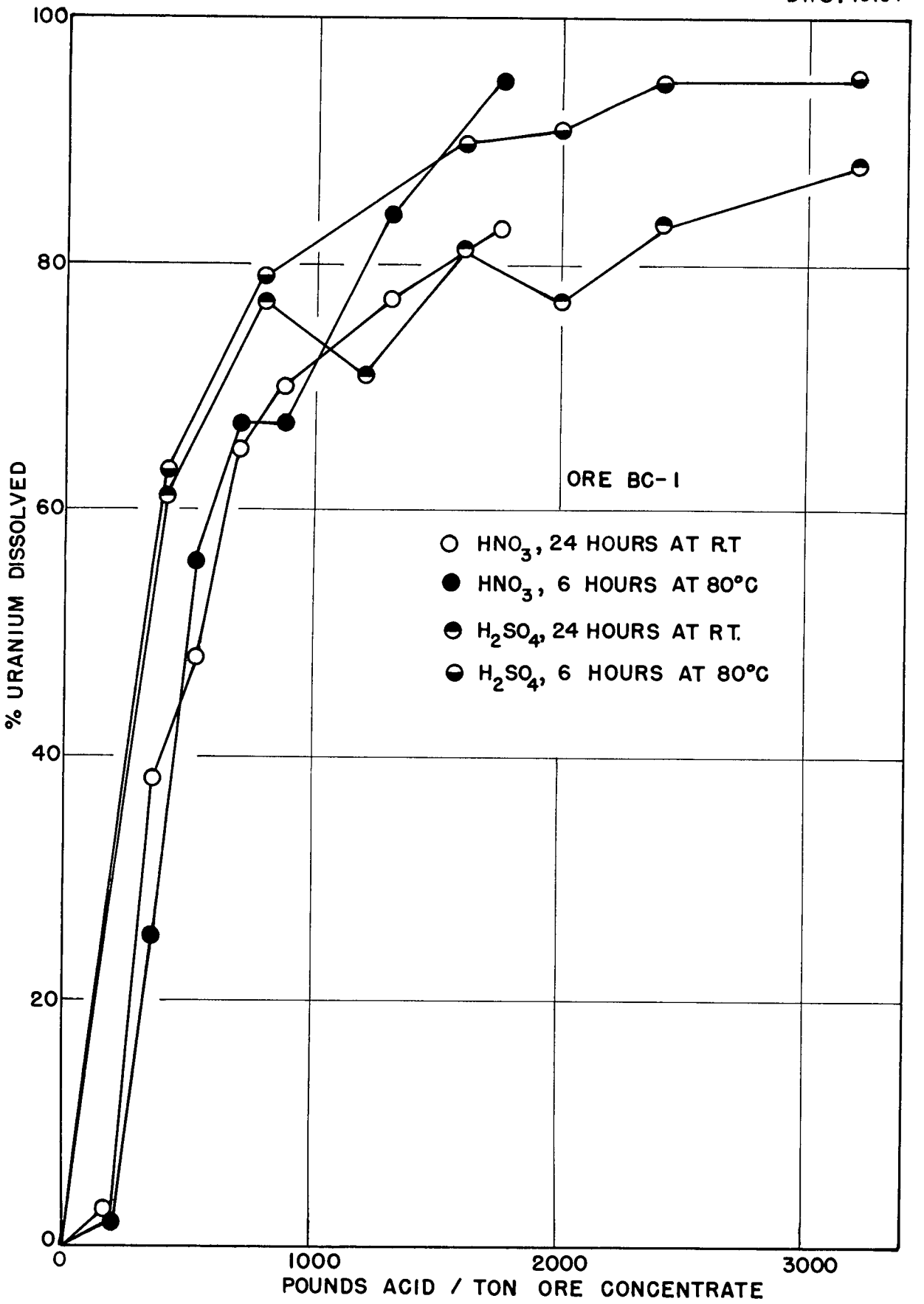
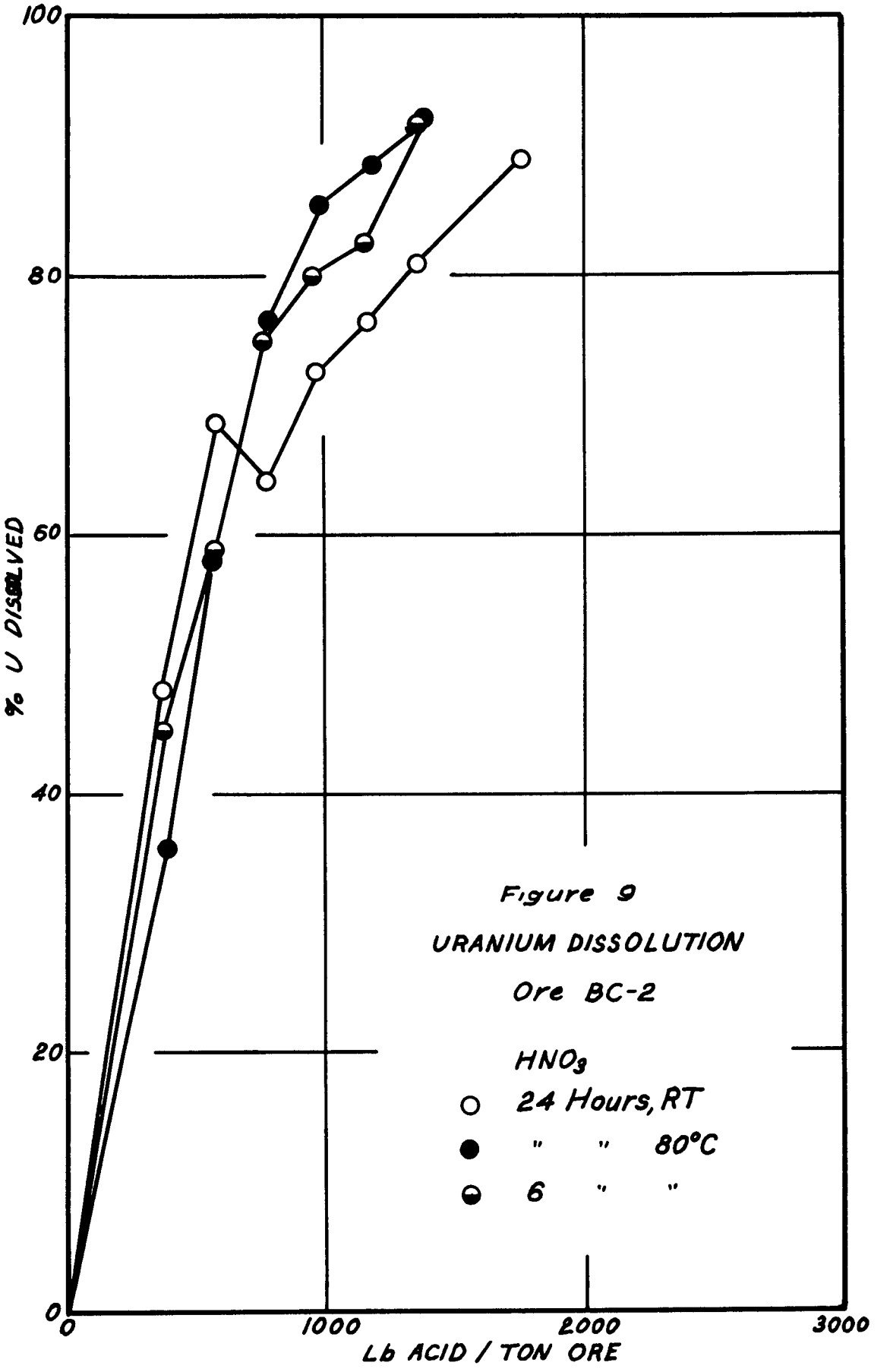


FIGURE 8 URANIUM DISSOLUTION


100
80
60
40
20
0
% U DISSOLVED
0
1000
2000
3000
Lb ACID / TON ORE
Figure 9
URANIUM DISSOLUTION
Ore BC-2
HNO3
24 Hours, RT
" " 80°C
6 " "

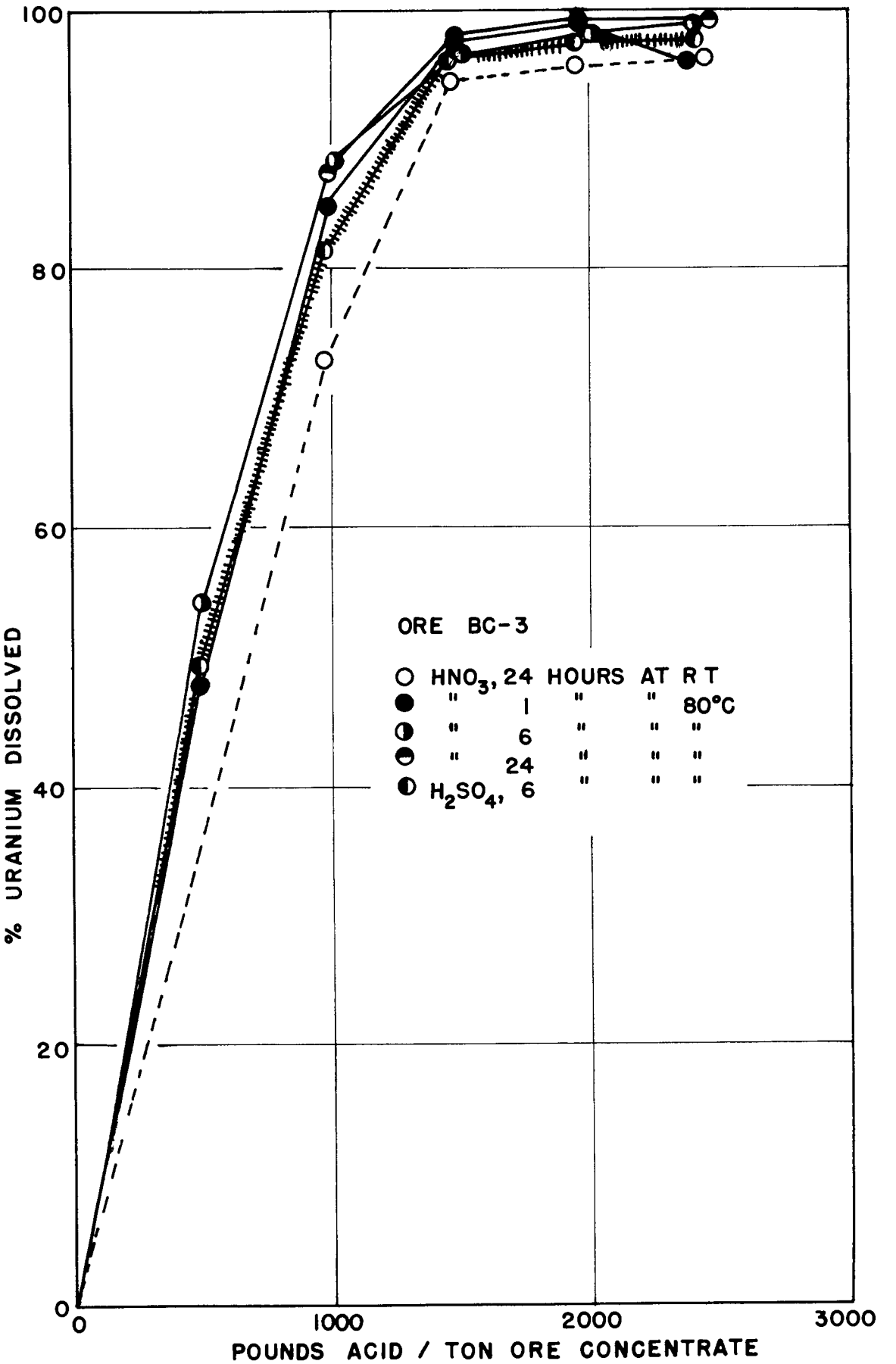


FIGURE 10 URANIUM DISSOLUTION

DWG. 18137

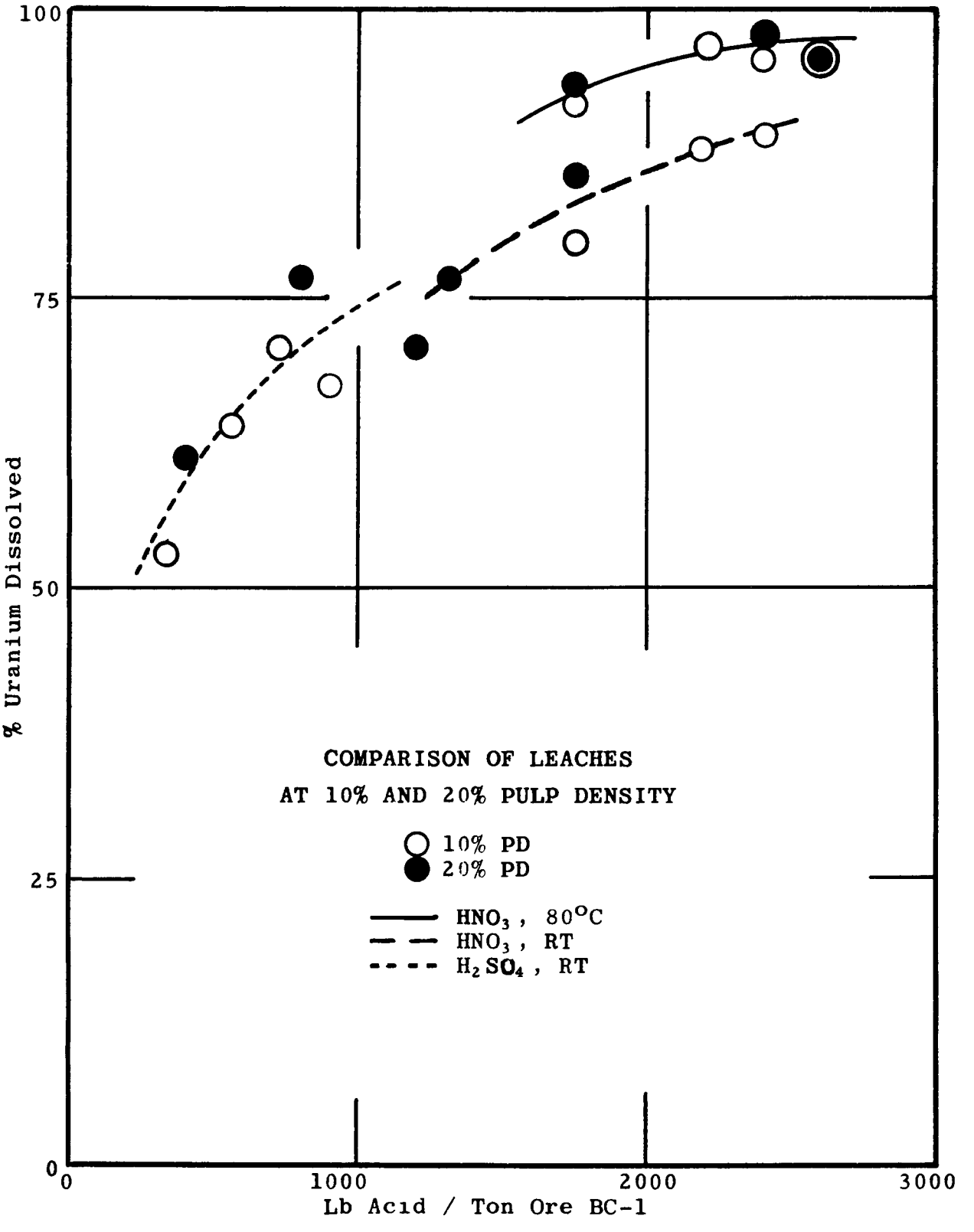
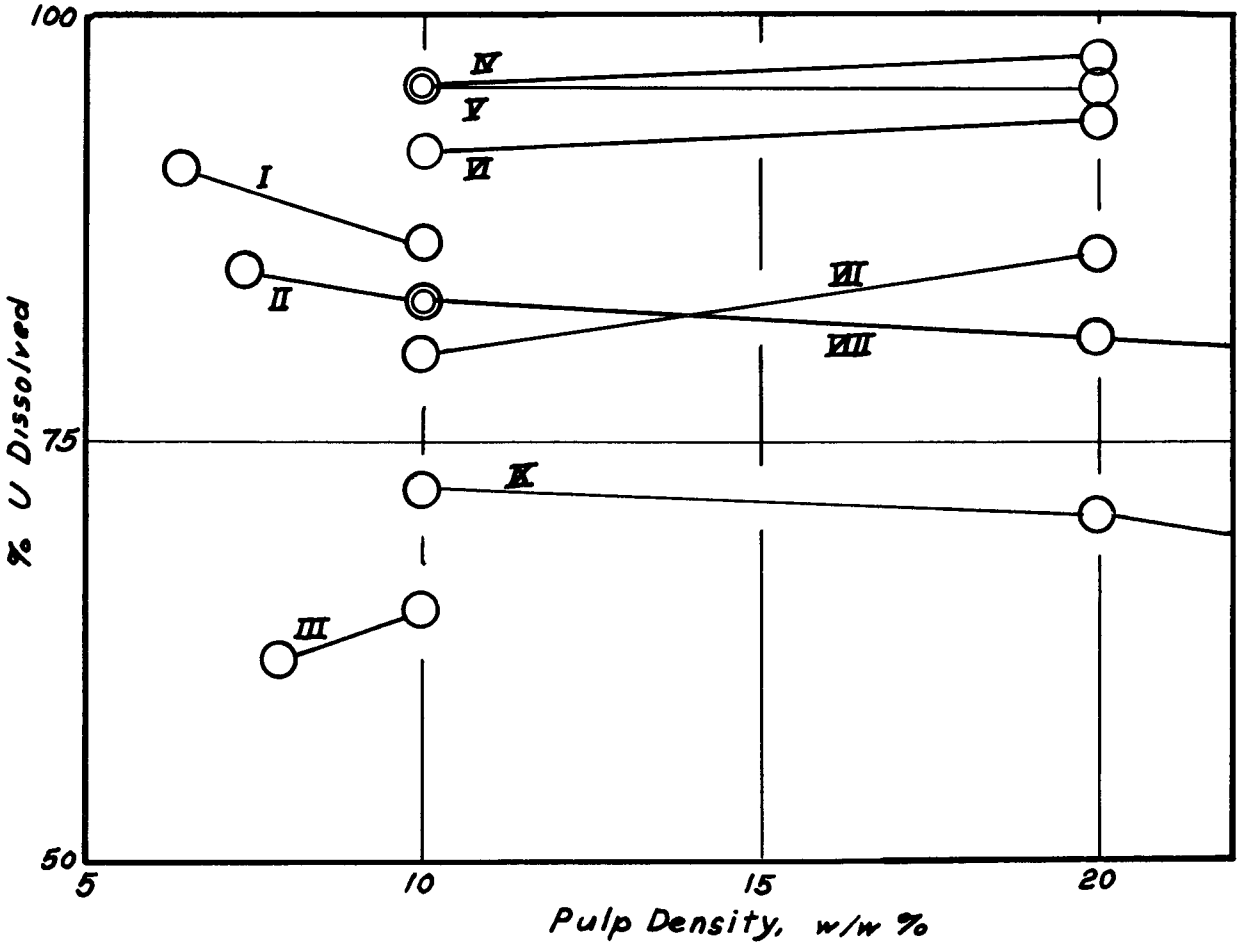


FIGURE 11



I	BC-OBI	1187	Lb	H_2SO_4 /	Ton	Ore	RT
II	"	730	"	"	"	"	"
III	"	340	"	"	"	"	"
IV	BC-1	2400	"	HNO_3 /	"	"	80°C
V	"	2600	"	"	"	"	"
VI	"	1750	"	"	"	"	"
VII	"	"	"	H_2SO_4 /	"	"	RT
VIII	BC-0	450	"	"	"	"	"
IX	"	"	"	"	"	"	80°C

Figure 12

EFFECT OF PULP DENSITY

into two groups for the two acids, separated in proportion to their equivalent weights of 49 and 63. Thus, the close agreement of the curves on the weight basis actually means that, on an equivalent basis, the sulfuric acid was slightly less effective than the nitric acid, probably because of the weaker ionization of its second hydrogen. The observed results make it convenient to refer all the leaching data to weight of acid used.

The final pH's* were usually slightly higher after leaching at 80°C than after leaching at room temperature, indicating more extensive attack on the bases at the higher temperature. This was also shown by the fraction of the total solids dissolved, which was considerably higher at 80°C than at room temperature when more than 1000 lb nitric acid per ton of ore was used.

Uranium dissolution points for ore BC-1 at two acid levels are plotted against temperature in Figure 13, and for ore BC-3 in Figure 14. With ore BC-1, all the final pH's for the leaches with 1750 lb acid per ton for six hours, and the two at 30°C and 50°C with 1750 lb acid per ton for 24 hours, were less than zero. The final pH's of the other leaches are shown in the figure. In both series with 1750 lb acid per ton (six hours and 24 hours), uranium dissolution was increased from about 80% at room temperature to about 90% at 50°C and to about 95% at 80°C and 95°C. Both series at 525 lb acid per ton showed some improvement from room temperature to 50°C (63% uranium dissolved), but impairment at higher temperatures. The 24 hour leach at 95°C fell below 40% uranium dissolution suggesting that reprecipitation of the dissolved uranium may have occurred as the free acid was used up by continued reaction with the gangue during the protracted digestion. However, the increase in the final pH for this leach did not appear great enough to make reprecipitation seem probable.

The difference between 24 hour leaches of ore BC-3 at room temperature and at 80°C (Figure 14) with 1000 lb acid per ton was about the same as was found with BC-1, but with 1400 lb acid per ton the room temperature leach was almost as effective as that of 80°C.

The effect of leaching time is shown for ore BC-1 in Figures 15 to 18, and for ore BC-3 in Figures 19 and 20. There was not much change in the results after about six hours, except for the dissolution of aluminum from ore BC-3. The aluminum

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*All the pH's shown in Figures 2, 13, and 15 were measured after the pregnant liquor had been diluted to twice its original volume. All the other pH's reported were measured before the pregnant liquor was diluted with washings.

[redacted]

DWG. 18139

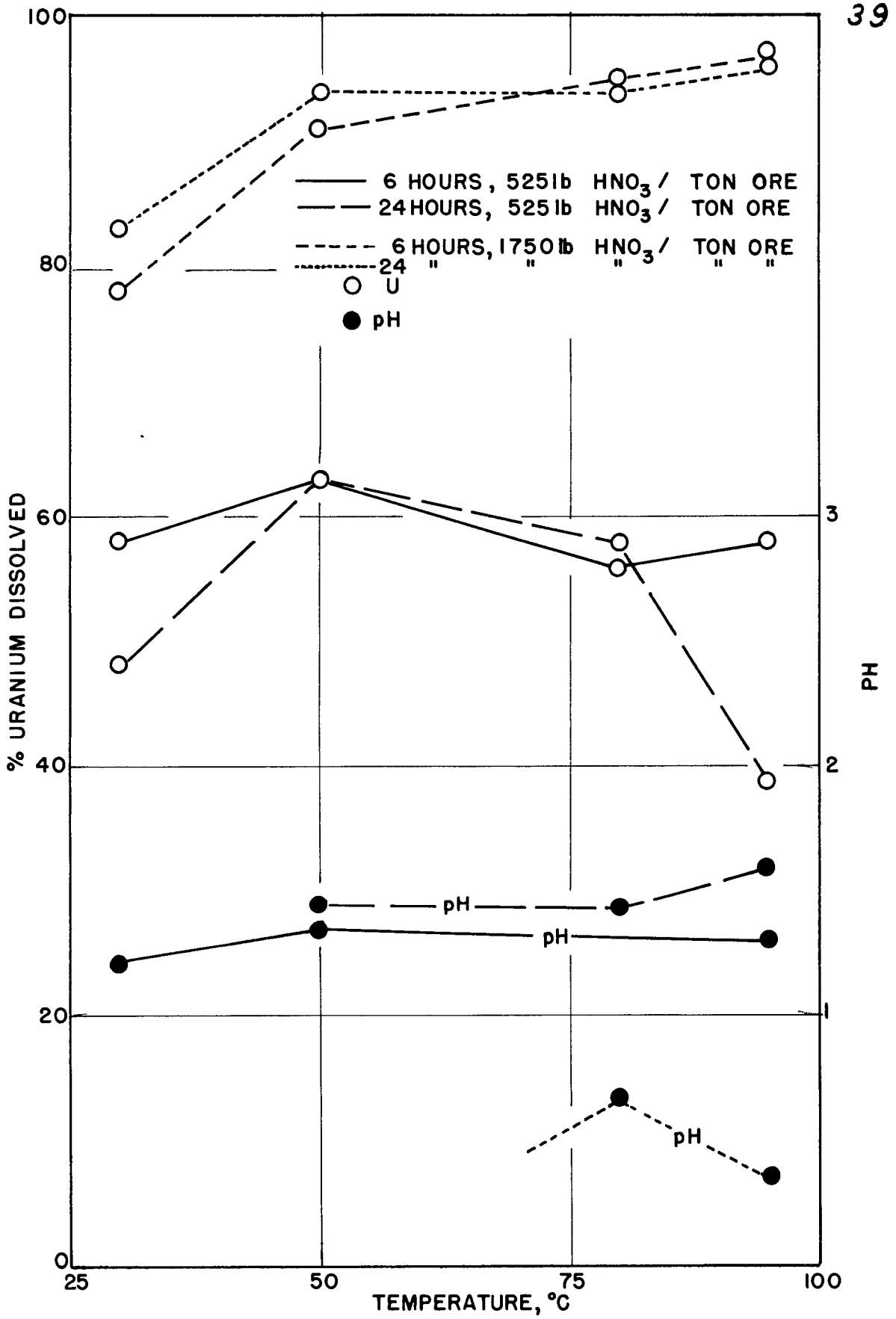


FIGURE 13 EFFECT OF TEMPERATURE ON NITRIC ACID LEACHING OF BC —1 ORE

[redacted] DWG. 18140 40

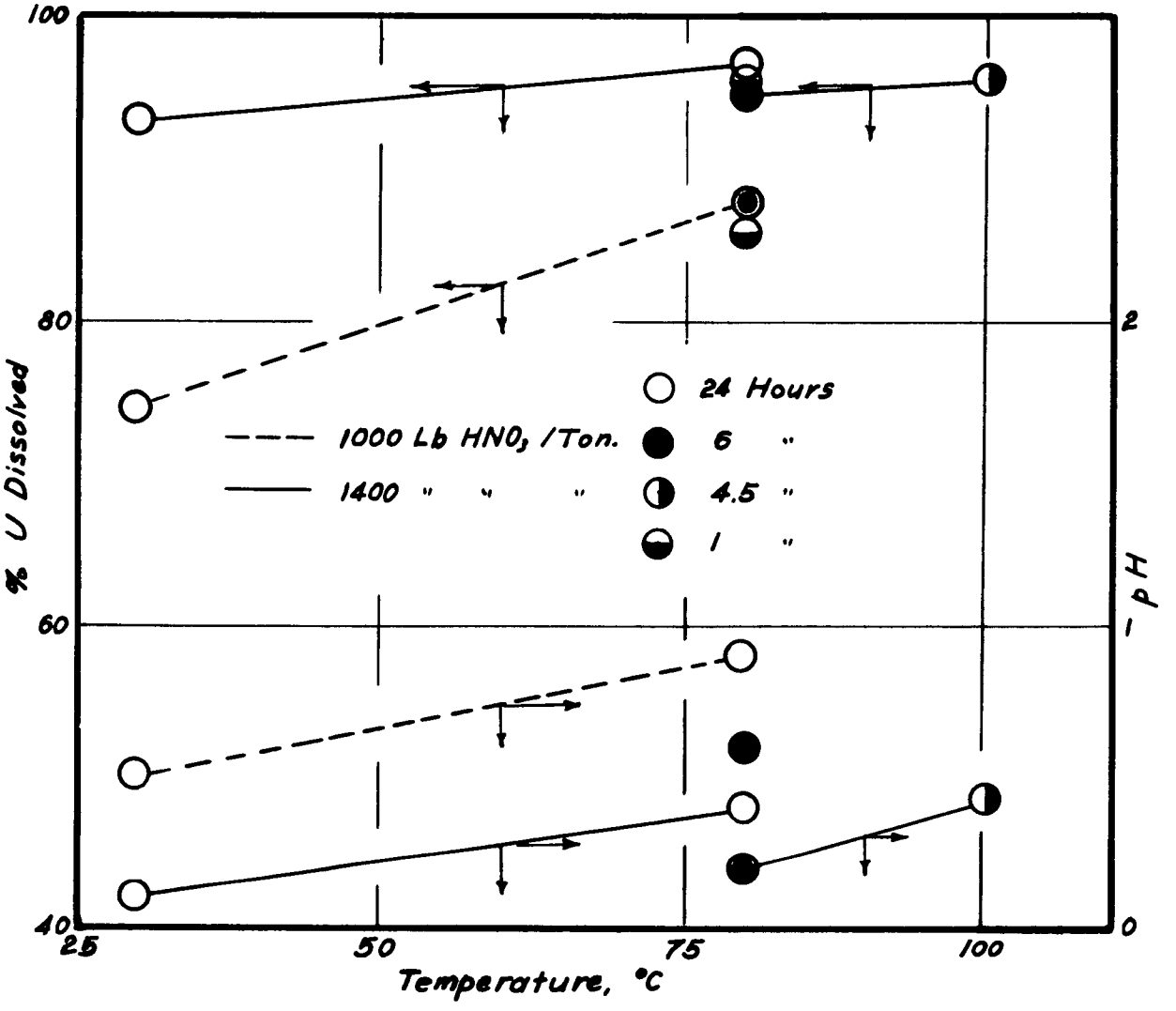


Figure 14

EFFECT OF TEMPERATURE

Ore BC-3

[redacted] DWG. 18141 41

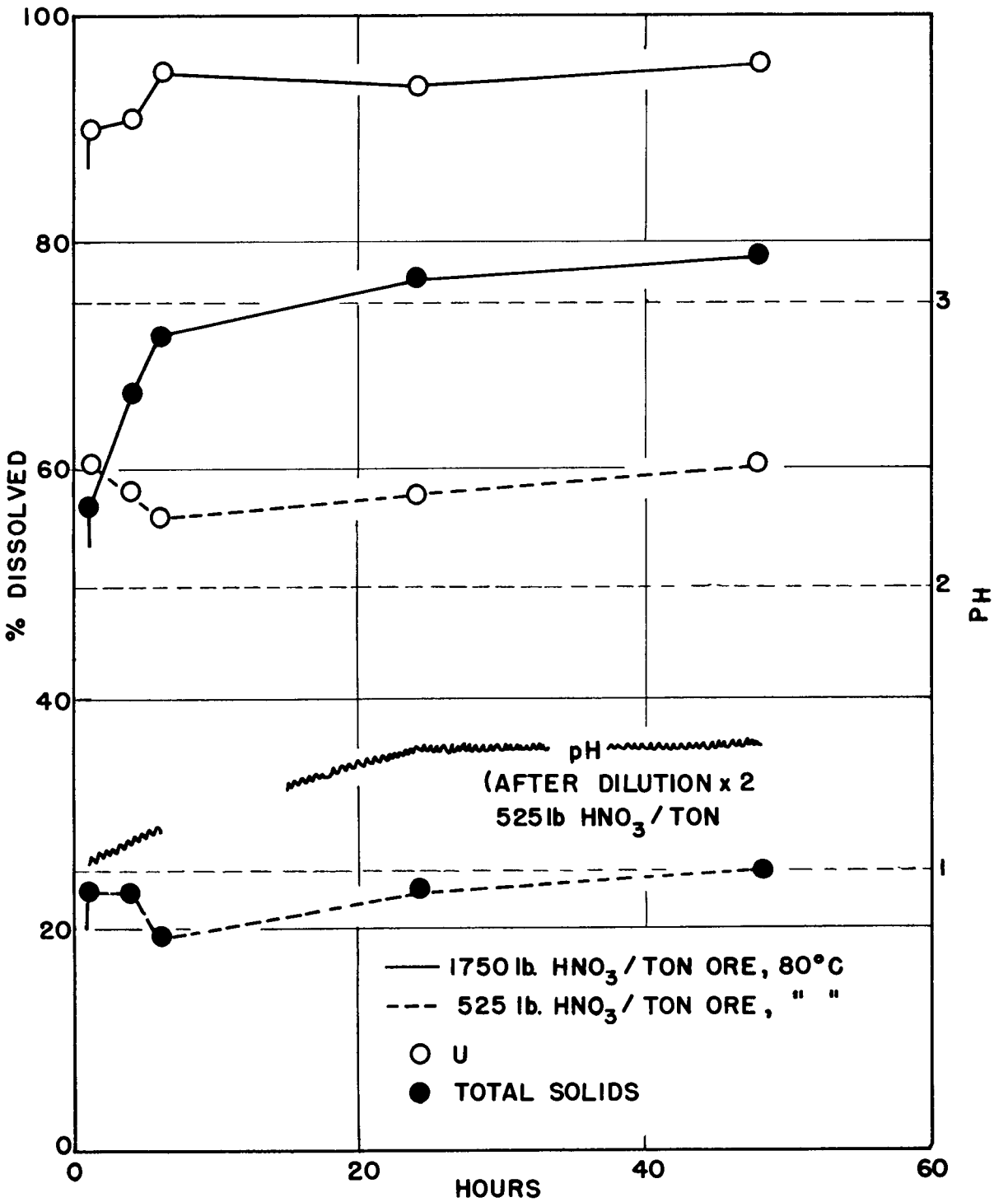


FIGURE 15 EFFECT OF TIME ON NITRIC ACID LEACHING OF BC-1 ORE

[redacted] DWG. 18142 42

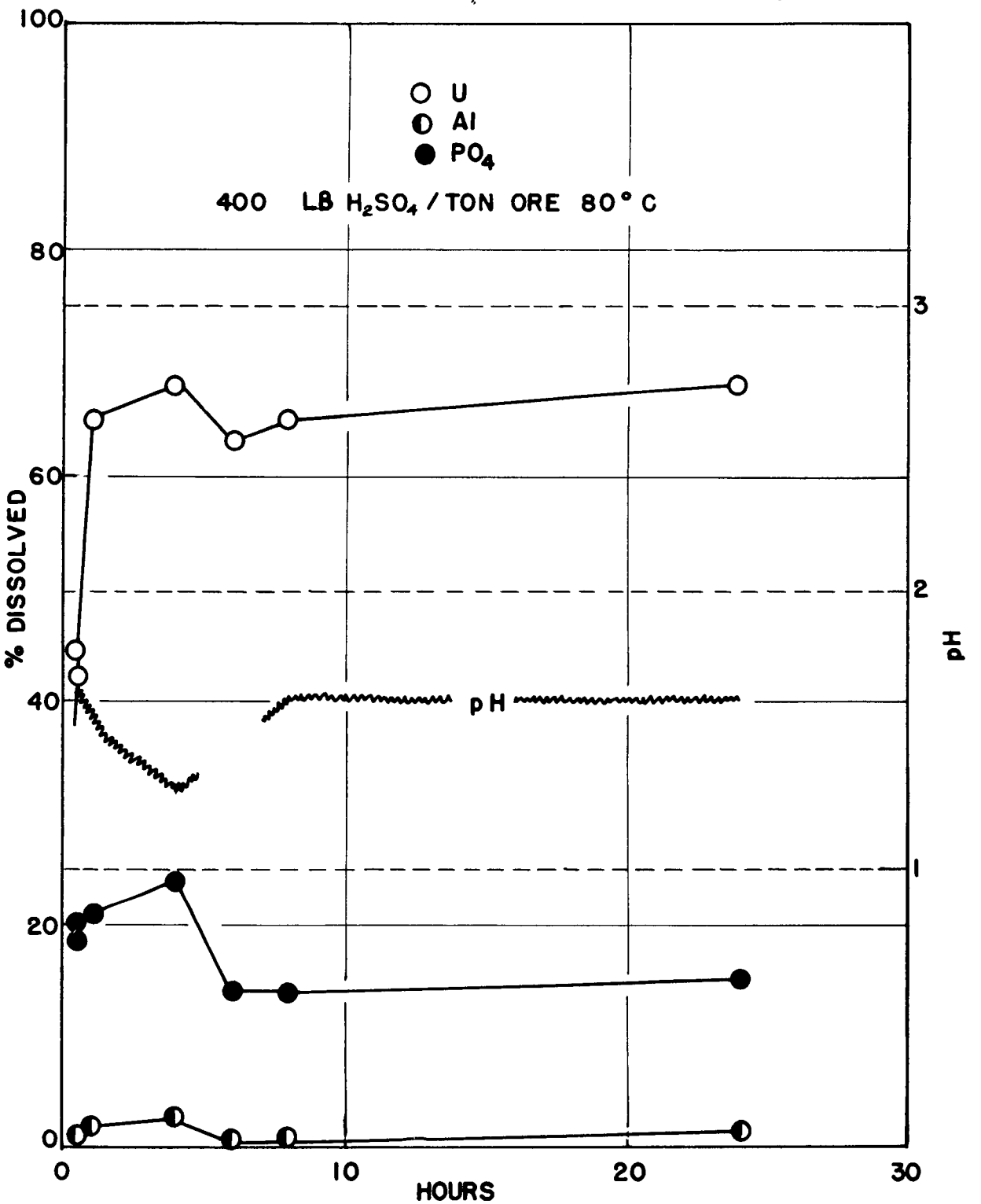


FIGURE 16 EFFECT OF TIME ON SULFURIC ACID LEACHING OF BC-I ORE

[redacted] DWG. 18143 43

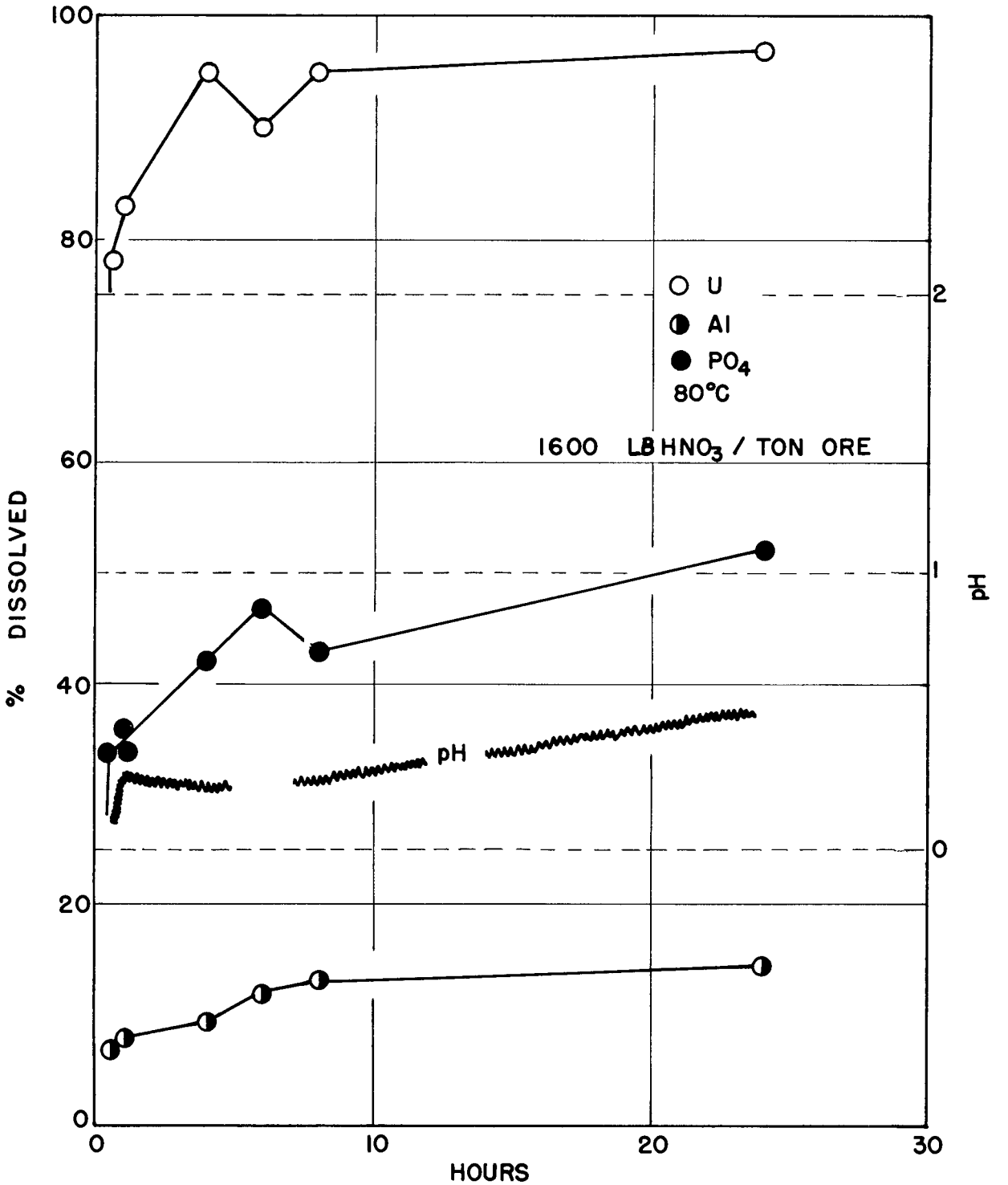


FIGURE 17 EFFECT OF TIME ON SULPHURIC ACID LEACHING OF BC-1 ORE

[redacted] DWG. 18144 44

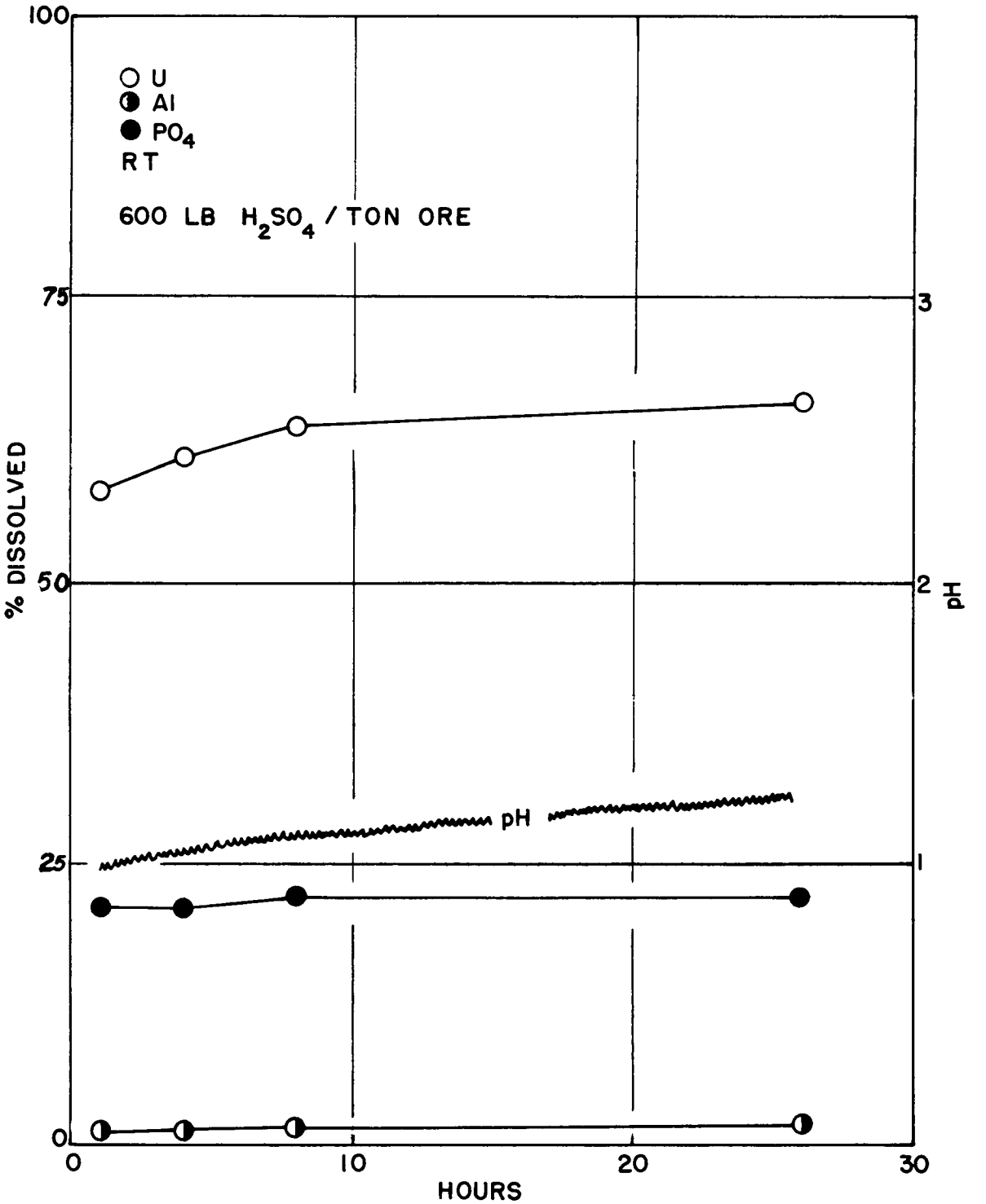


FIGURE 18. EFFECT OF TIME ON SULPHURIC ACID LEACHING OF BC-1 ORE

[redacted]

DWG. 18145 45

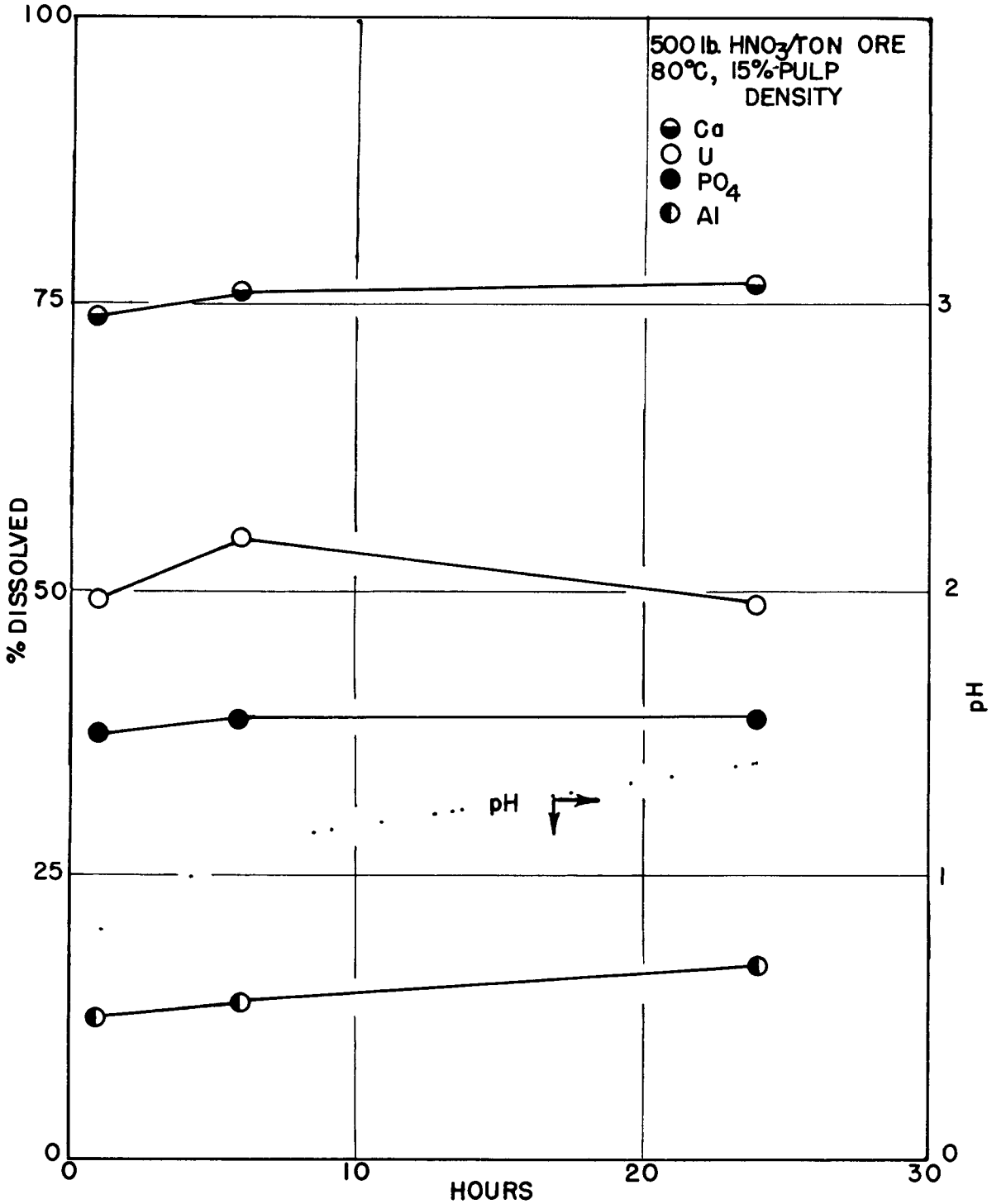


FIGURE 19. EFFECT OF TIME ON NITRIC ACID LEACHING OF BC—3 ORE

[redacted] DWG. 18146 46

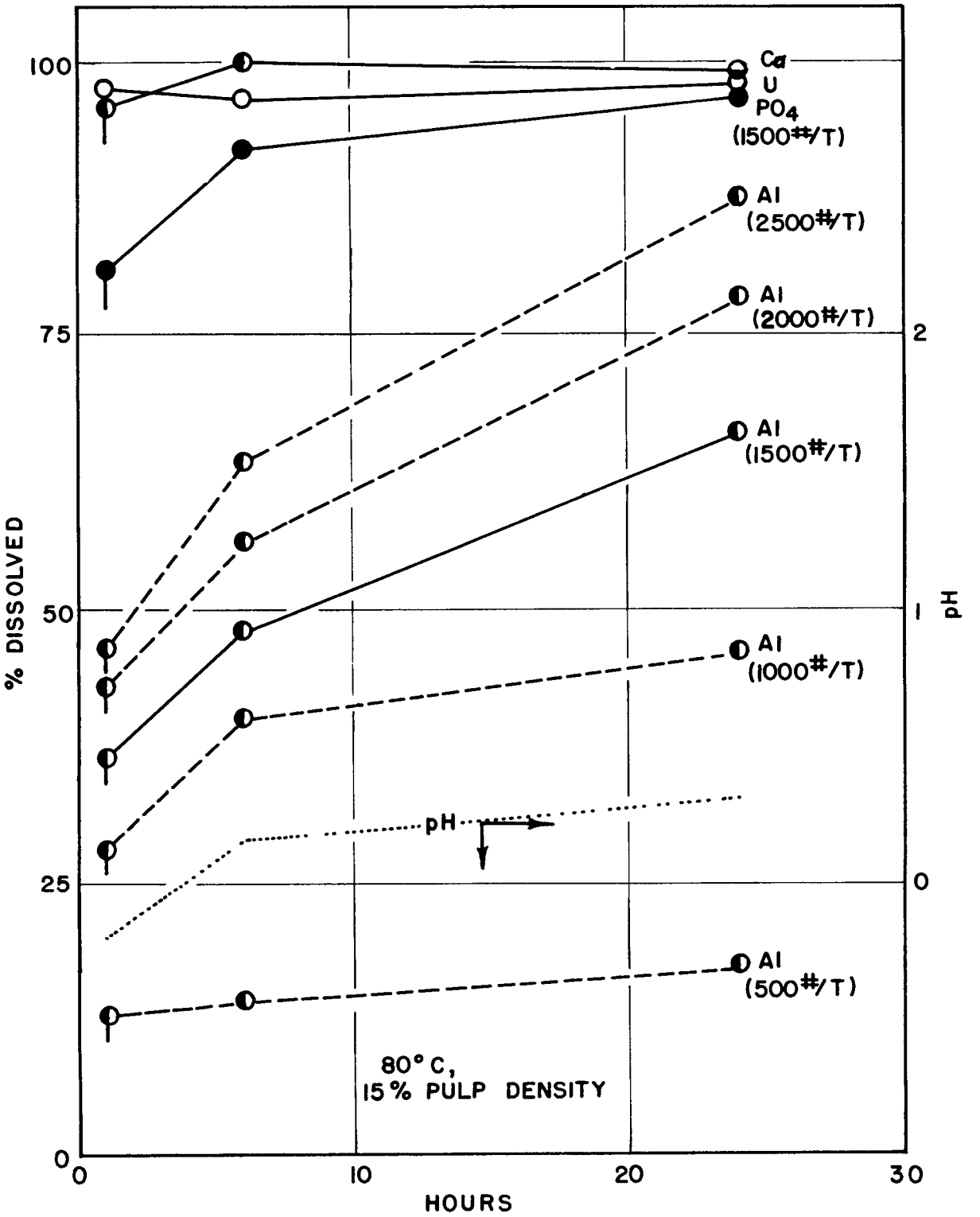


FIGURE 20. EFFECT OF TIME ON NITRIC ACID LEACHING OF BC-3 ORE

extractions for several acid levels are included in Figure 20, showing continued rise throughout 24 hours, especially at the higher acid levels. This was interpreted as indicating a protracted attack on aluminum silicate minerals. For ore BC-1, which was reported to be essentially free of clay, the aluminum curves are parallel to curves for the other constituents.

These time curves together with the temperature curves of Figures 13 and 14 indicate that six hours was sufficient leaching time at 80°C, and that much longer leaches might be harmful if a minimum of acid were to be used. At room temperature there was little change beyond eight hours, but 24 hours was not detrimental.

Figures 21 to 26 show the dissolution of uranium, calcium, aluminum, and phosphate for some of the nitric acid leaches shown above, and the dissolution of uranium, aluminum, and phosphate for the corresponding sulfuric acid leaches.

In all the nitric acid leaches, calcium dissolution was highest at any given acid level, and aluminum dissolution was lowest, with phosphate intermediate. Uranium dissolution paralleled the calcium, usually falling between the calcium and the phosphate. Iron was determined in some of the leaches, and showed about the same relative dissolution as the aluminum. Calcium dissolution was of course slight in the sulfuric acid leaches; the results for the other constituents were similar to those of the nitric acid leaches.

Although the general results were similar, several differences were noted between the responses of BC-1 and BC-3. With BC-1, very little aluminum was dissolved by the lower quantities of acid, where the calcium dissolution was increasing rapidly, and aluminum dissolution became proportional to the additional acid after most of the calcium had been dissolved. With BC-3, this lag in aluminum dissolution was much less noticeable, in accordance with the lower calcium content of this ore head. The phosphate dissolution from BC-3 rose toward completion almost as rapidly as did the calcium dissolution, whereas with BC-1 the phosphate curve was more nearly parallel to the aluminum curve. These differences, as well as the differences in overall acid consumption and dissolution of total solids, may be ascribed at least in part to the slow acid attack on the aluminum silicate minerals in ore BC-3.

The scatter of results in a series of tests, whether from inherent variations in the dissolution or from analytical imprecision, was sometimes greater than the average differences between series. The scattering appeared worst for the 24 hour leach at room temperature (Figures 8 and 23), perhaps indicating greater sensitivity to unrecognized variables at low temperature.

[redacted]

DWG. 18147

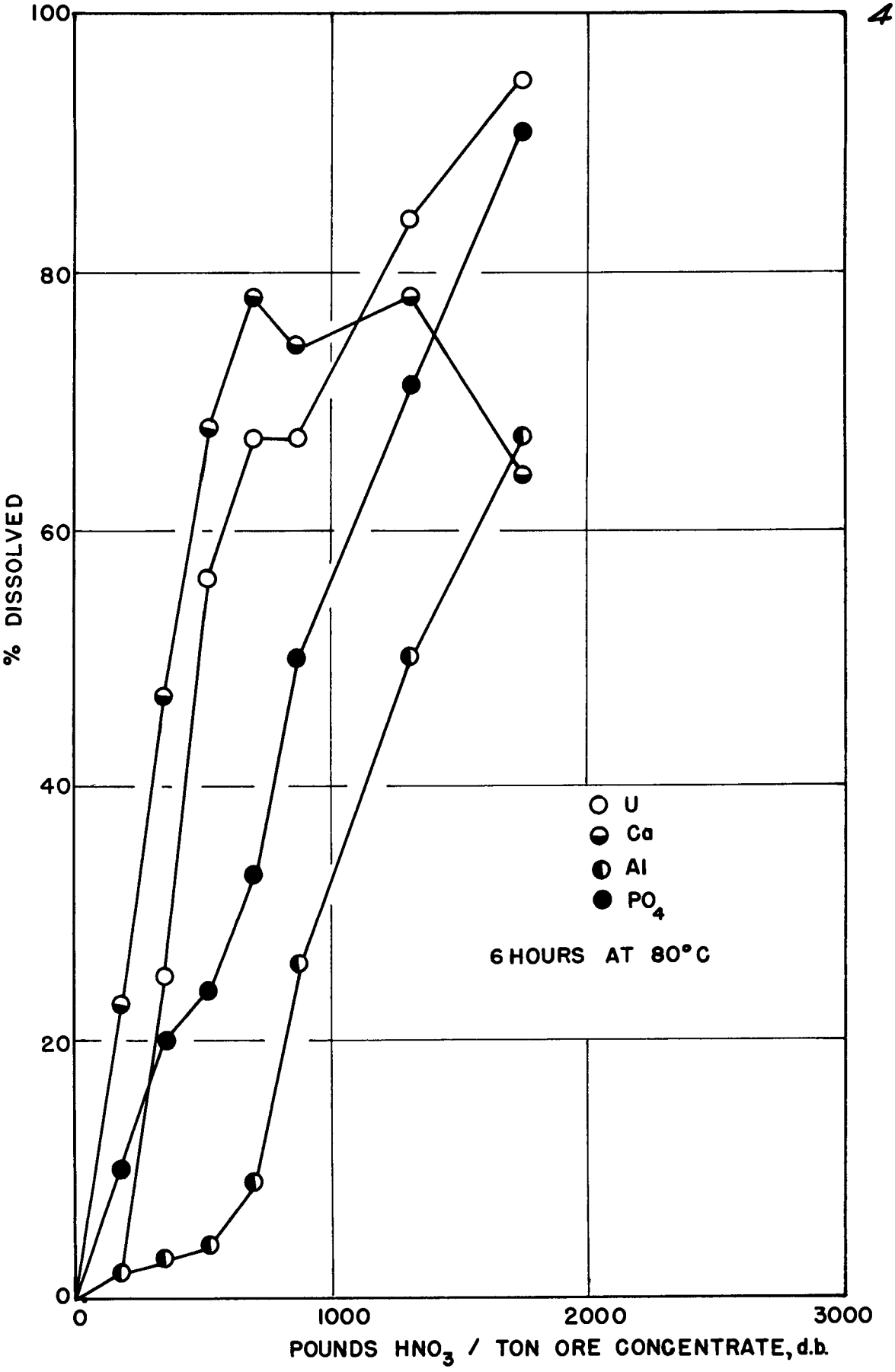


FIGURE 21. NITRIC ACID LEACHING OF ORE BC—I

[redacted] DWG. 18148 49

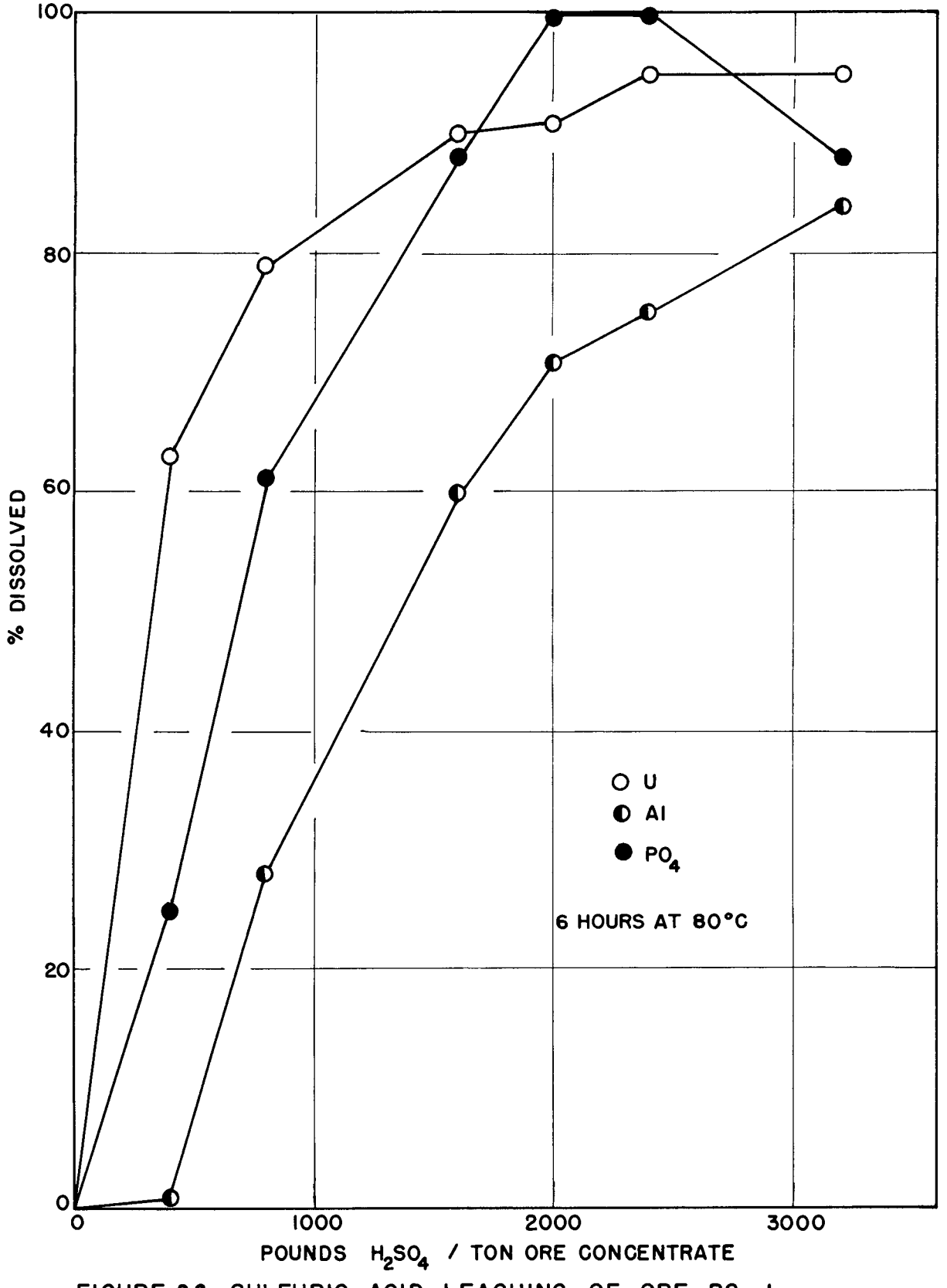


FIGURE 22. SULFURIC ACID LEACHING OF ORE BC—I

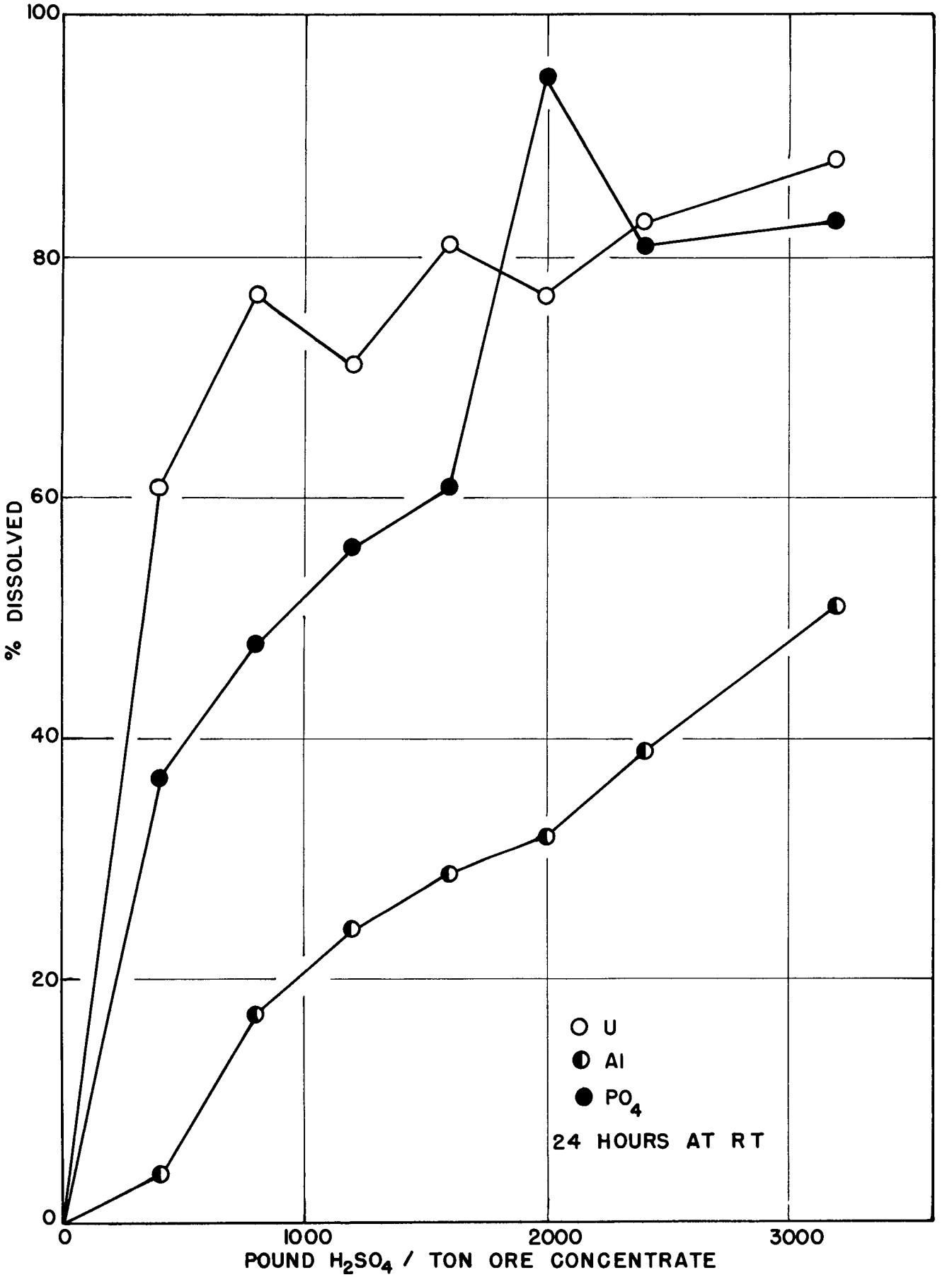


FIGURE 23. SULFURIC ACID LEACHING OF ORE BC-1

[redacted]

DWG. 18150 51

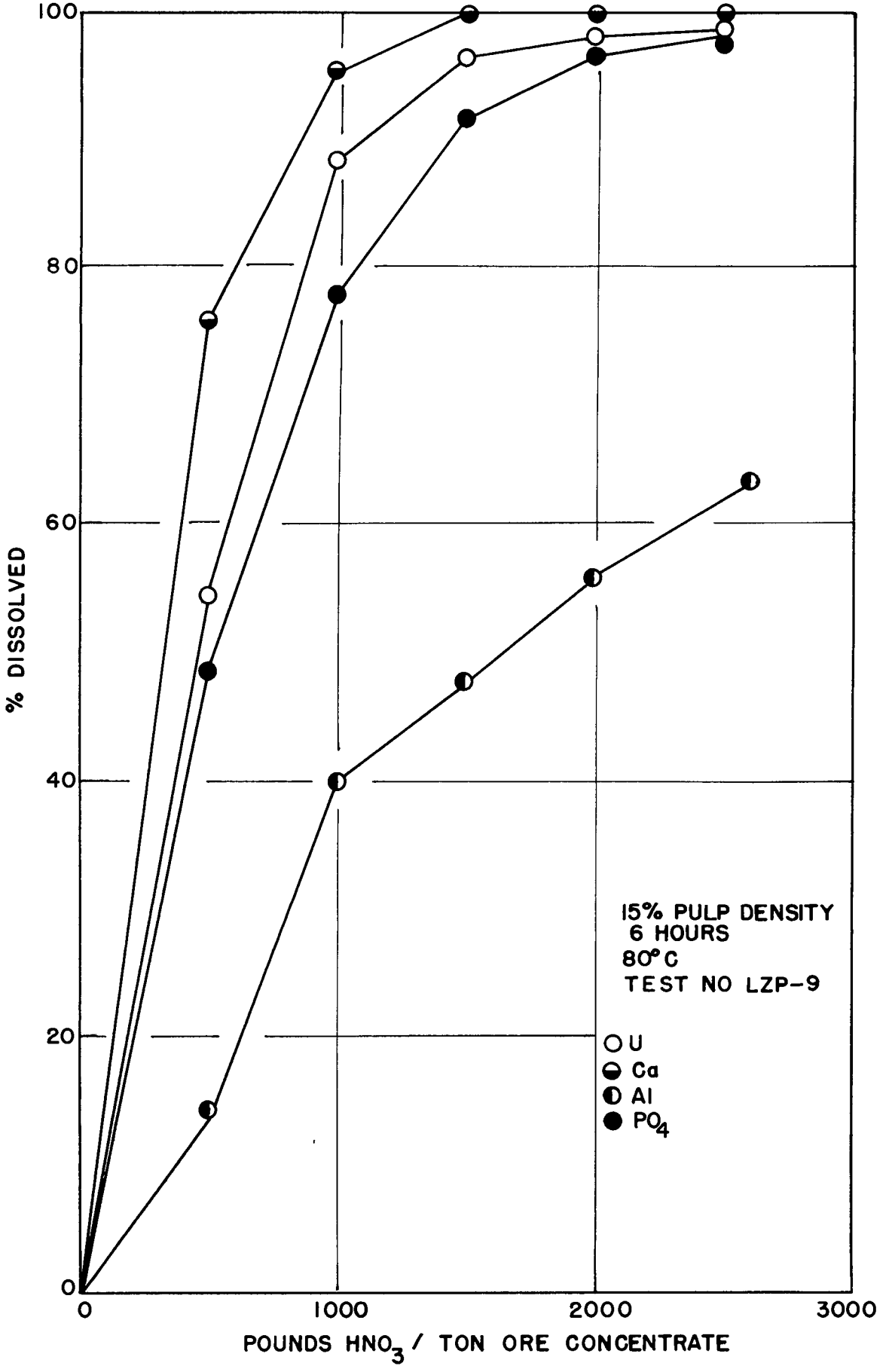


FIGURE 24. LEACHING OF BC-3 ORE WITH NITRIC ACID

[redacted]

DWG. 18151

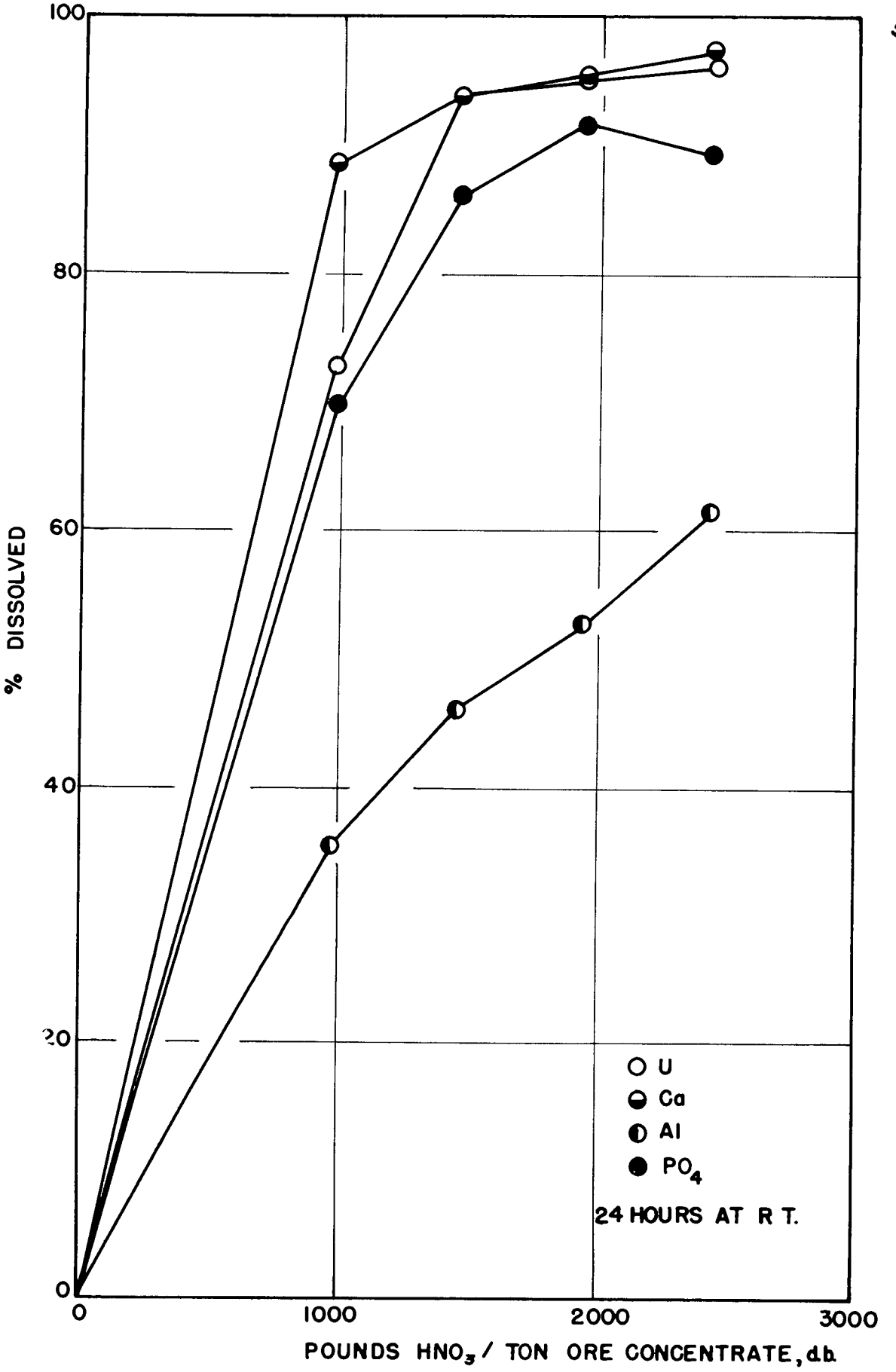


FIGURE 25. NITRIC ACID LEACHING OF ORE BC-3

[redacted]

DWG. 18152

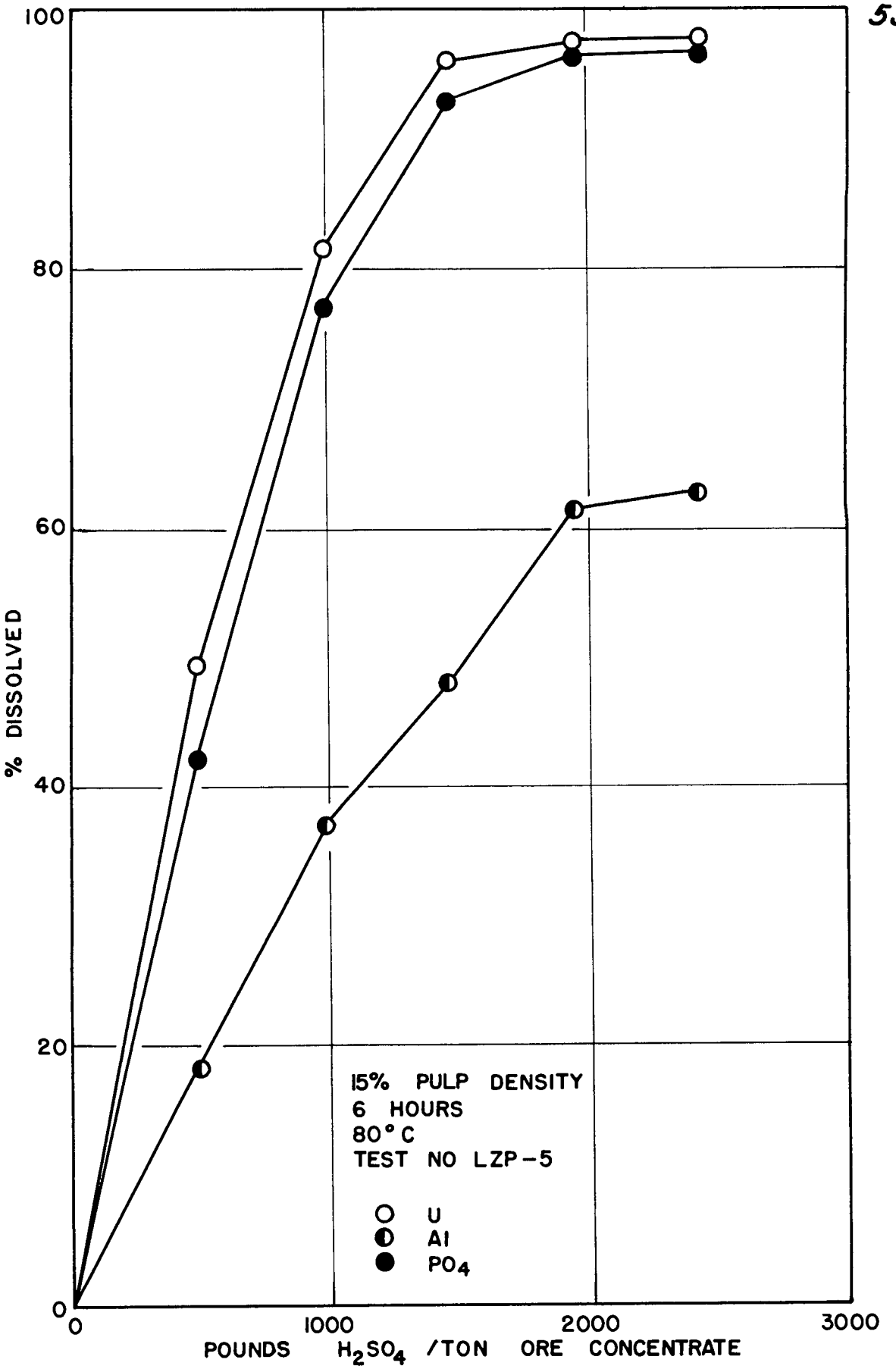


FIGURE 26. LEACHING OF BC-3 ORE WITH SULFURIC ACID

Phosphoric Acid. Leaching tests similar to but less extensive than the foregoing tests were made with phosphoric acid on ores BC-1 and BC-3. The results showed less material dissolved and higher final pH's than were obtained with the same weights of nitric or sulfuric acid, in keeping with the weaker nature of phosphoric acid. Complexing of uranium by the phosphoric acid, if effective at all, was not sufficient to bring the extractions up to those obtained with the strong acids.

Constant-pH Leaches

Attempts were made to increase the efficiency of uranium extraction at low acid levels by means of constant-pH leaching and resin-in-pulp leaching. The dissolutions of solids shown in Figures 5, 6 and 7 indicated that the acid consumption by the bases in the gangue minerals depended rather strongly on pH. This suggested that the acid consumption could be minimized by adding the acid only as required to maintain a constant pH throughout a leach rather than adding the same total quantity of acid all at one time, giving initially a much lower pH but ending at a higher pH. If the uranium were present as discrete minerals or in surface concentrations, so as to be accessible to the acid without extensive dissolution of the gangue, then decreased acid consumption by the gangue should permit higher efficiency in extraction of uranium. It was also considered possible that in the direct leaches some of the uranium dissolved at low pH might be reprecipitated as the free acid was depleted and the pH rose. If this were occurring, the extractions might be improved by continuous removal of the uranium as it was dissolved, e.g., by anion exchange sorption from the slurry or by slurry-liquid extraction.

Both the maintenance of constant pH and the presence of a uranium acceptor were tested in the same set of leaches. In these tests, several minus 200 mesh ore samples were leached, with anion exchange resin in the pulp, at constant pH's of 1.0, 1.5, or 2.0, and similar ore samples were leached directly with the same quantities of acid. The experimental procedures are described below. The final pH's obtained in the direct leaches (Figure 28) were a little higher than the corresponding constant pH's (Figure 27), but the uranium extractions did not show any systematic differences large enough to be distinguished from the random variations which were encountered to about the same extent in both types of leach. The uranium extractions are shown in Figures 31 to 39, with open and blackened circles for the direct and the constant-pH leaches, respectively. The failure to obtain enhanced uranium extraction, although not constituting a very sensitive test, can be considered evidence that at least the greater part of the uranium was either occluded or dispersed in other minerals.

[redacted]

DWG. 18153

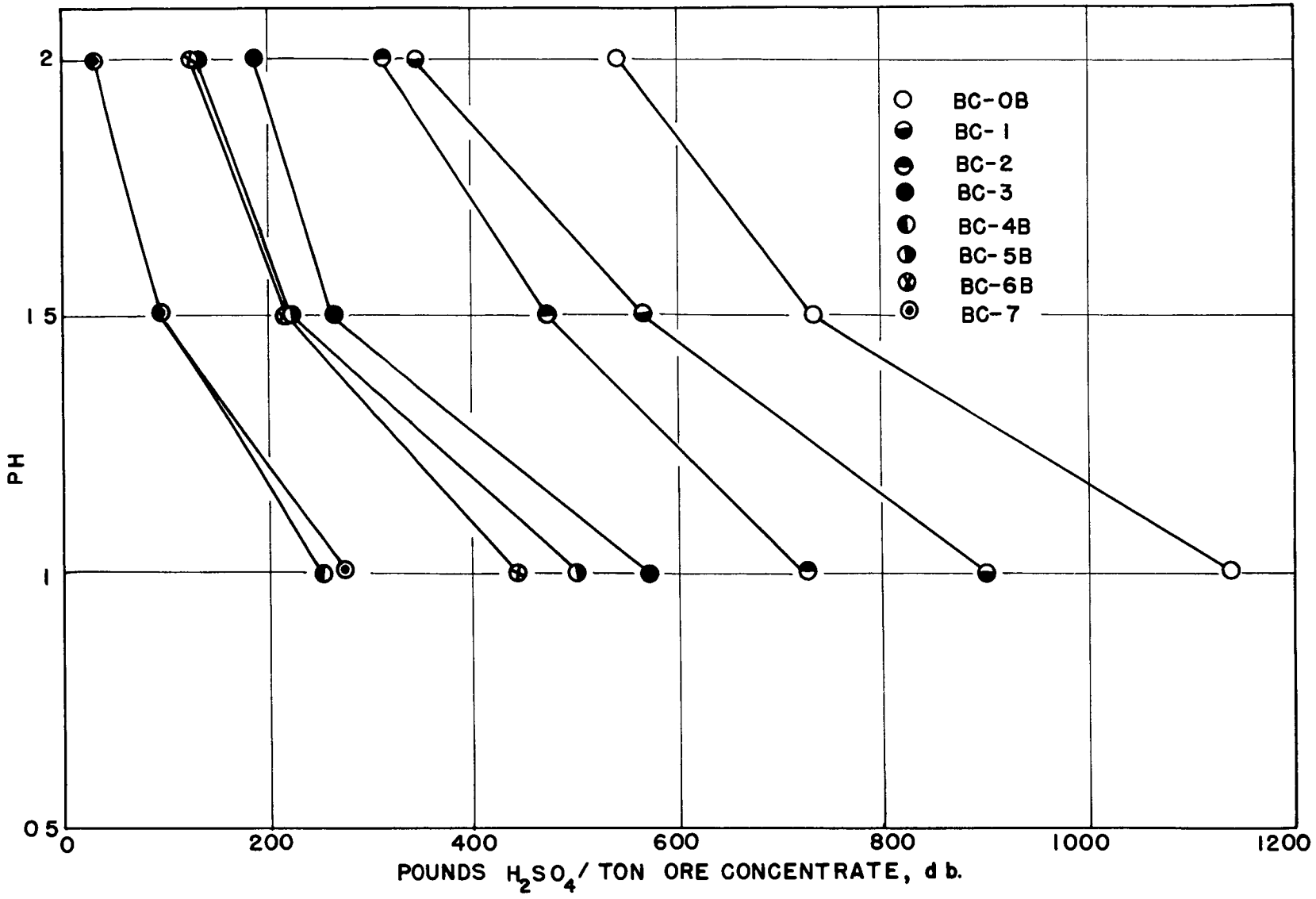


FIGURE 27. ACID CONSUMPTION IN CONSTANT pH LEACHES

[redacted]

DWG. 18154

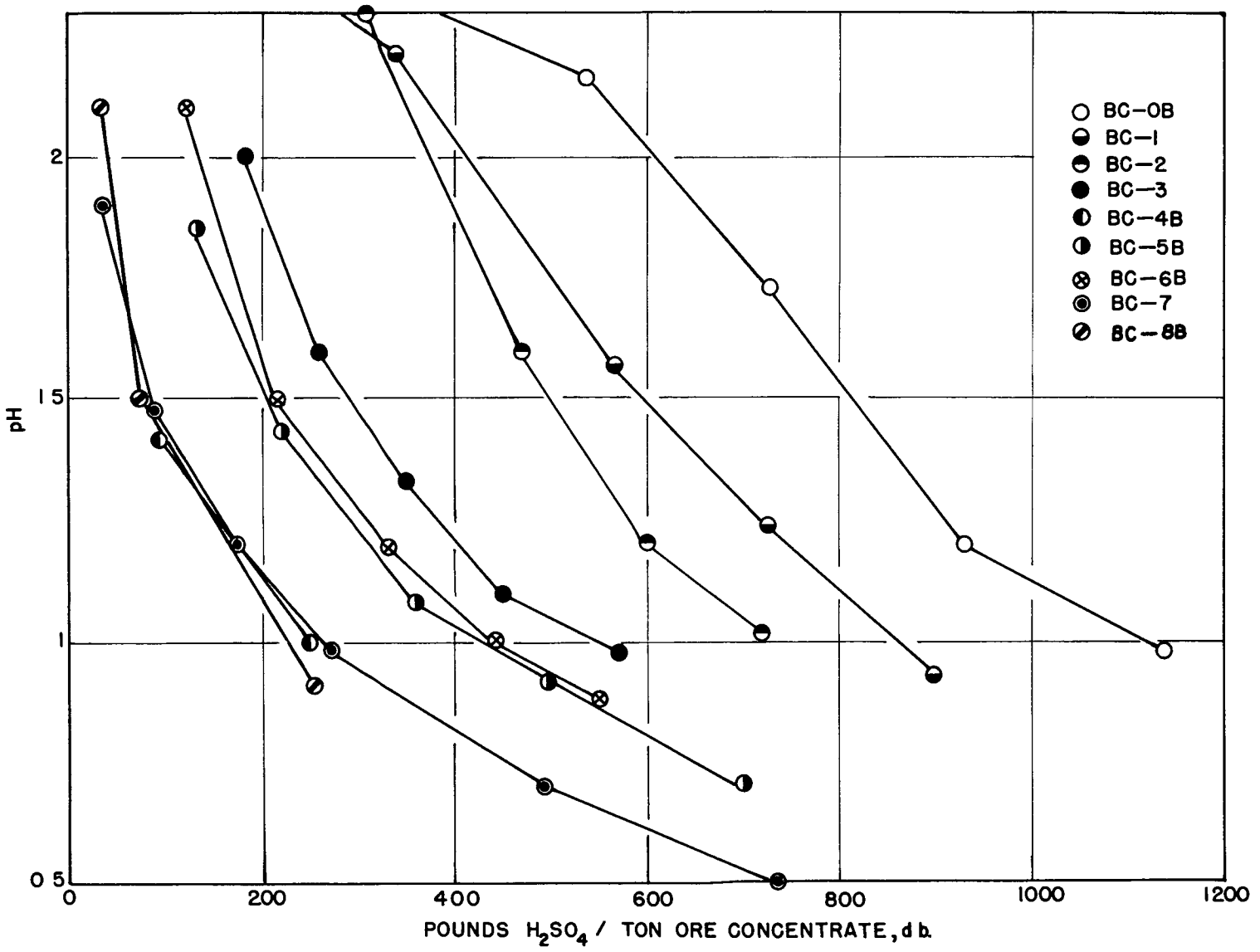


FIGURE 28. ACID CONSUMPTION IN DIRECT LEACHES

These comparative leaching tests were carried out as follows:

(1) Constant-pH Leach with Anion Exchange Resin. A weighed amount of anion exchange resin in the sulfate form (Dowex-1 or Dowex-2, 40-60 mesh, 8 meq for 20 g ore, dry basis) was added to the ore sample, which was slurried at 10% pulp density. Sulfuric acid was then added to each stirred sample as required to keep the pH at 1.0, 1.5, or 2.0 for 24 hours at room temperature. The acid consumption was very small after the first few hours. The exchange resin was removed by means of a small 100-mesh screen, and a second similar batch of resin was added. After the second batch of resin was removed, the leached slurry was filtered. The washed residue, the slurry filtrate, and the loaded resin batches were each analyzed for uranium. Nearly all of the dissolved uranium was taken up by the resin. Since it was the total uranium extraction from the ore that was of primary interest, the amounts of uranium found in the resin and in the solution were added together for the percent extraction data shown in the figures in this section. The sorption data for the separate resin stages are presented in another section (see Table 25), together with other tests of resin-in-pulp leaching.

(2) Direct Leach. The total quantity of sulfuric acid used in each constant-pH leach was recorded, and a direct leach was made with the same quantity of acid added at one time to the 10% pulp density slurry. The acidified slurry was stirred for 24 hours at room temperature, then filtered and washed for solution and tailings analyses. Tests at a few other acid levels were included with those corresponding to the constant-pH leaches.

These direct leaches were made up to be 10% initial pulp density (weight basis) including the acid. For the constant-pH leaches, dilute acid was added to a slurry initially at 10% pulp density; hence, the slurry was diluted to a degree corresponding to the amount of acid used. The greatest dilution occurred with ore BC-0B1, where the pulp density (initial weight of ore over final weight of slurry) dropped to about 6%. A second set of direct leach tests was made with this ore with pulp densities matching those for the constant-pH leaches. The uranium extractions for this set are included in Figure 31. In one test the extraction was higher from the 10% pulp density leach, in the other two, from the more dilute leach, and in all three the differences were within the range of variations usually encountered.

The resin-in-pulp leaches were made with sulfuric acid only, since nitrate solutions are not favorable for anion exchange sorption of uranium. Some of the direct leach tests were repeated with nitric acid. The results, shown in the same figures, were generally similar to those with sulfuric, showing

that in these tests the presence of a strong oxidizing agent gave no advantage. The sample which approached closest to pure wavellite, BC-4B, was entirely consumed in the five sulfuric acid leaches, and hence was not tested with nitric acid. However, ore BC-5 was picked to approach the same mineral composition, and the nitric acid leaches of BC-5B did not show any specific effects.

Amenability to Low Sulfuric Acid Leaching

The amounts of acid required to maintain constant pH varied greatly for the different ore samples, from 30 to 535 pounds sulfuric acid per ton at pH 2, and from 250 to 1140 at pH 1 (Figure 27). If these quantities of acid are referred to the amount of calcium in each ore instead of to the total weight, as in Figures 29 and 30, the variation among the ore samples becomes much less. Most but not all of the acid-consumption curves are grouped together in a fairly narrow band, with the acid consumption at pH 1.5 being close to the amount of sulfuric acid equivalent to the calcium. The curves which fail to conform are those for BC-6B, which contained much non-phosphatic acid-consuming gangue, and BC-7 and BC-8B, which proved refractory to the acid attack. Preliminary results with BC-11B and BC-12B appeared similar to those with BC-7 and BC-8B.

When the quantity of acid is referred to the calcium content, the uranium extraction curves for most of the ore samples also group together. This is illustrated by the curves in Figure 40, which are the smoothed curves from the preceding figures. Each of these curves shows more or less of a break between the most easily dissolved portion of the uranium and the subsequent portions which required higher relative consumptions of acid for extraction. For most of the ores these breaks occurred near or a little below the quantity of acid equivalent to the calcium (2.45 pounds 100% sulfuric acid per pound of calcium) For some the sharpest curvature occurred at an acid consumption of about one-half of that equivalent to the calcium, suggesting that it might correspond to conversion of the calcium compounds to acid salts. These results, like the relative dissolutions of calcium and aluminum from ore BC-1, described above, appear to indicate that the fraction of the uranium in the ore which was most easily extracted with a minimum quantity of sulfuric acid was that which was associated with the calcium minerals, and also that the quantity of acid for leaching in a process designed to use the minimum acid per pound of uranium dissolved could probably be based on the calcium content of the ore.

The results obtained with ores BC-7 and BC-8B cannot be included in the foregoing generalization, and these ores appeared not to be amenable to a low-acid leach process. As shown in Figures 38 and 39, they were surprisingly refractory to leaching

[redacted]

DWG. 18155

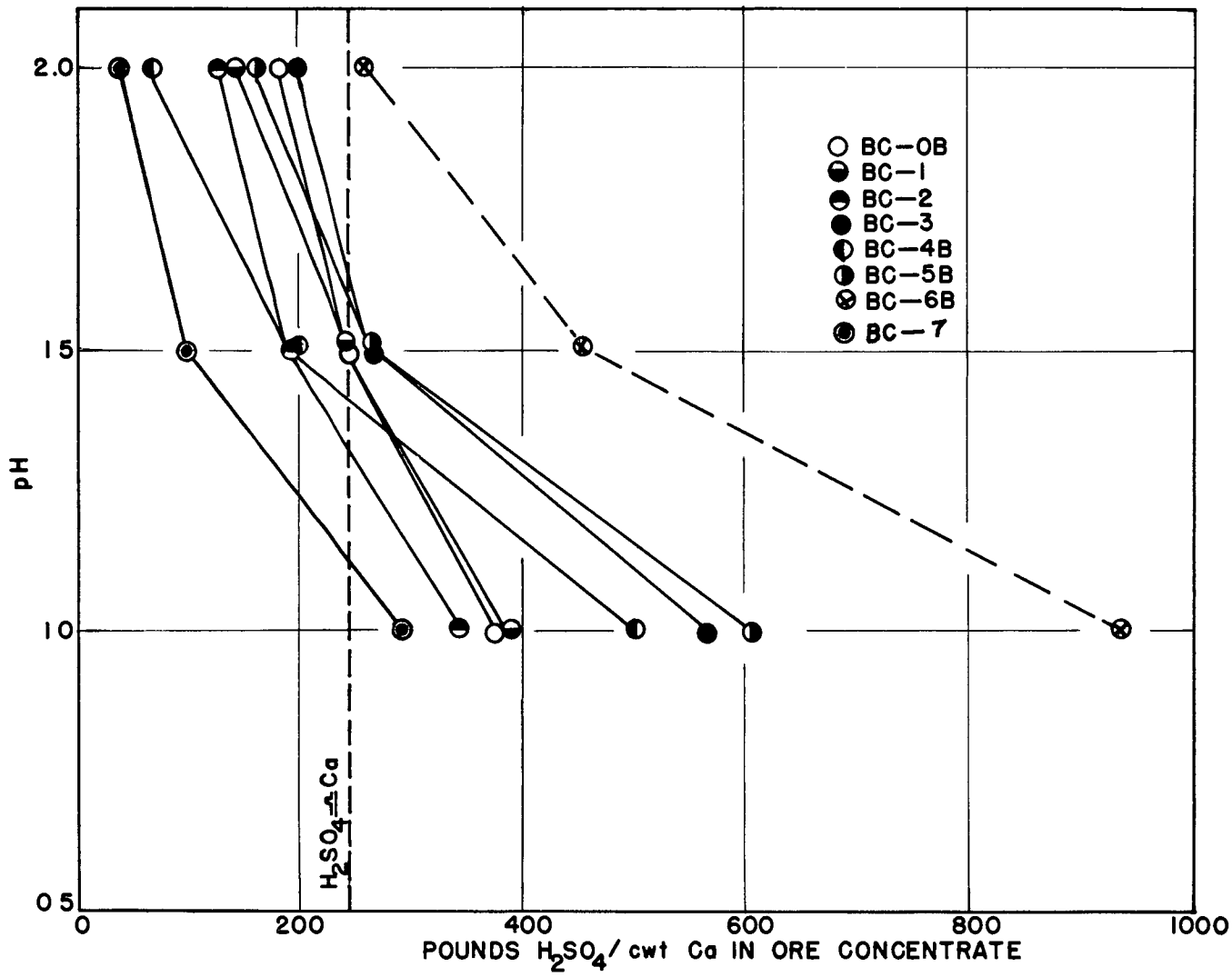


FIGURE 29. ACID CONSUMPTION IN CONSTANT pH LEACHES REFERRED TO CALCIUM CONTENT

[redacted]

DWG. 18156

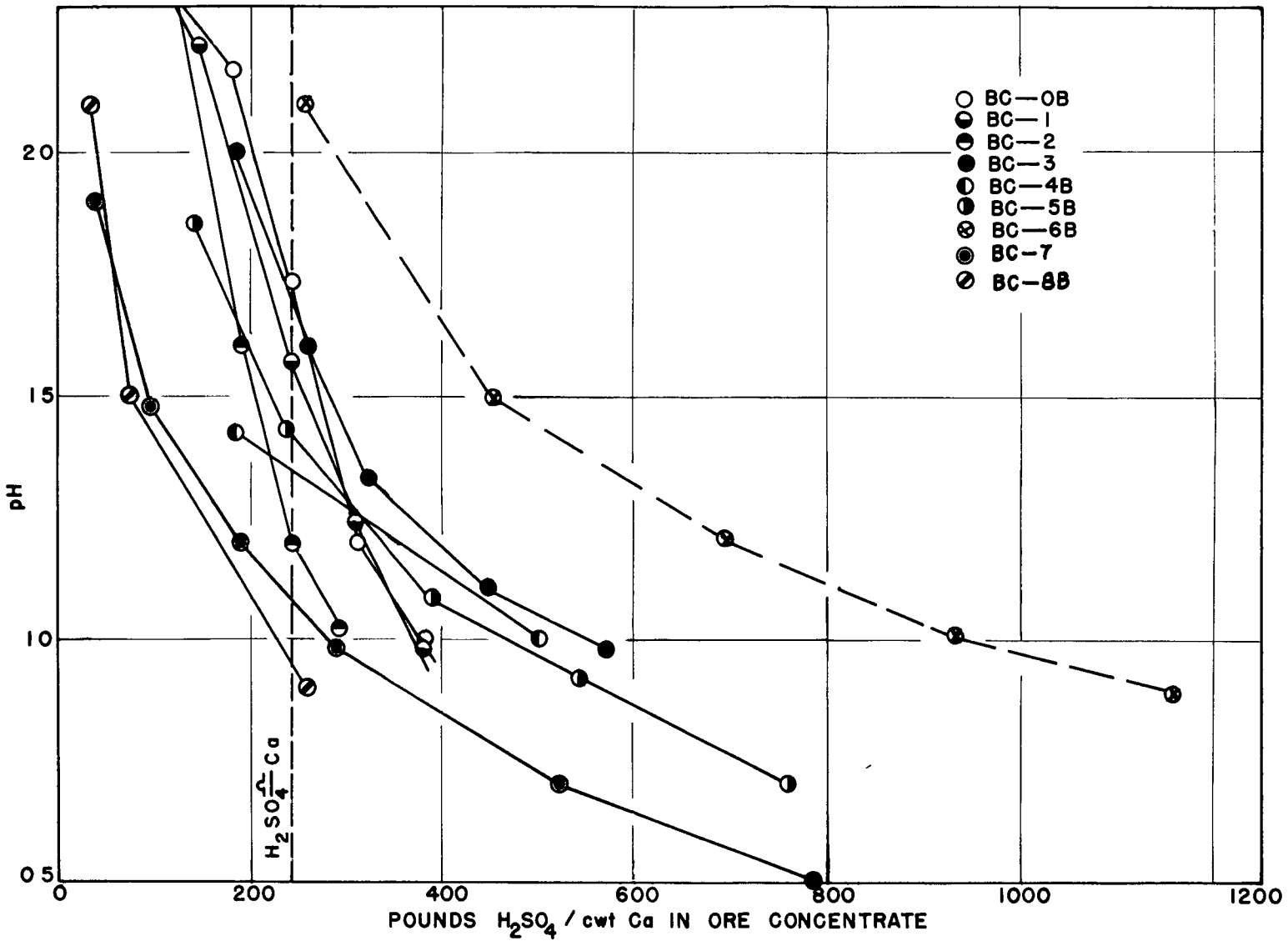


FIGURE 30. ACID CONSUMPTION IN DIRECT LEACHES, REFERRED TO CALCIUM CONTENT

[redacted]

DWG 18157

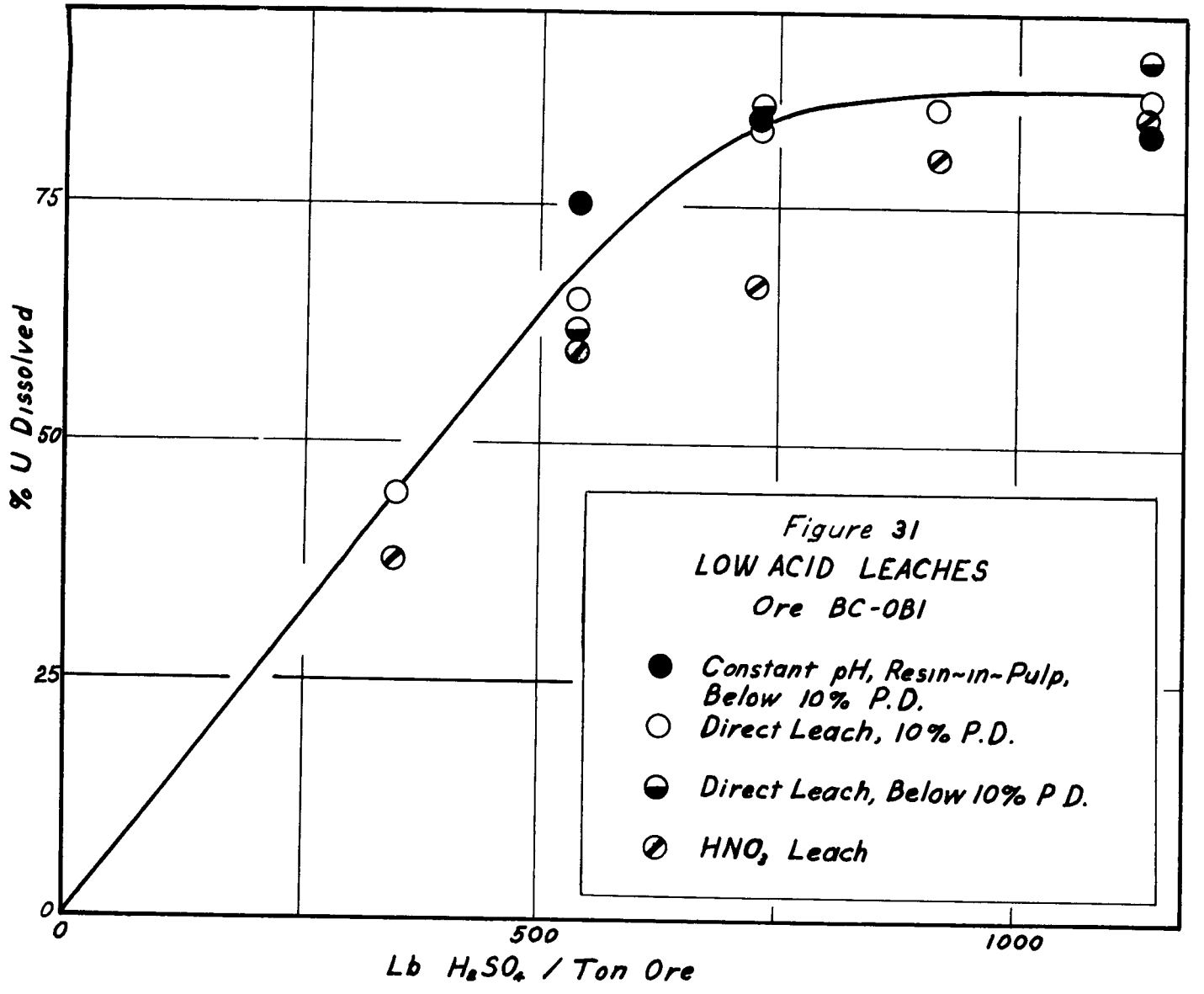


Figure 31
LOW ACID LEACHES
Ore BC-OBI

[redacted]

DWG. 18158

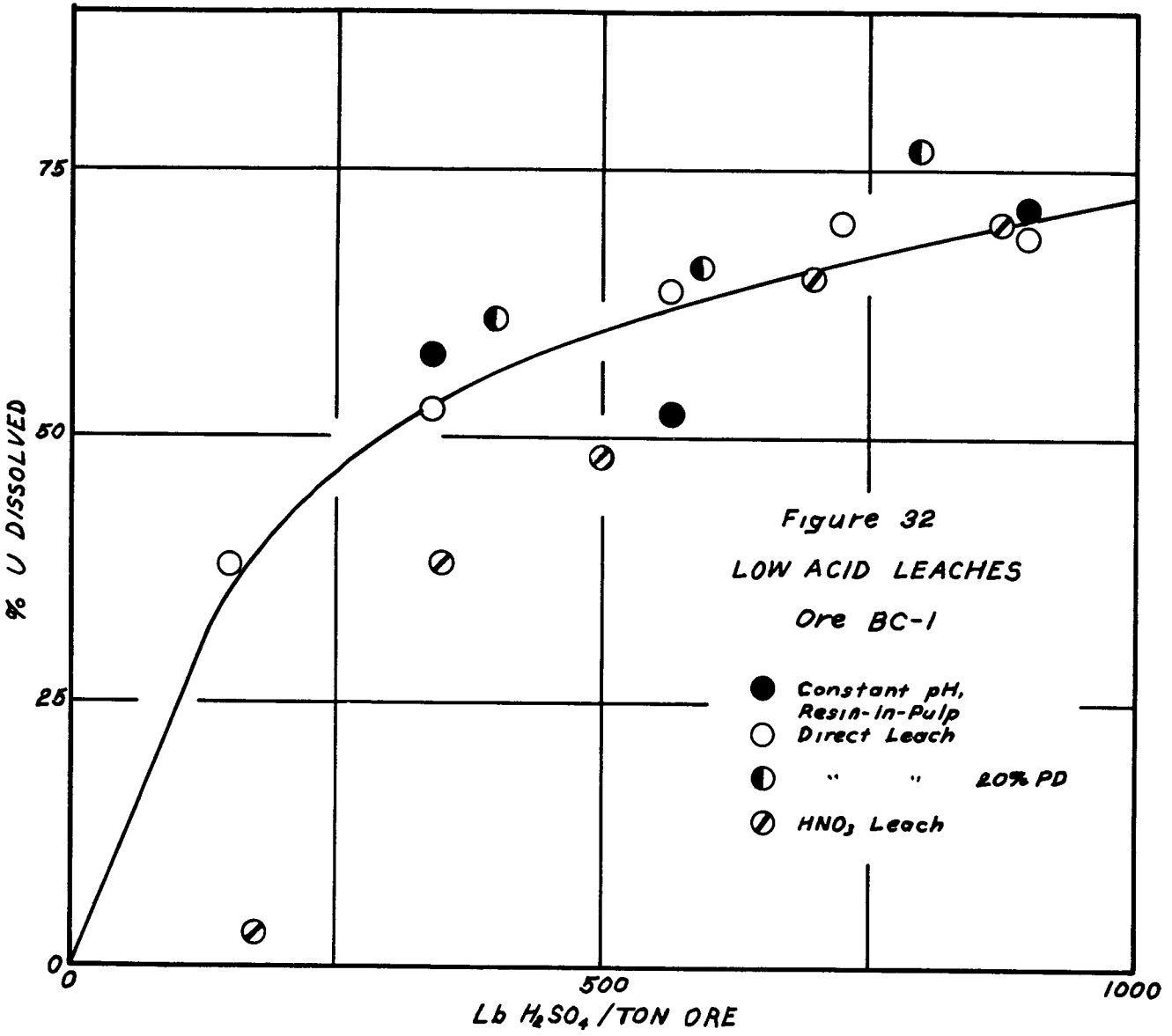


Figure 32

LOW ACID LEACHES

Ore BC-1

[redacted]

DWG. 18159

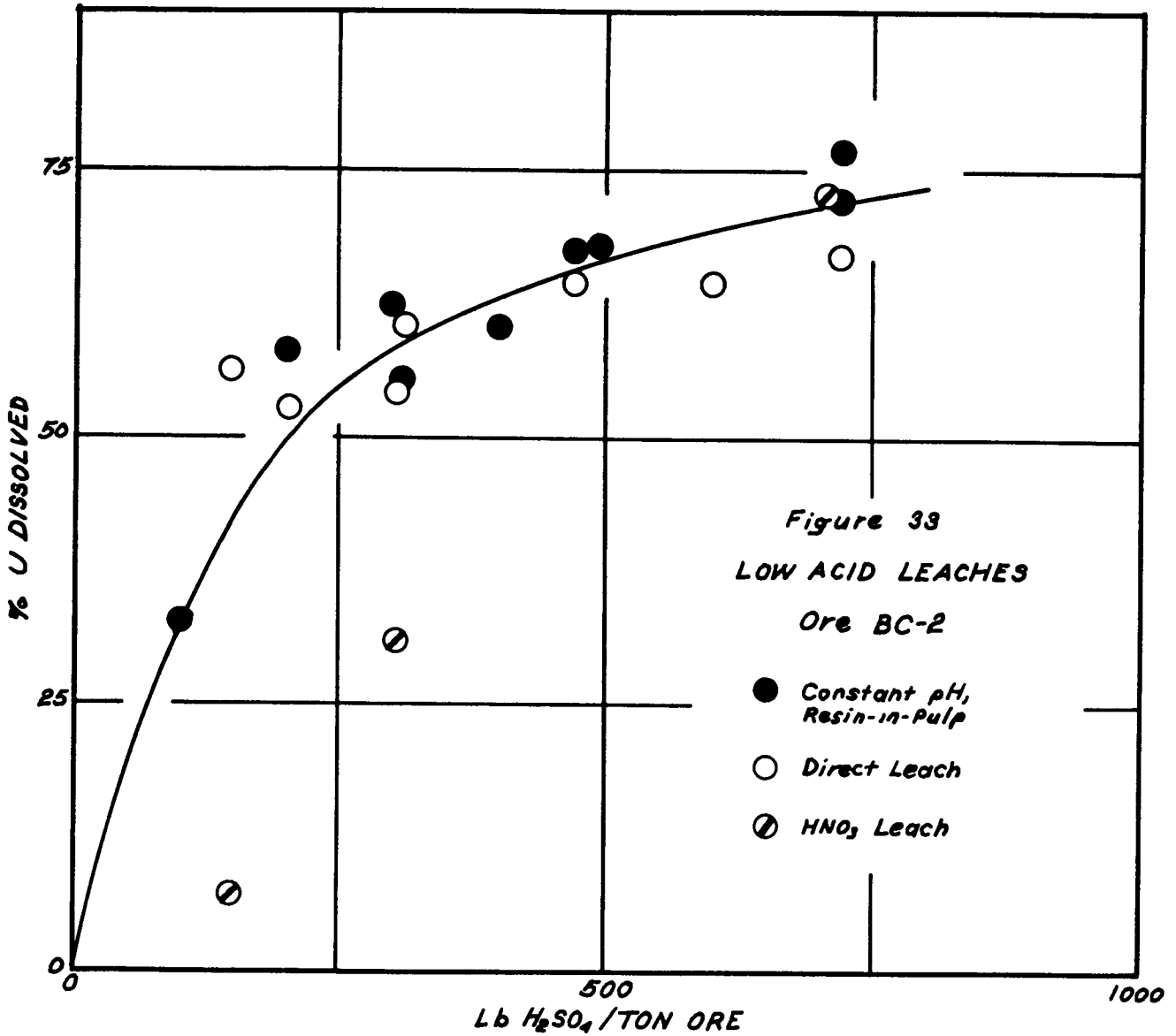


Figure 33

LOW ACID LEACHES

Ore BC-2

[redacted]

DWG. 18160

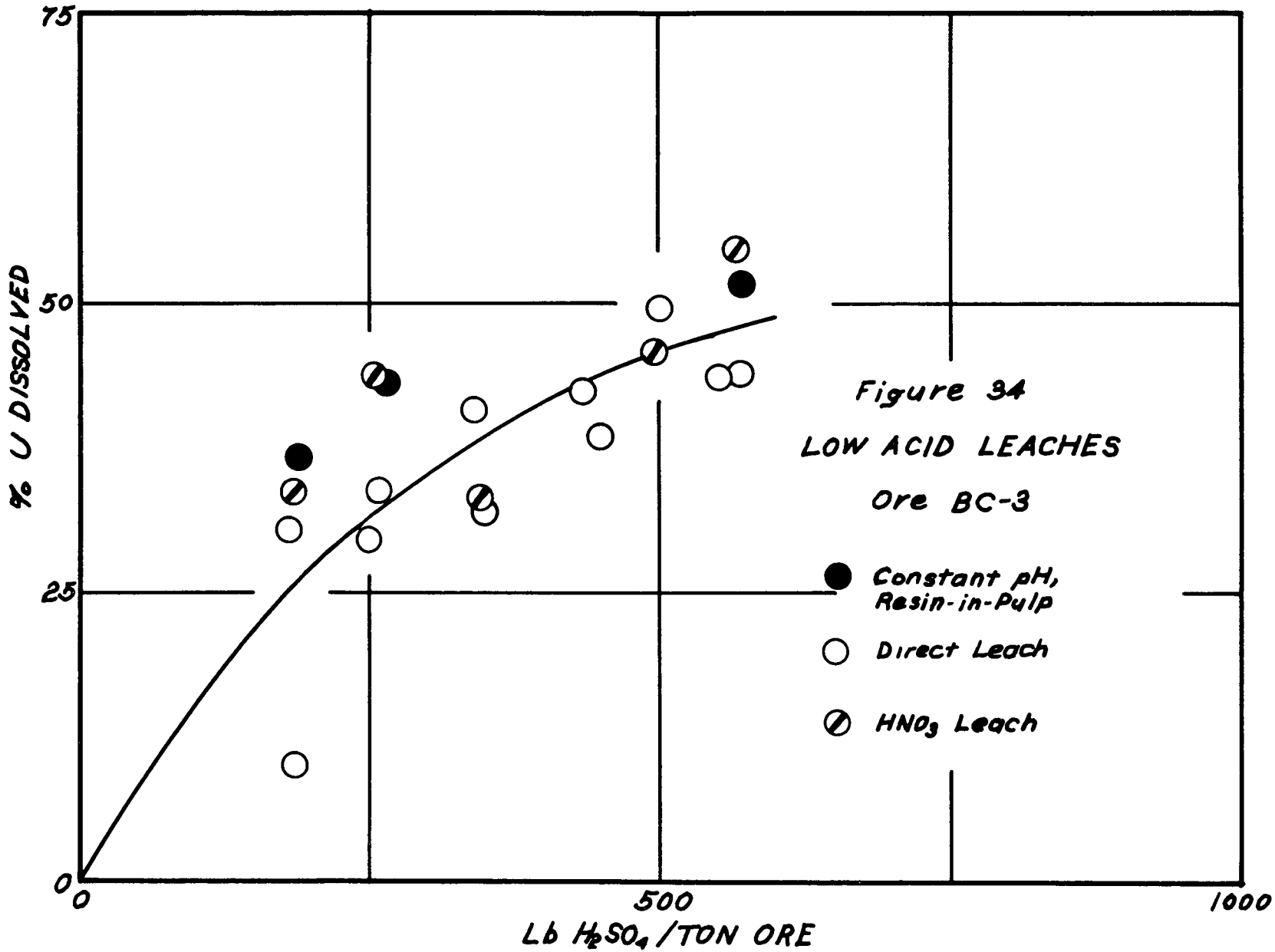


Figure 34

LOW ACID LEACHES

Ore BC-3

[redacted]

DWG. 18161

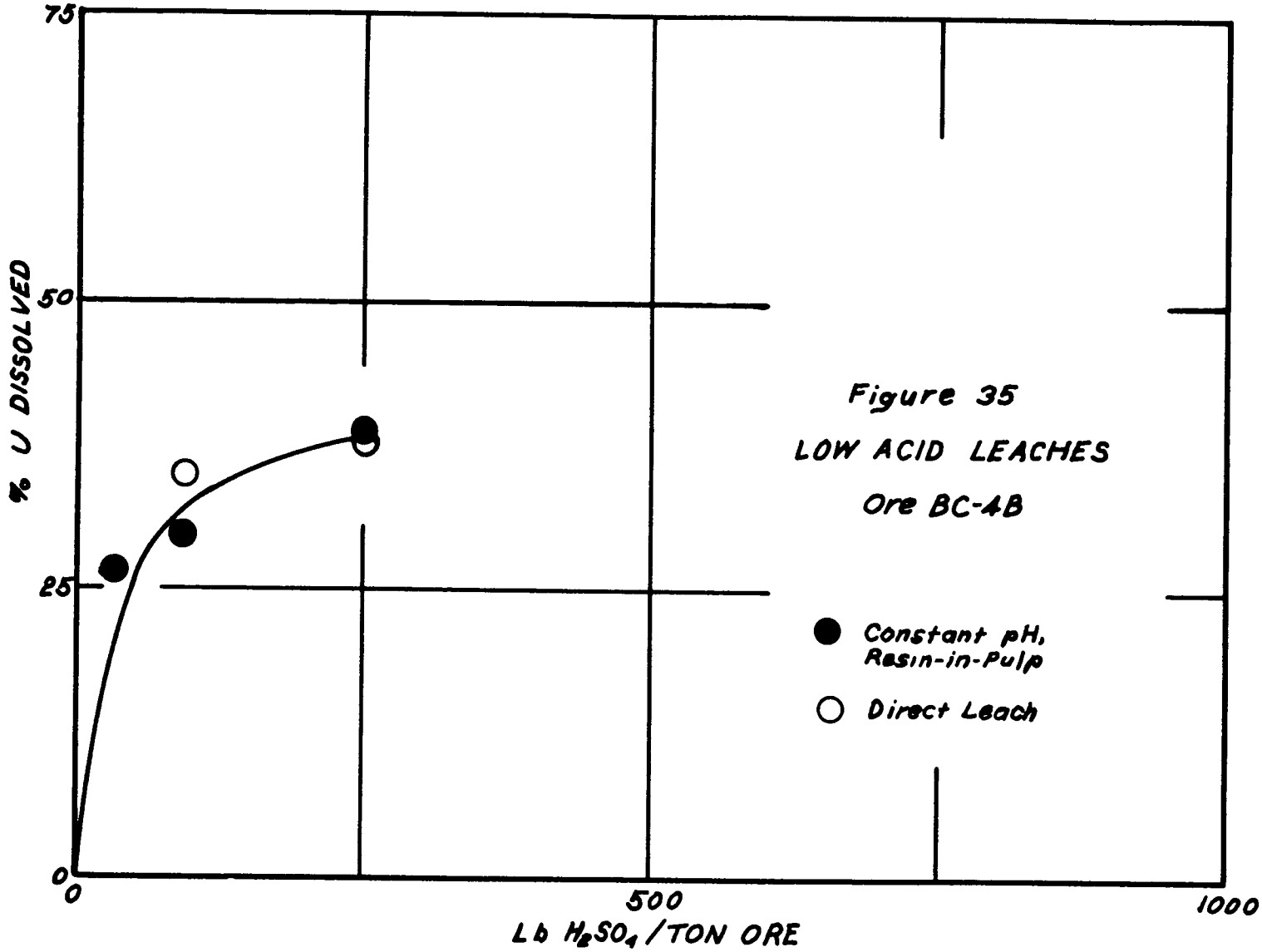


Figure 35

LOW ACID LEACHES

Ore BC-4B

[redacted]

DWG. 18162

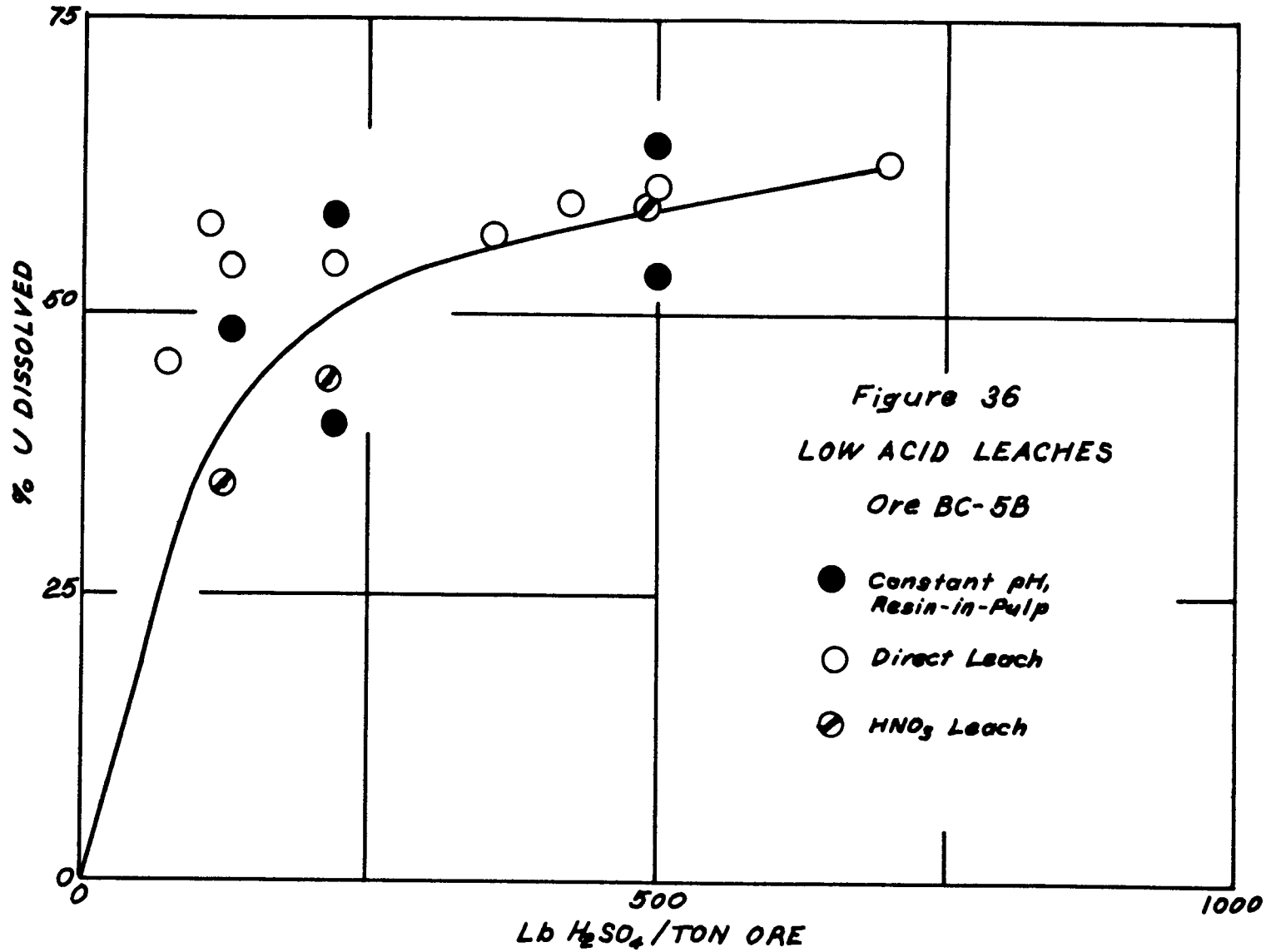


Figure 36

LOW ACID LEACHES

Ore BC-5B

[redacted]

DWG. 18163

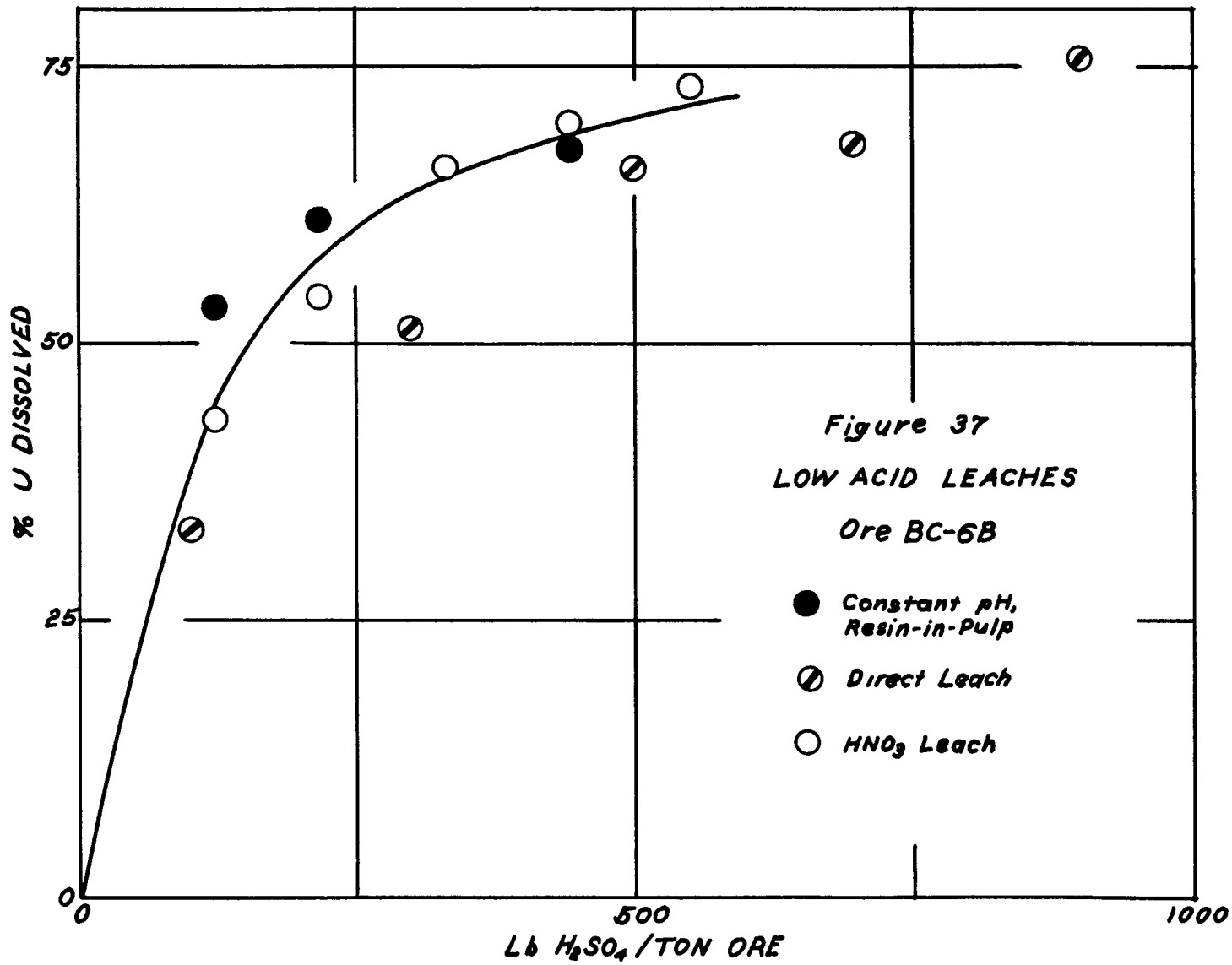


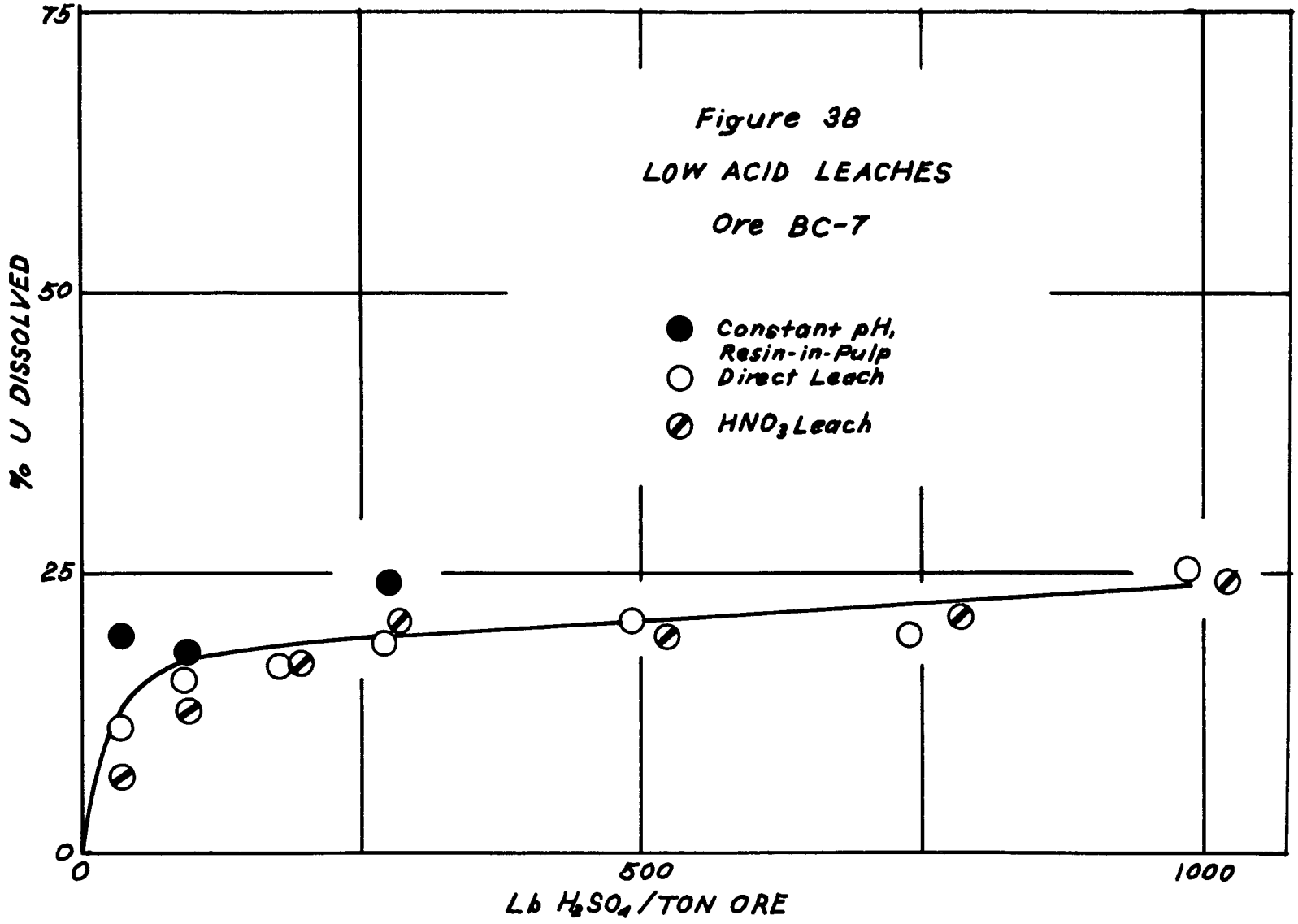
Figure 37

LOW ACID LEACHES

Ore BC-6B

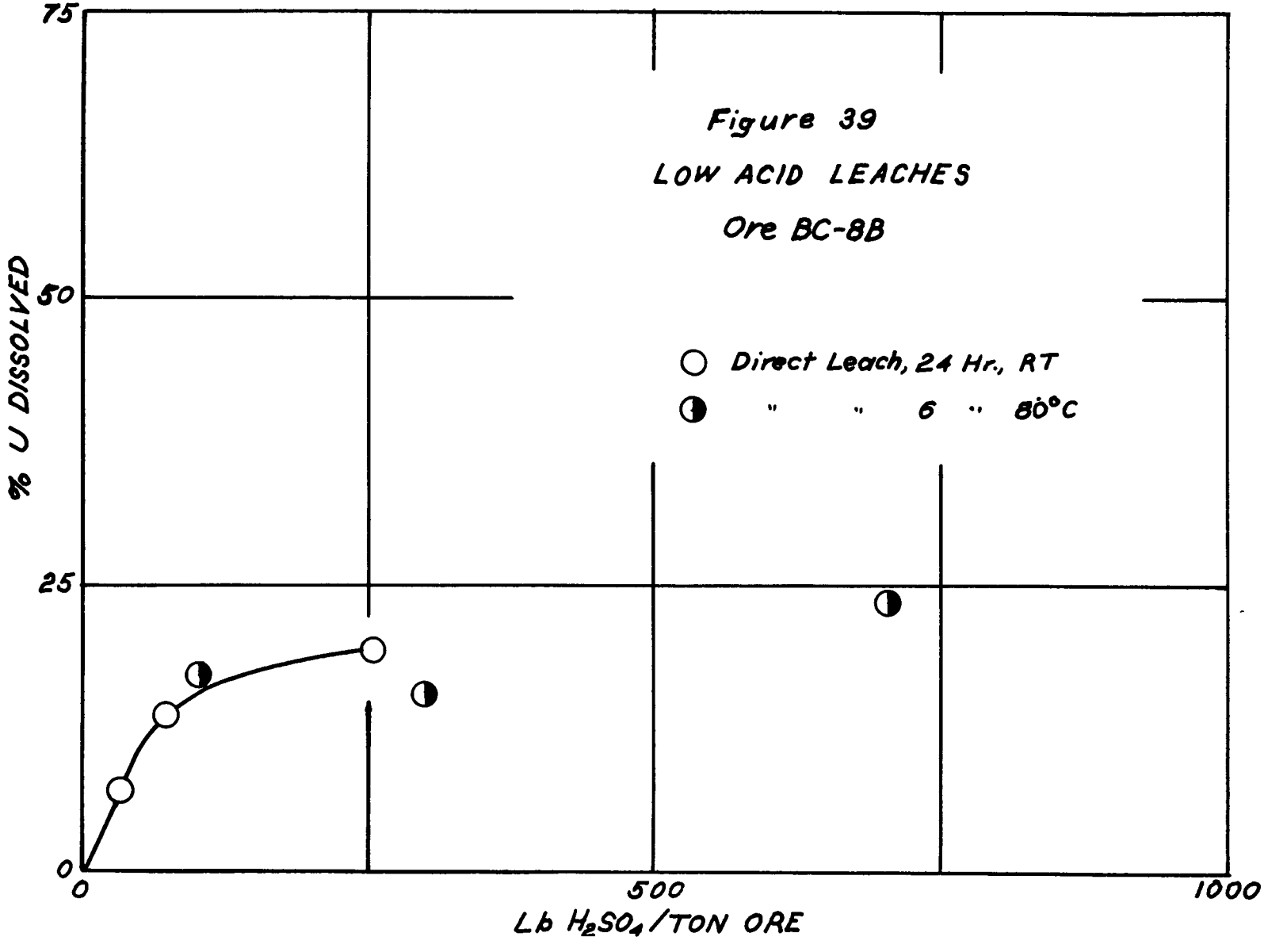
[redacted]

DWG. 18164



[redacted]

DWG. 18165



[redacted]

DWG. 18166 70

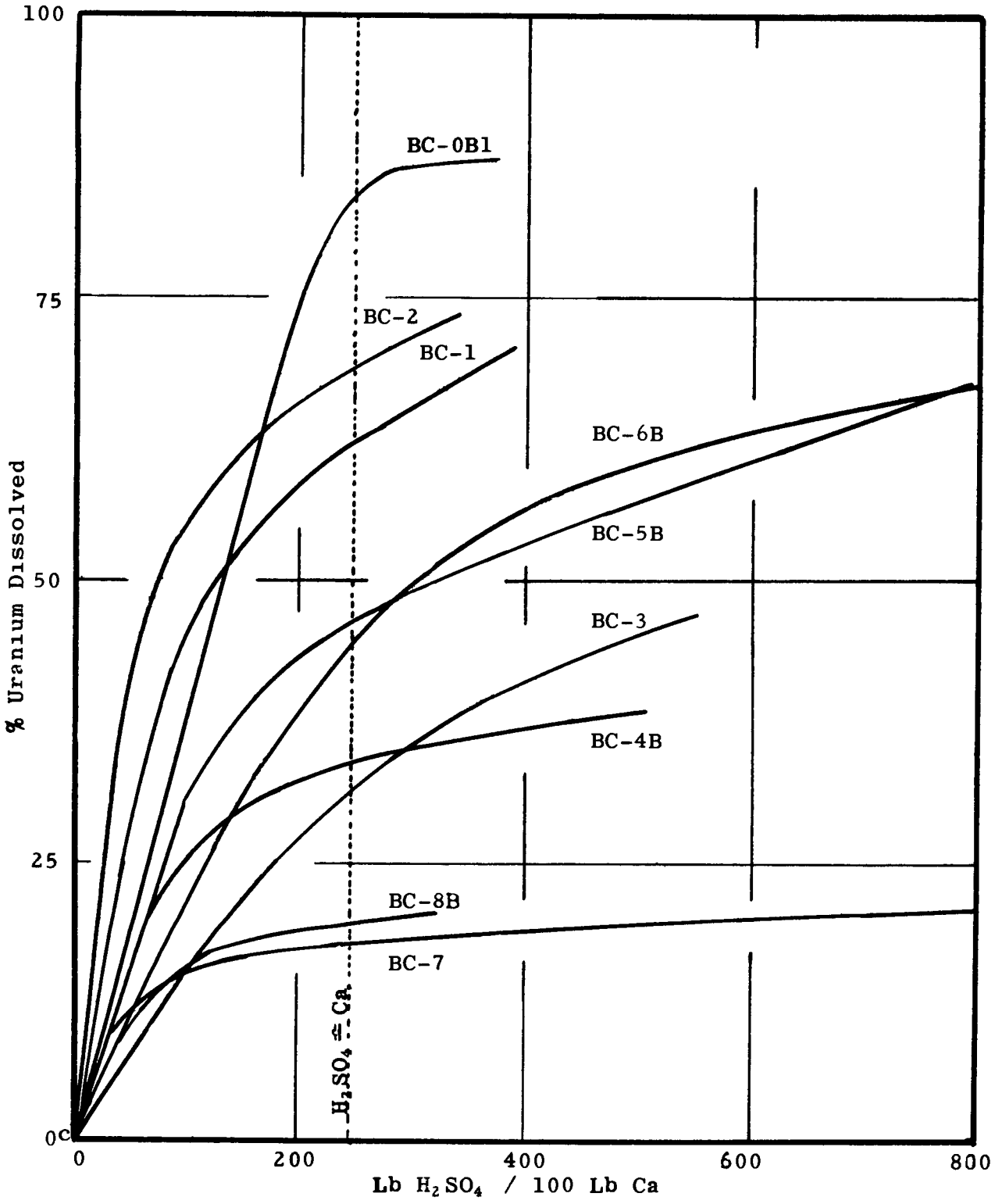


Figure 40. LOW ACID LEACHES OF LZ ORES

by sulfuric or nitric acids in the cold, even at high acid levels.* These ores have given improved extractions at high acid levels in hot leaches (see Figure 43), and still better extractions after calcination, but the improvement found at low acid levels by hot leaching did not appear sufficient to make these ores more than barely tolerable for a low-acid leach.

The points at which the various curves of Figure 40 intersect the 245-pound acid line, i.e., the percent of the uranium extracted from each ore by sulfuric acid equivalent to its calcium content, are plotted against those calcium contents in Figure 41. Corresponding points from low-nitric acid leaches are also shown. With the exception of ores BC-7 and BC-8B, and perhaps also BC-3, these points fall fairly well along a straight line. This relationship illustrates the basis for the suggestion given above that the amount of acid to be used for a given head might be based empirically on its calcium content.

Figure 42 shows curves for the same leach series as are shown in Figure 40, plotted in a manner to emphasize the importance of the ore grade. The abscissa is the pounds of sulfuric acid used per pound of uranium dissolved, and the ordinate is the tons of ore (here the minus 200 mesh material) per pound of uranium dissolved. Each curve is marked with the point at which the acid used was equivalent to the calcium, and the point at which the final pH was about 1.5, showing the fair agreement between these two Qualitatively, the ores whose curves fall closest to the origin would give the lowest cost for uranium product.** The high grade and low acid consumption of ore BC-4B put it in a favorable position in spite of its low percent uranium extraction, whereas the high uranium extraction from ore BC-0B1 did not completely offset its high acid consumption and its lower grade. The curve for BC-7 (room temperature leach) lies far from the origin, illustrating again that it was not amenable to a low sulfuric acid process. Ore BC-3 is intermediate in this figure as also in Figure 41. Some feed of this type could probably be tolerated, but it would be unfavorable.

---

* The principal phosphatic mineral in ores BC-7 and BC-8 was reported to be millisite, which is tentatively presumed to be responsible for the refractoriness to acid

** If the coordinates of Figure 42 were re-scaled to show the costs of sulfuric acid and of ore per pound of uranium dissolved, plus allocation of processing costs proportional to each, the resulting curves would show the optimum extent of leaching for each ore sample.

[redacted]

URANIUM DISSOLVED BY ACID EQUIVALENT TO CALCIUM DWG. 18167

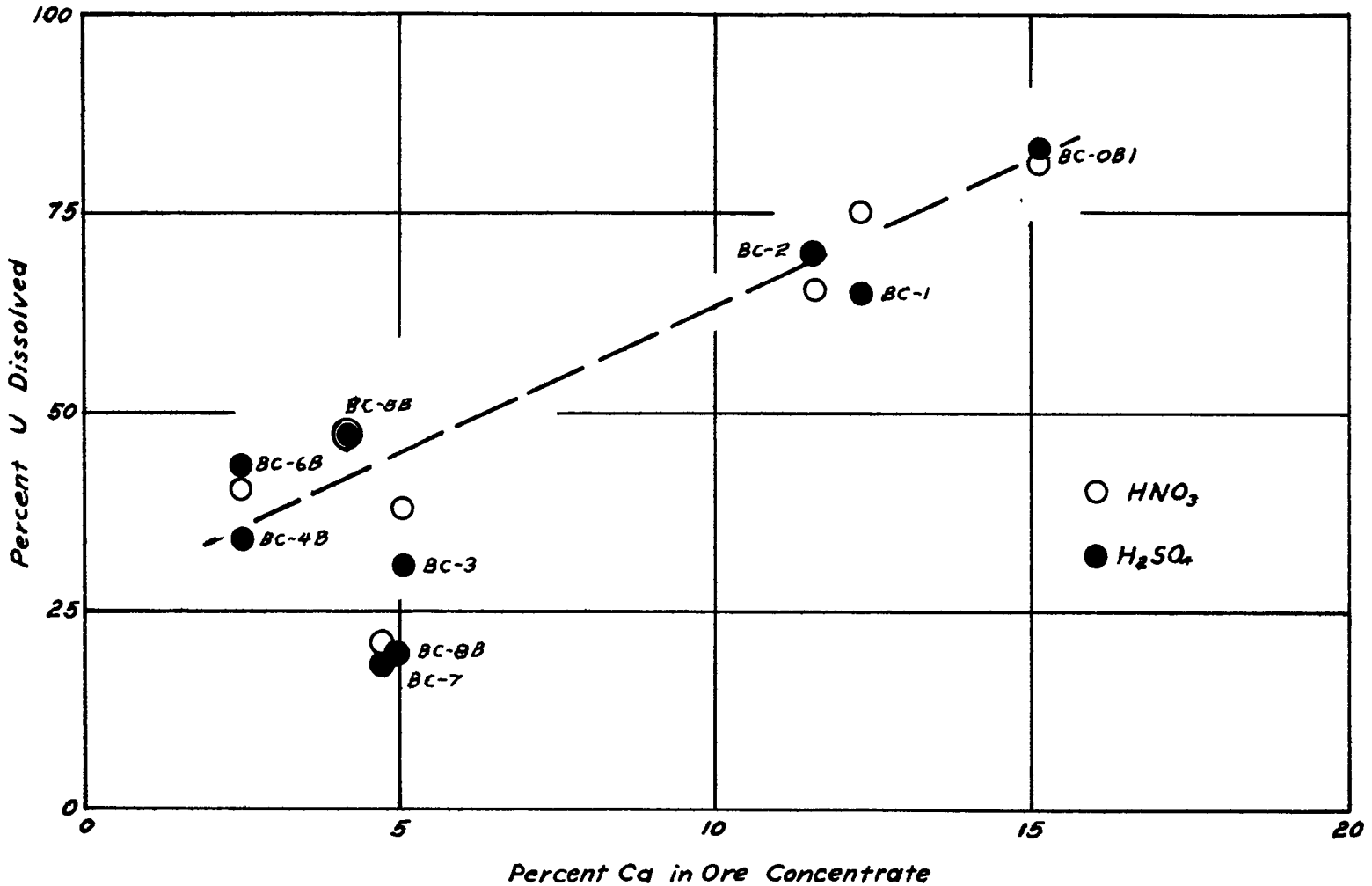
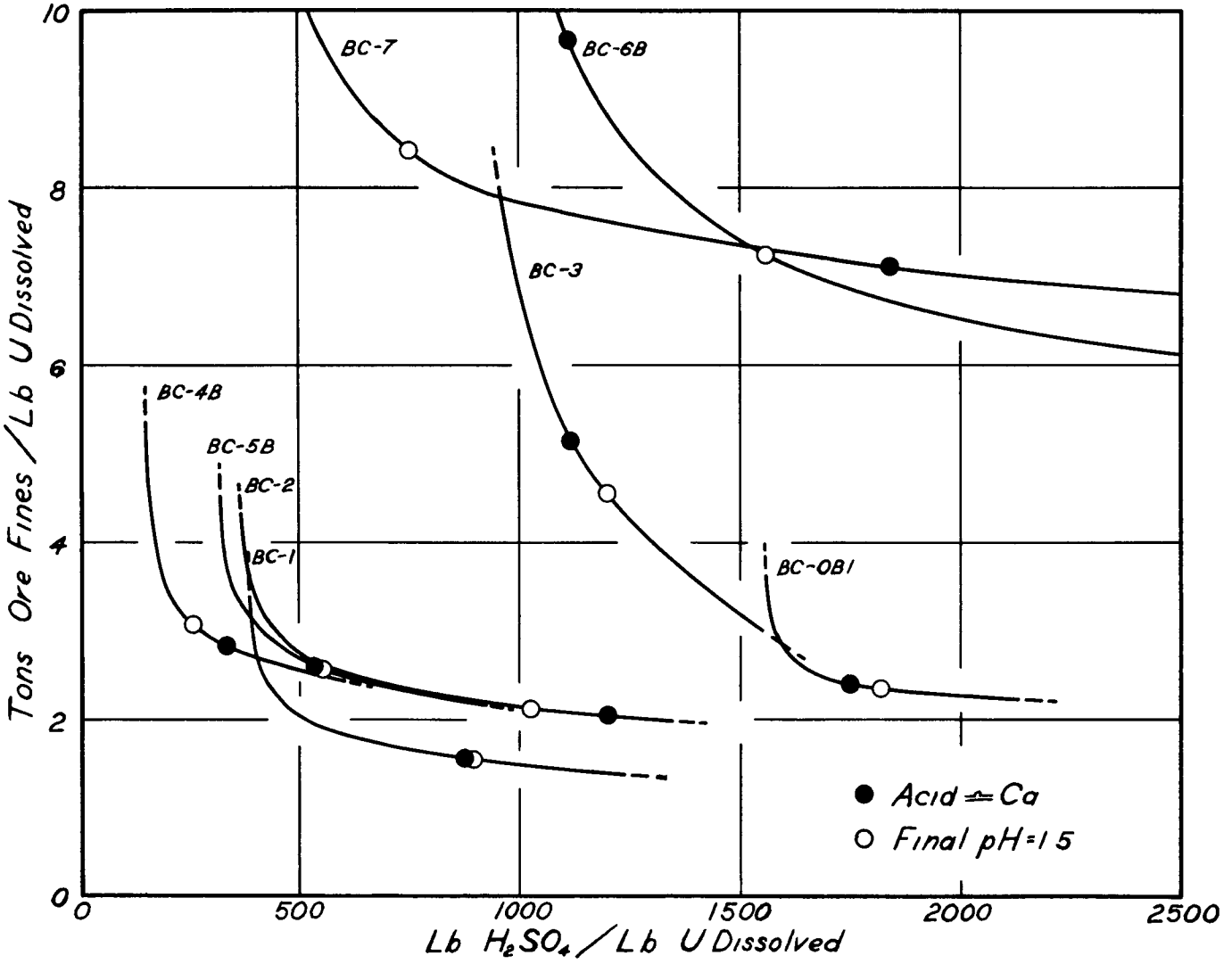


Figure 41

(x)

[redacted]

DWG 18168



COMPARISON OF ACID AND ORE CONSUMPTION

Figure 42

Uranium extractions from some of the unclassified ores are shown in Figure 43. These extractions are plotted against (pounds acid per 100 pounds calcium in ore), so that the curves can be compared directly with those of Figure 40. On this basis, the percent extractions were similar from the unclassified ores and from the corresponding ore fines. These extractions are also shown in Figure 44, which is the same type of plot as Figure 42.

Bench-Scale Leaches

The largest scale of leaching practicable in the laboratory was limited to about 2 kg of minus 200 mesh ore stirred at 20% pulp density in a battery jar. Slightly larger batches were handled by using several jars in parallel. The bench-scale leaches were made primarily to supply pregnant leach liquor for tests of uranium recovery methods, as described below. The conditions used for these leaches are shown in Table 8, and analyses of the pregnant liquors are shown in Tables 9 and 10. "Percent uranium extracted" in Table 8 includes credit for uranium found in the washes, whether or not the washes were combined with the pregnant liquor.

Filtration

A few filtrations of the low sulfuric acid leach slurries were timed in order to compare the effects of ore type and filtration conditions. Some of the results are shown in Figures 45, 46, and 47. These tests were made in laboratory filters, and the results may differ by a wide margin from results which would be obtained in process equipment. They are presented to show the relative effects of slurry temperature and of ore type. There was no obvious correlation between the widely-varying rates found for the different ores and their chemical or mineral compositions.

The vacuum filtrations were made in "coarse" sintered glass Buchner funnels with approximately 0.06 ft^2 filtering area, at indicated vacuum of 25 inches. The entire batch of slurry was poured into the funnel at one time. The leach slurries contained about 170 ml (0.045 gal) of total liquid. Hot slurries, from leaching at 80°C, were transferred at about 75°C and were cooled to 50-55°C by evaporation. The cakes formed were about one-third of an inch thick.

The pressure filtrations were made in a laboratory pressure filter* with approximately 0.2 ft^2 filtering area,

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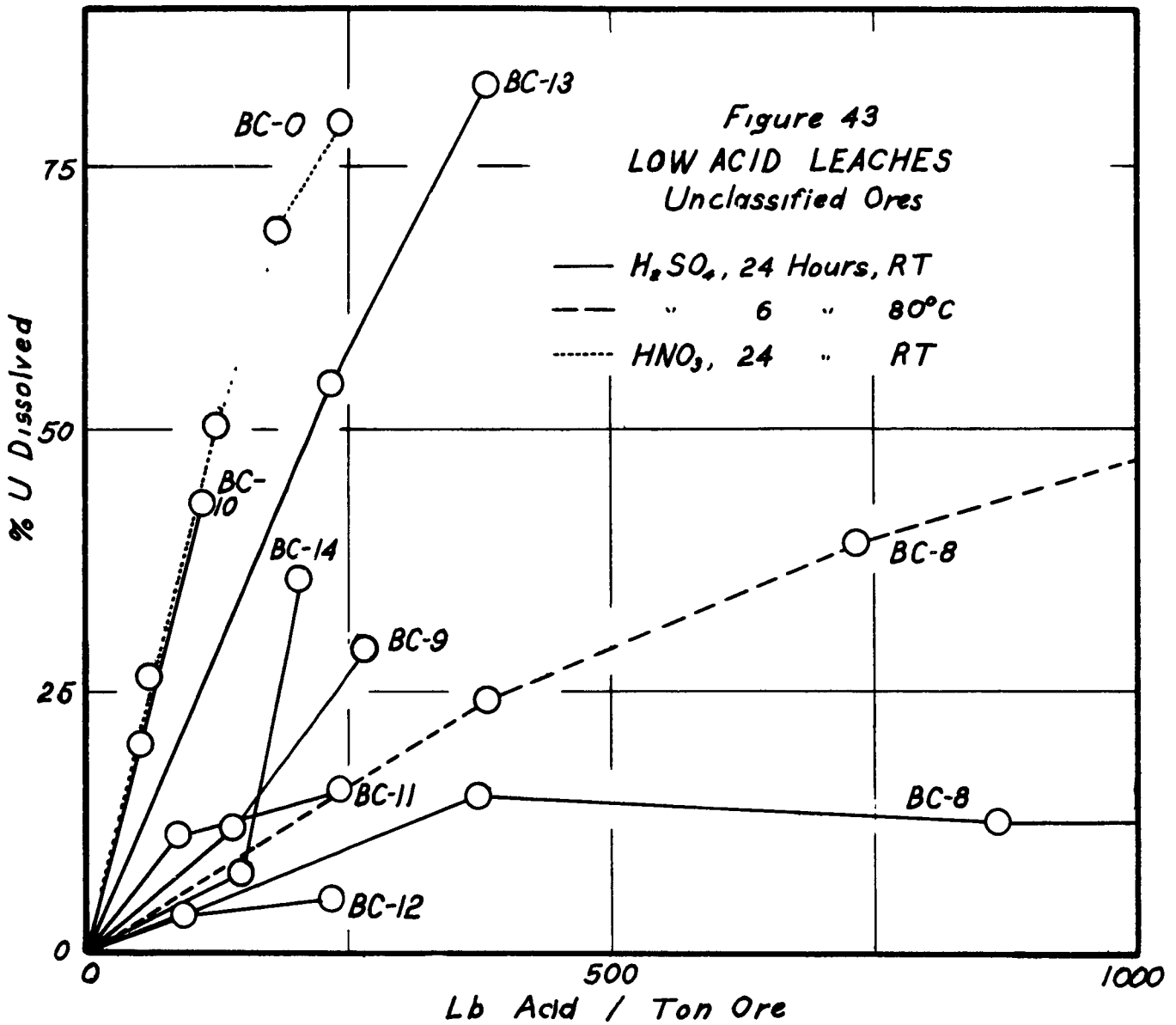
*Denver Equipment Company

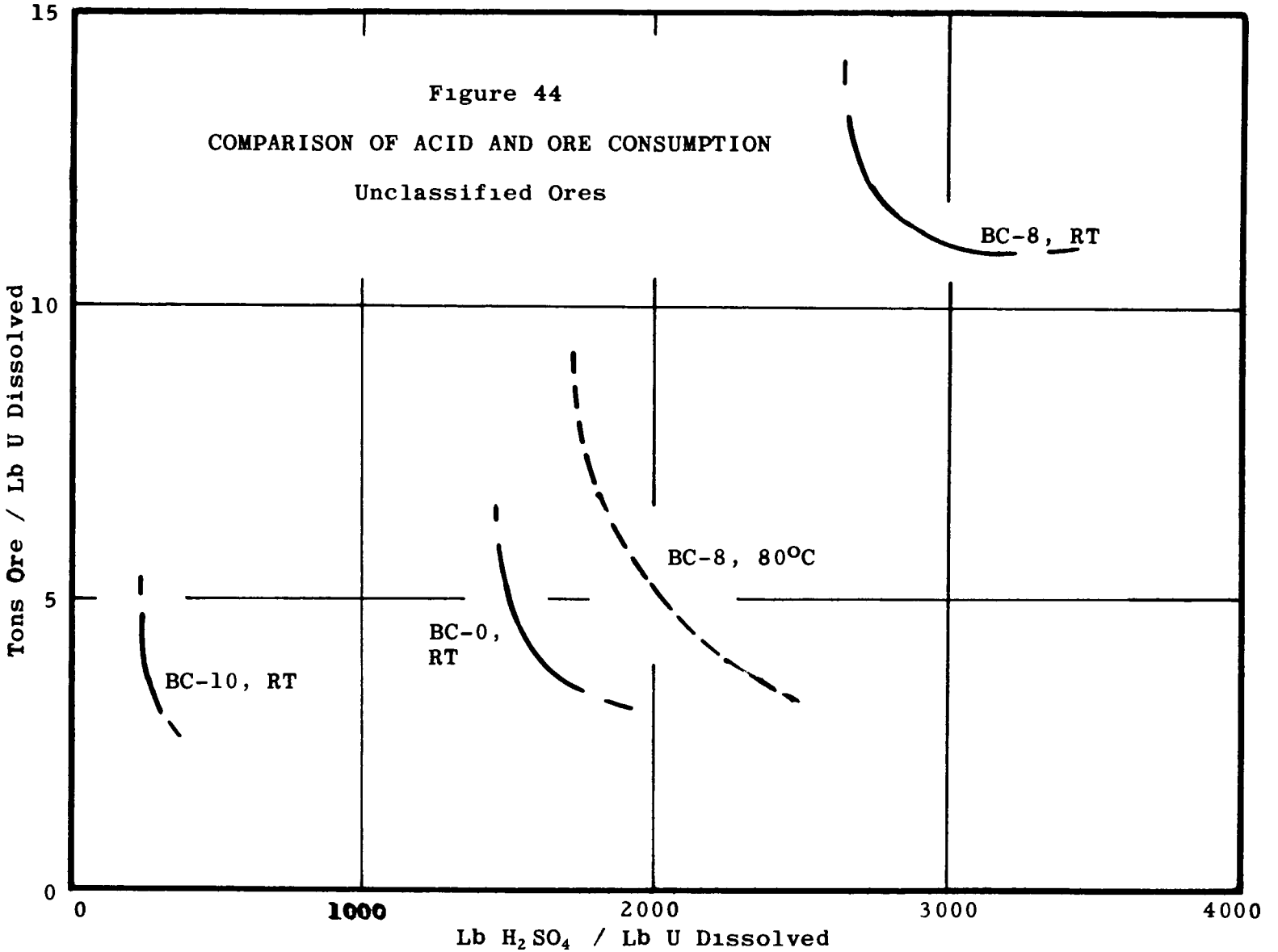
[redacted]

DWG. 18169



[redacted]

DWG. 18170



[redacted]

DWG 18171

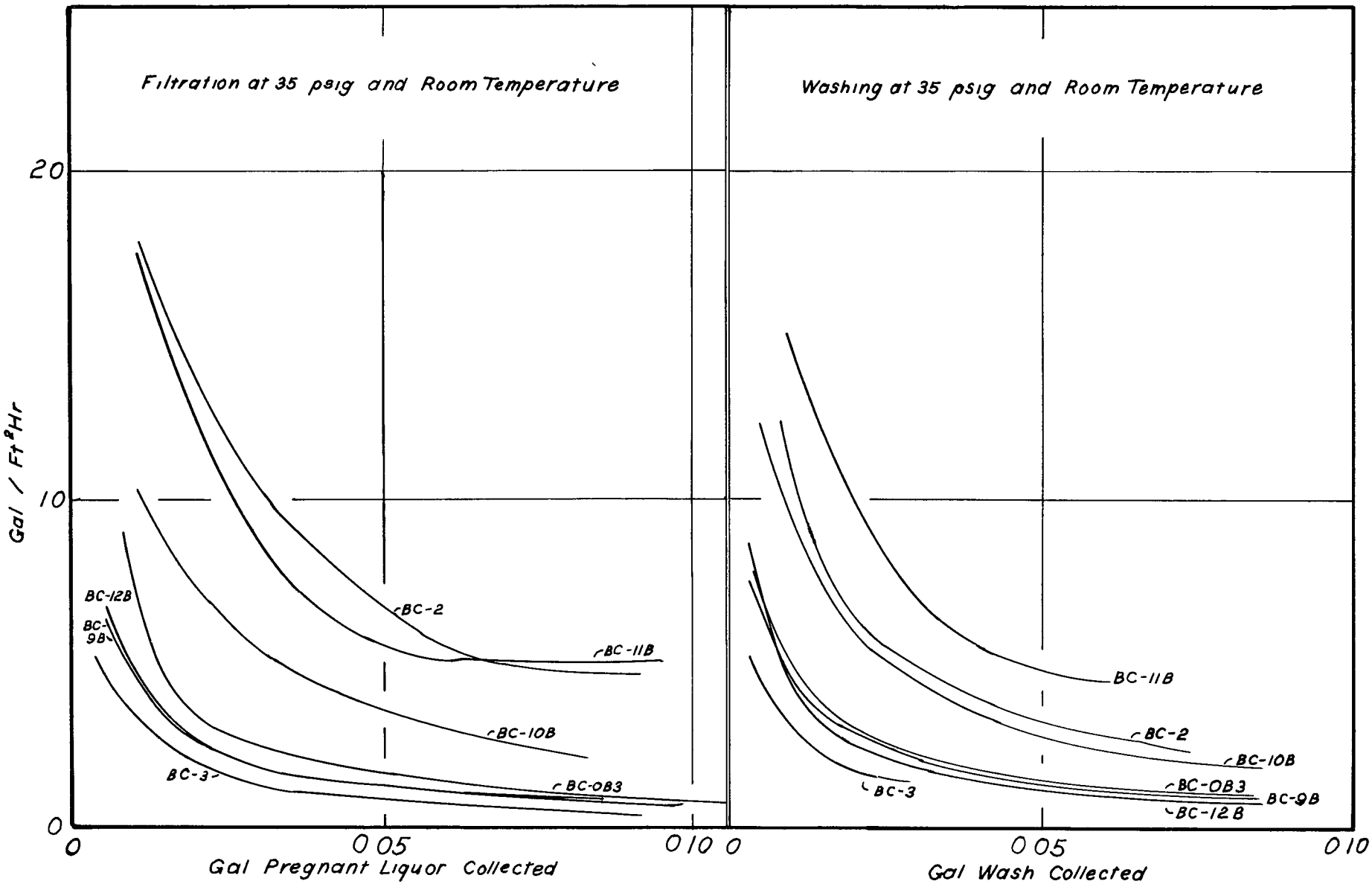


Figure 45

PRESSURE FILTRATION OF LOW SULFURIC ACID LEACH SLURRIES

[redacted]

DWG 18172

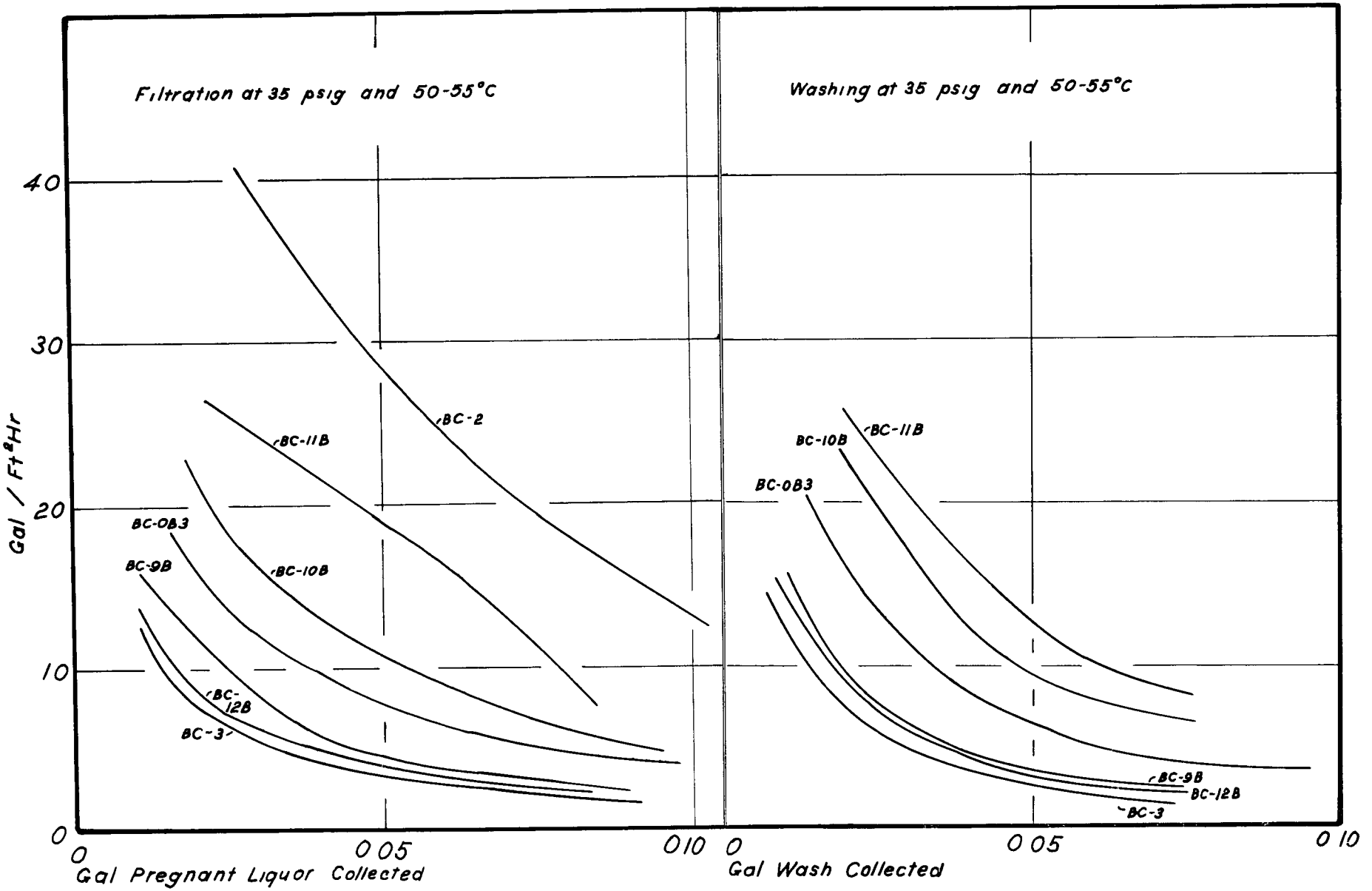


Figure 46

PRESSURE FILTRATION OF LOW SULFURIC ACID LEACH SLURRIES

[redacted]

DWG 18173

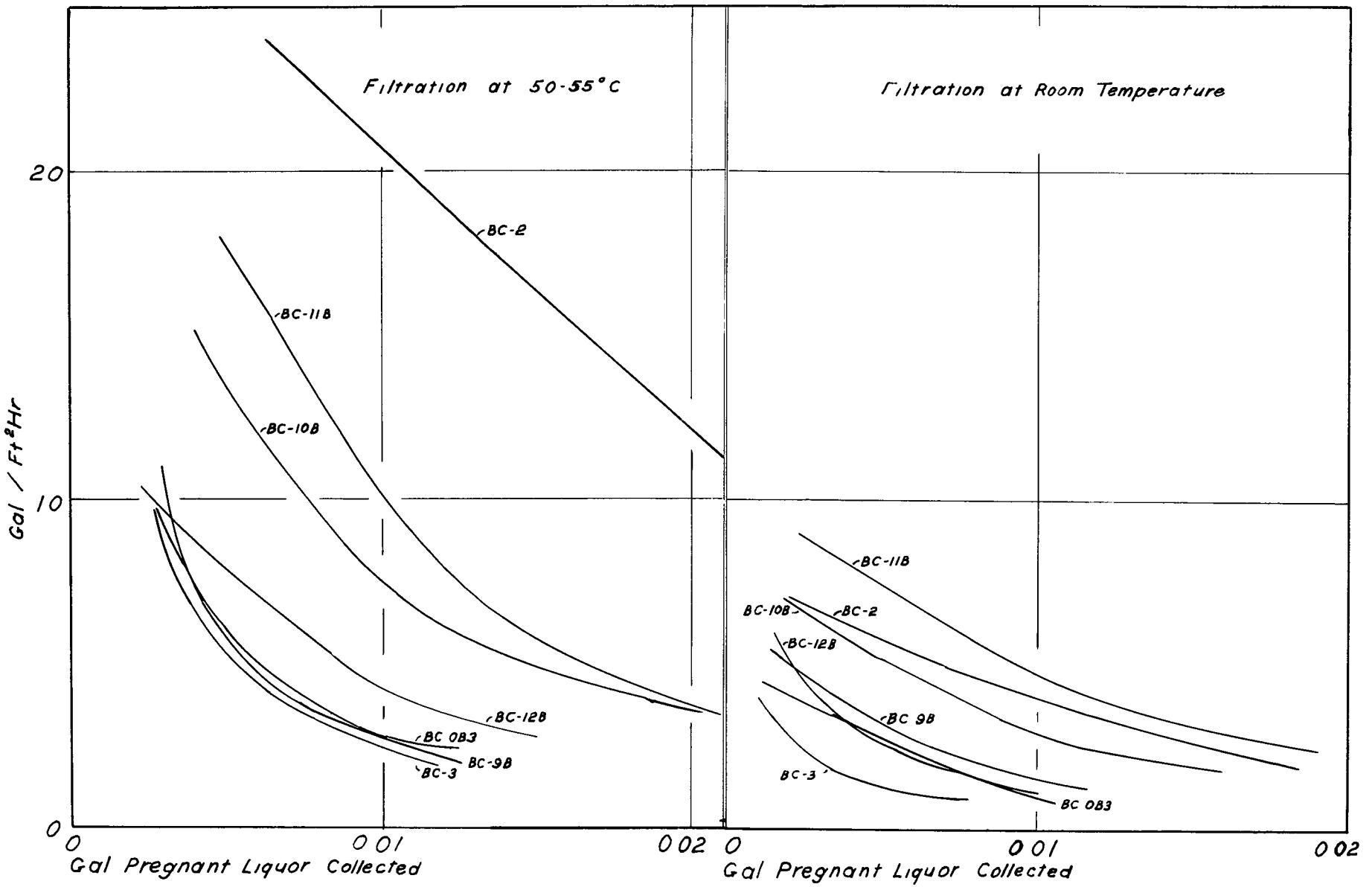


Figure 47

VACUUM FILTRATION OF LOW SULFURIC ACID LEACH SLURRIES

Table 8

BENCH-SCALE LEACHES: LEACHING CONDITIONS

Leach No.	BC-32	BC-41	BC-59-1	BC-59-2	BC-73
Head Ore:	BC-2	BC-2	BC-3	BC-3	BC-3
Kg (d.b.)	4	8	0.2	0.2	6
Acid:	H_2SO_4	H_2SO_4	H_2SO_4	H_2SO_4	H_2SO_4
lb/ton	600	600	800	400	600
Pulp Density %	20	20	20	20	20
Leach Time, Hrs.	4	16	16	16	20
Temp., °C	RT	RT	80°	80°	RT
Filtrate without Washing, Vol, liters	-	23	-	-	-
Filtrate without Washing, pH	0.9	0.9	1.0	1.4	0.8
Filtrate with Washing, Vol, liters	20	-	0.9	0.9	19.5
Filtrate with Washing, pH	0.8				0.8
% U Dissolved	58*	~55*	67**	41**	~40*
% U Balance			105*	111*	

* Based on head analysis

** Based on total uranium found

Table 9

BENCH-SCALE LEACHES. ANALYSES OF PREGNANT LIQUORS

Leach No.	BC-32	BC-41	BC-59-1	BC-59-2	BC-73
			Percent		
U	0.006	0.007	0.005	0.004	0.004
Al	.17	.33	1.32	.54	.64
Fe	.05	.06	.09	.05	.06
Ca	.08	.06			.07
Mg	.007				
Ni	.0002				
Na		.02			
K		.001			
SiO_2	.002	.015			
PO_4	2.5	3.4	3.0	1.5	2.1
SO_4	2.7	2.7			4.8
F	.16	.21			.12

Table 10

BENCH-SCALE LEACHES: ANALYSES OF PREGNANT LIQUORS

Spectrographic Analysis*

Percent

	BC-32	BC-41		BC-32	BC-41
Al	0.12	0.066	Mo	<.0005	<.001
B	<.0001	<.0001	Na	.01	
Ba	<.0005	<.0005	Nd	<.005	
Ca	.01	.02	Ni	.003	<.003
Cd	<.001	<.001	Pb	<.001	<.001
Co	<.001	<.001	Pr	<.01	
Cr	<.001		Si	<.001	
Cu	.0005	.0006	Sm	<.01	
Dy	<.002		Sn	<.00005	
Eu	<.002		Sr	<.002	
Fe	.03		Ta	<.02	<.03
Gd	<.002		Ti	<.001	
K	.0002		V	<.001	
La	<.002		W	<.02	
Li	.0002		Y	<.003	
Mg	.007	.01	Yb	<.002	
Mn	.002	.005	Zn	<.007	

* "The spectrographic test results reported herein are semi-quantitative estimates which were obtained for use as a guide to chemical analysis and should not be interpreted or construed to be precise quantitative determinations."

at 35 psig. Whatman No. 42 paper was used on top of a light duck. The leach slurries contained about 500 ml (0.13 gal) of total liquid. Hot slurries were transferred at about 75°C and were cooled by contact with the metal filter to 50-55°C. The cakes formed were about one-quarter of an inch thick. They were washed by reslurrying with water acidified to about pH 1.5. The filtration rates for the washes were similar to those for the pregnant liquors.

RECOVERY OF URANIUM FROM SOLUTION

Three types of treatment were tested for recovery of the uranium from the low sulfate leach liquor---anion exchange, liquid-liquid extraction, and precipitation. The low sulfate liquor is more favorable for anion exchange sorption of uranium than are liquors obtained by more complete dissolution of the ore with larger quantities of acid, because the excess anions compete with the complexed uranium for positions in the resin, and the competition is the more severe the higher the concentration of the excess anions. It is also advantageous that this liquor is essentially free of chloride and nitrate, which would compete more seriously with uranium sorption than do sulfate and phosphate.

Brief exploratory tests of cation exchange sorption of uranium from the sulfate liquor with Dowex-50 were less promising than anion exchange. Exploratory tests with a phosphorus-containing resin, Duolite C-60*, showed almost no pickup.

Reagents for use in liquid-liquid extraction as a method for removing uranium and other metal ions from various types of aqueous solutions are being studied in this laboratory.(5) Extraction of uranium from phosphoric acid and from some related materials has been studied by workers at the Dow Chemical Company.(10) Several organophosphorus compounds have shown promise for recovery of uranium from nitric acid and sulfuric acid liquors.

A study is also being made in this laboratory of the liquid-liquid extraction of uranium from aqueous solution by secondary and tertiary amines in organic solvents.(5c) The partition appears to be analogous to anion exchange with weak-base resins, and has shown high uranium extraction from reagent solutions. Single-stage uranium extractions from low-sulfate LZ liquor were also high, but in multistage extractions with the first amines tested the losses to the raffinates were high. Other amines showing much lower loss to the aqueous phase have been tested with reagent solutions, but not yet with LZ liquors.

Hydrolytic precipitation gave nearly complete recovery of uranium, but only in very low grade cakes. The precipitates consisted mainly of aluminum phosphate, the uranium probably being present as uranyl ammonium phosphate or as a uranous phosphate. Precipitation was improved when the sulfate liquor was reduced. Several methods were tested for upgrading the primary cakes, none of which gave good enough results to make precipitation appear a promising recovery method.

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*Research sample obtained from the Chemical Process Company, Redwood, California.

Recovery of Uranium from Sulfate Leach Liquor by Anion Exchange

The effects on uranium sorption of excess concentrations of various anions, including sulfate, phosphate, nitrate, and chloride have been previously reported.[6] The tests with sulfate and phosphate, both separately and together, suggested that uranium sorption should be satisfactory from sulfuric acid leaches of LZ, especially from those resulting from use of a minimum quantity of acid, provided that there be no important interference by any other constituent of the liquors.

Preliminary tests were made with the small quantity of liquor available from one of the beaker-scale leach tests (No. BC-4-2, 800 lb. H_2SO_4/T) in column sorption and in batch equilibration with Dowex-1 phosphate. The equilibration of 40 ml of the liquor with 4.7 meq of the resin showed over 90% pickup, giving resin loading of 0.5 mg uranium/meq resin, and a distribution coefficient of 120 (mmole U/meq R)/(M U). The preliminary column test qualitatively indicated good sorption, but the quantity of liquor was not sufficient to saturate the resin (326 ml through 7.6 meq). The last effluent fraction was 10 ppm in uranium, 18% of the head concentration. The column was cut into quarters for analysis; the uranium found was (1, top) 3.5, (2) 2.8, (3) 1.6, and (4) 1.0 mg uranium/meq resin.

Tests were continued with larger quantities of sulfate liquor from leaches No. BC-32 and BC-41 (Table 9). Batch equilibrations were made to determine the importance of liquor concentration and pH. In all these tests, 2 meq of Dowex-1-PO_4 resin was used per 100 ml of solution. The improvement in the single-stage pickup of uranium as the pH was raised with sodium hydroxide is shown in Figure 48. The pH dependence was strong up to at least 1.5, and appeared to be leveling off around 2.0. Hydrolytic precipitation at slightly higher pH prevented further extension of the range.

The use of magnesium carbonate to raise the pH was expected to give still higher sorption, because the magnesium ion was expected to complex some of the excess sulfate or phosphate and decrease its interference. The result in a single test was slightly higher than the results with sodium hydroxide, as shown in Figure 48, but the difference found is within analytical error.

Simple dilution of the sulfate liquor raised the pH considerably, as shown in Figure 49. In general, dilution would be expected to decrease the sorption of uranium by a given amount of resin if the distribution coefficient remained constant. In these tests the ratio of resin to uranium was kept constant; the sorption increased, but not as much as when the pH was raised without dilution. When the diluted solutions were adjusted to pH 2 with sodium hydroxide, the sorption was about the same as

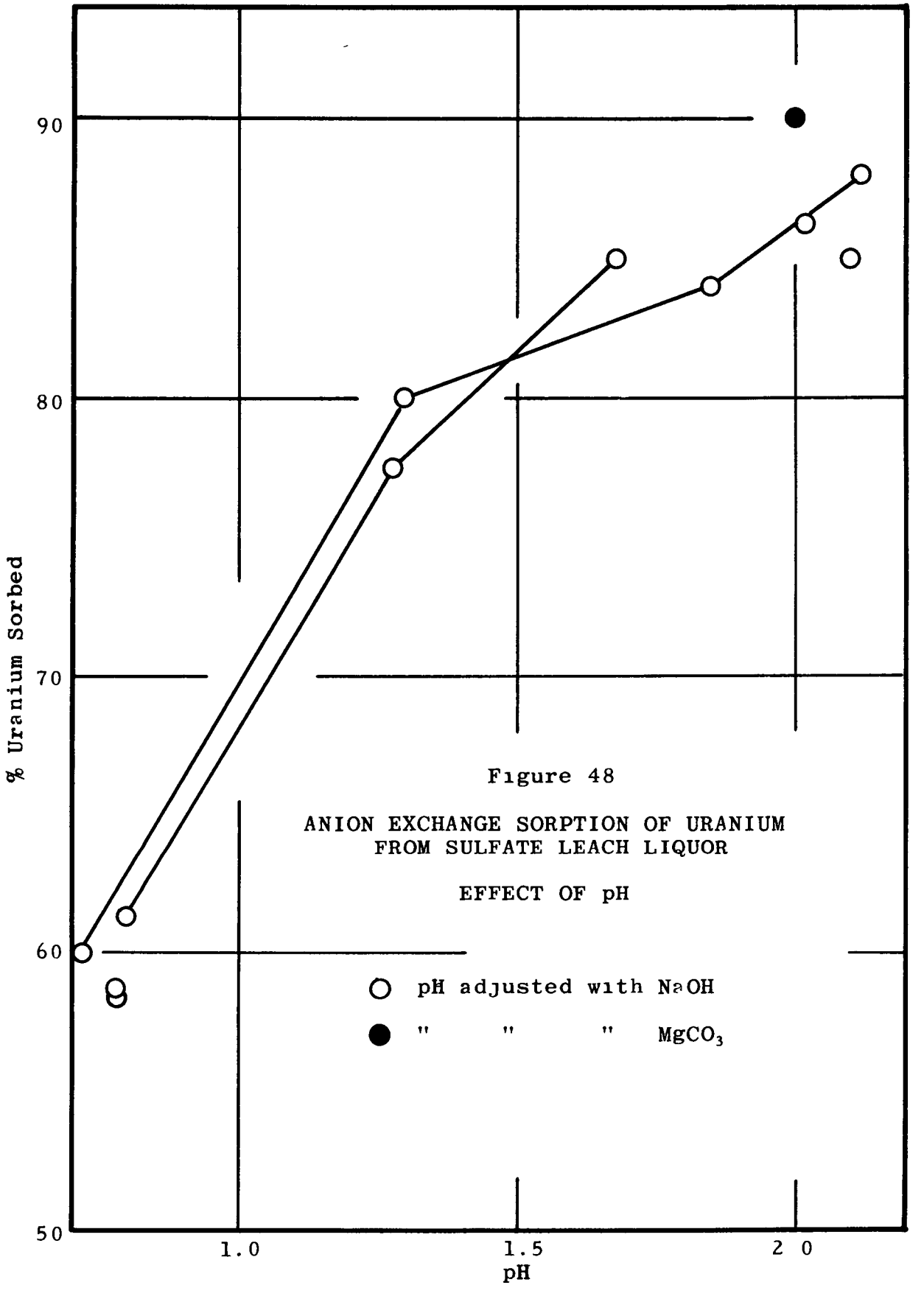


Figure 48

ANION EXCHANGE SORPTION OF URANIUM
FROM SULFATE LEACH LIQUOR

EFFECT OF pH

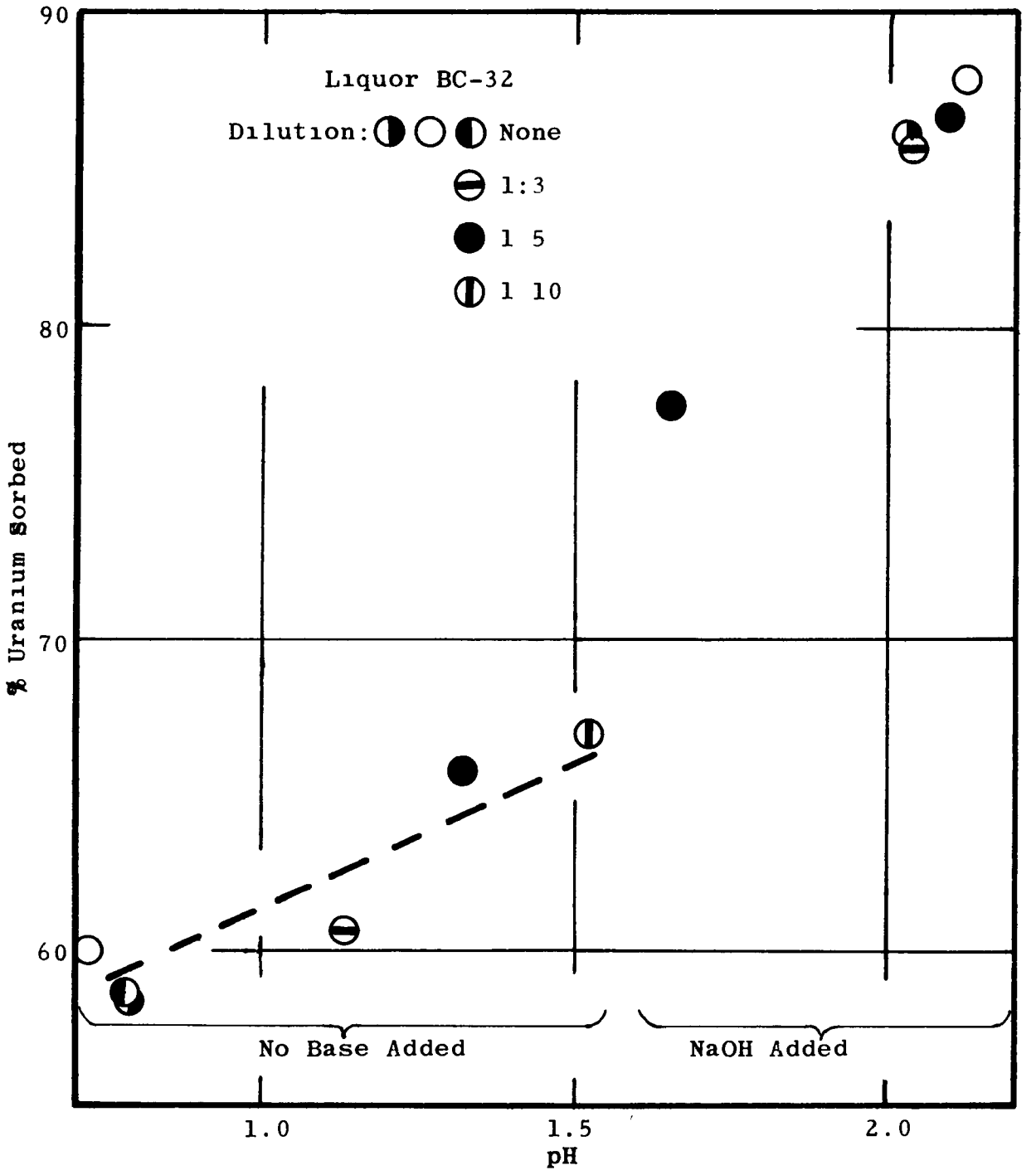


Figure 49

ANION EXCHANGE SORPTION OF URANIUM FROM LEACH LIQUOR
EFFECT OF DILUTION

from undiluted liquor at the same pH. These tests show that for a process the pregnant liquor should go to the resin columns at pH 1.5 or above if that can be reached without danger of precipitation, and also that the uranium concentration of the pregnant liquor is not of primary importance, so that a low pulp density can be used in the leach if needed. (This does not imply that the ratio of uranium to sulfate and phosphate could be decreased without impairing the uranium sorption.)

As an approximation to the results to be expected from much higher sulfate liquors, expected to dissolve much of the aluminum minerals as well as the calcium minerals, aluminum sulfate equivalent to the aluminum in the tailings from leach No. BC-32 was added to an aliquot of the pregnant liquor. A batch equilibration of the resulting liquor with Dowex-1-phosphate showed the uranium pickup decreased from 58% to 33%, with the loading correspondingly decreased from 1.8 to 1.1 mg uranium per meq of resin. This lowered pickup is not necessarily prohibitive for a process, but it would increase the amount of resin needed, and decrease the uranium concentration obtainable in the subsequent elution.

Comparison of several commercial resins in batch equilibrations showed slightly better uranium pickup by Amberlite IRA-400 and Dowex-1 than by Amberlite IRA-410 and Dowex-2, all strong-base resins. Amberlite IR-45, a weak-base, bead-form resin, showed considerably lower pickup. These results are all referred to the ionic capacities of the resins, measured as previously described.[6a]

Column Sorption Tests

In the preliminary column test described above, saturation was not reached because too much resin was present for the small amount of liquor available. More extensive tests, but still on a limited scale, were made with liquor from the larger bench-scale leaches BC-32 and BC-41.

A test with a flow of 1 ml/min through 4.0 meq of Dowex-1-phosphate (retention time of about 1.5 minute) showed rapid breakthrough and a slow, almost linear rise of the uranium concentration, indicating too rapid flow. The test was terminated when the effluent uranium concentration reached 70% of the head, which was at 360 ml throughput. The calculated average loading was 3.4 mg (0.014 mmole) uranium per meq of resin. A similar column test was made with the pH of the head liquor adjusted from 0.8 to 2.0 with sodium hydroxide, and with the flow rate decreased to 0.3 ml/min or less, giving a retention time of about 5 min. This test was terminated after a throughput of 850 ml, when the effluent uranium concentration was still only 25%

of the head. The column was cut into quarters for analysis, with the results shown in Table 11. The average loading of the top quarter was 17.4 mg uranium per meq of resin. While the uranium loading still showed a steep gradient from top to bottom, the iron and aluminum were essentially constant throughout the column. Ionic charge balances on these analyses were not possible because the degree of hydrolysis of the anions in the resin phase was not known, and was probably different from the degree of hydrolysis in the equilibrium solution.

On the basis of the foregoing results, tests were made with column units in series. The scale of the tests was made still smaller than before, in accordance with the high ratio of solution to resin indicated as desirable by the foregoing test. Each unit prepared for the column series contained 1.0 meq of resin in a glass tube 4 mm O.D. by about 75 mm, with the wet-settled resin occupying about one ml gross volume. Dowex-1-sulfate was used, since the single-column tests had shown that the throughput would be sufficient to bring the resin into equilibrium with the sulfate and phosphate of the head solution early in the run. (Sulfate and phosphate are both favorable for uranium sorption. Resin initially as chloride or nitrate, on the other hand, might permit loss of some uranium through the bed before the chloride or nitrate could be all displaced by the incoming sulfate and phosphate.) The column units were connected in series by short lengths of rubber tubing. A large dropping funnel with a constant-head air inlet was used as the solution reservoir, and effluents were collected in graduates which were kept covered to minimize evaporation. Samples were removed from between column units by means of a stainless steel hypodermic needle, about 0.4 ml being collected for each sample. For the saturation tests shown in Figure 50 the flow was manually controlled by means of a screw pinch clamp. The flow-rate decreased gradually when the equipment was left unattended, as at night, probably because of collection of suspended solids at the control point. Thus the flow varied greatly for this series test, but it was not allowed to increase above 0.1 ml per minute, which corresponded to about 4 min. retention time in each unit. The beginning and end of each curve in Figure 50 show when the corresponding column unit was added to the bottom or removed from the top of the series. The results show that a series of four units, with about 5 min. retention time in each, was sufficient for saturation of the head unit before breakthrough from the fourth unit.

Figure 51 shows sorption in a similar series of column units and under similar conditions, except that the pH was adjusted to 1.7 instead of to 2.0. In the series shown in Figure 52, the flow was maintained at 1 ml per minute by means of a squeegee pump, and all column units remained present in the series throughout the portion of the run which is shown in the figure. As expected, the faster rate caused early breakthrough from all column units, and slow rise of the loading toward saturation in each. For simplicity, smoothed curves for only four of the ten units are shown.

Table 11

Loading of Resin Column

VS-262

(Terminated when effluent U concentration = 25% head)

(mg/meq R^+)

Column Fraction	U	Fe	Al	PO_4	SO_4
1 (Top)	17.4	1.6	1.9	45.1	58.8
2	11.8	1.8	1.9	44.6	60.2
3	8.2	1.7	2.0	43.0	60.9
4 (Bottom)	4.8	1.6	2.1	43.3	66.1

(mmole/meq R^+)

1	0.073	0.030	0.070	0.47	0.61
2	.050	.032	.070	.47	.63
3	.034	.030	.074	.45	.63
4	.020	.029	.078	.46	.69

FIGURE 50

ANION EXCHANGE SORPTION FROM SULFATE LZ LIQUOR

SATURATION OF COLUMNS IN SERIES

Slow Flow
(Retention Time 5 Min or More)
Liquor BC-32, pH 2 0
Dowex 1 Sulfate
VS-268

[redacted]

DWG. 18176

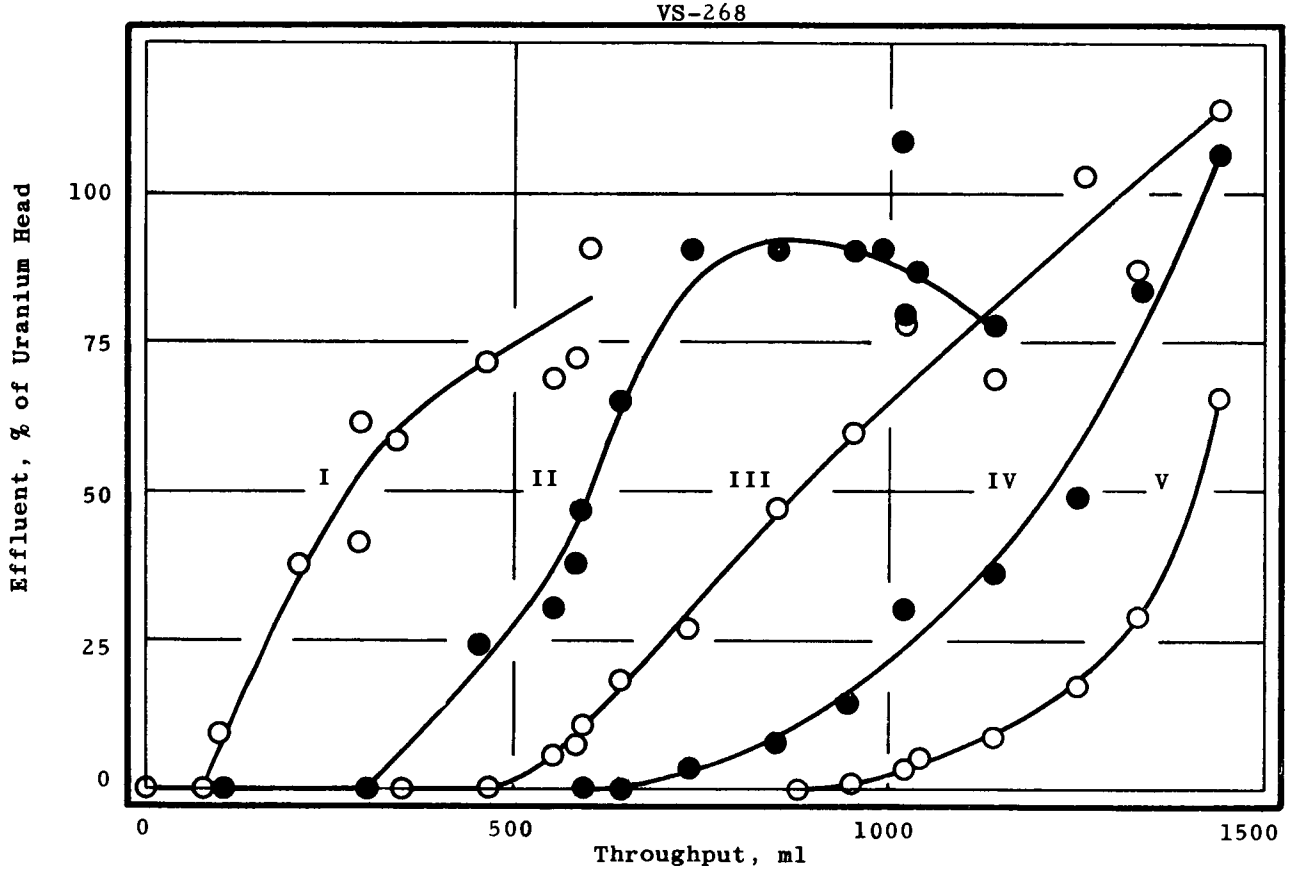


FIGURE 51

ANION EXCHANGE SORPTION FROM SULFATE LZ LIQUOR

SATURATION OF COLUMNS IN SERIES

Slow Flow
(Retention Time 5 Min. or More)
Liquor BC-32, pH 1.7
Dowex 1 Sulfate
VS-270

[redacted]

DWG. 18177

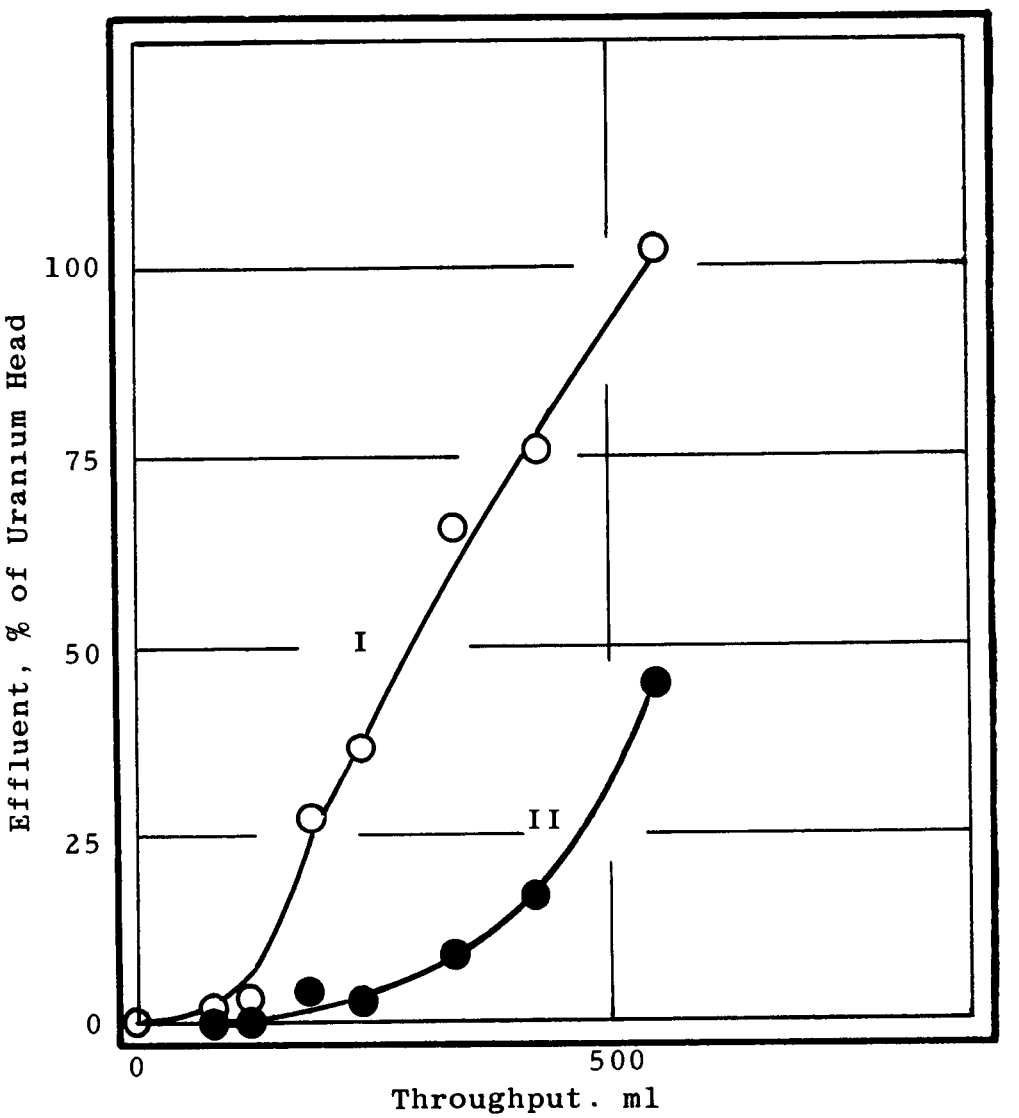


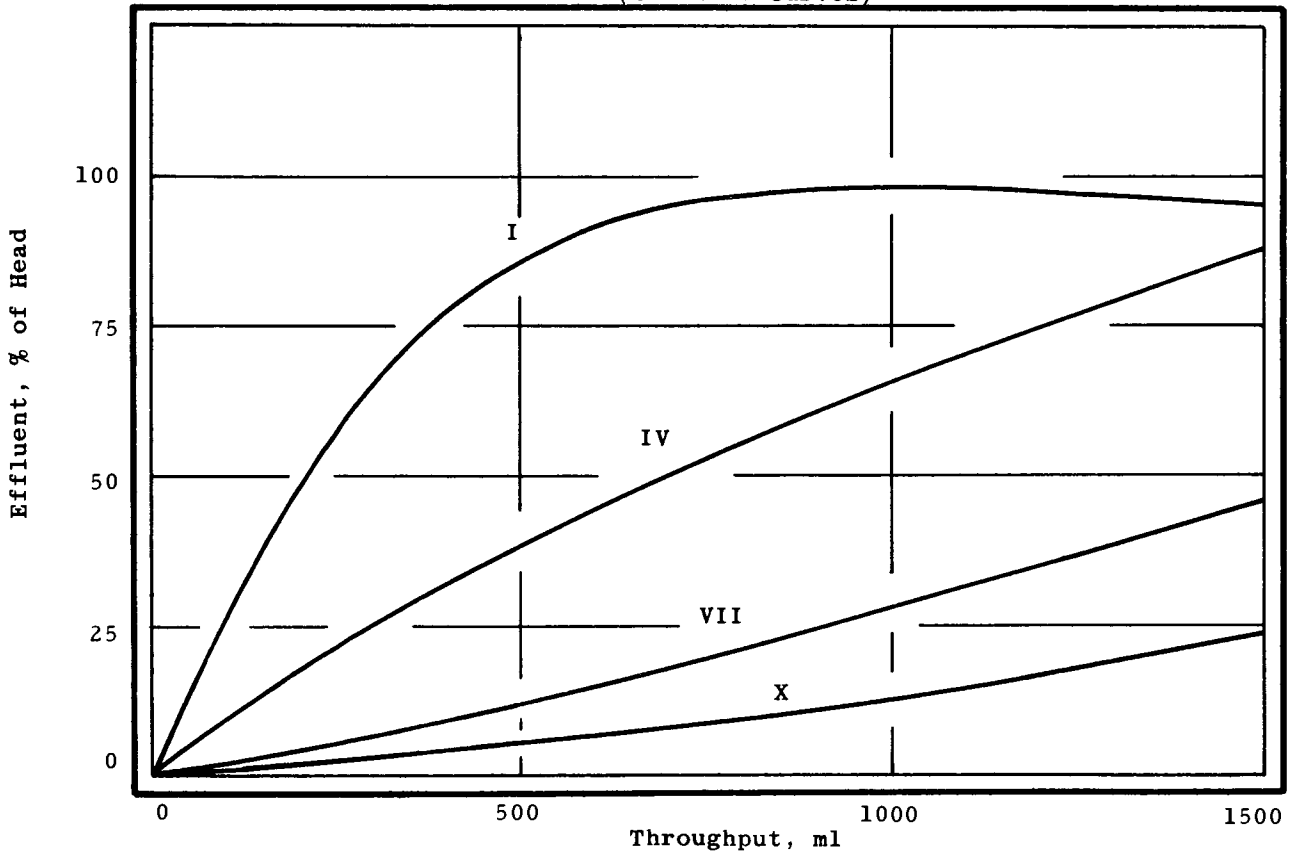
Figure 52

ANION EXCHANGE SORPTION FROM SULFATE LZ LIQUOR
SATURATION OF COLUMNS IN SERIES

Fast Flow
(Retention Time 0 25 Min)
Liquor BC-32, pH 1 7
Dowex 1 Sulfate
VS-271
(Smoothed Curves)

[redacted]

DWG. 18178



Elution of Loaded Columns

Figure 53 shows the elution of a single column unit by acidified chloride solution (0.1M hydrochloric acid, 0.9M sodium chloride). This was Column Unit I of Figure 50. The flow was limited to 0.1 ml per minute (retention time of at least 4 minutes) by manual control, but it should have been still slower, as shown by the high uranium concentrations obtained after overnight stoppages.

On the basis of this single-unit test, a series elution test was set up as shown in Figure 54. The eluent was 0.1M hydrochloric acid, 0.9M sodium chloride, as in the previous test. The column units were those loaded in the tests shown in Figure 50 and 51. The uranium concentration curve dropped to zero after each column unit was added, as the liquor already in the unit was displaced. Instead of attempting to maintain a very slow flow for this test (a flow much less than 0.1 ml per minute was desired), an intermittant flow was used. samples of approximately 0.3 ml, which was less than the estimated void space in the resin bed of each unit, were withdrawn at intervals of not less than one hour. The resulting uranium concentration built up too high locally for the acidity of the eluent, and before the test was completed a precipitate, apparently a uranyl phosphate, was formed in each of the last three units.

The resin in the first three units, after completion of the elution as shown in Figure 54, was found to contain 0.03, 0.1, and 0.5 mg. uranium, or about 0.2, 0.7, and 3.5%, respectively, of the average unit loading. Thus only the first and perhaps the second unit were ready to be removed from the series at this time.

Figure 55 repeats the last section of Figure 54 together with effluent curves for the other important ions. These curves show how the uranium elution was suppressed until most of the sulfate and phosphate was removed, accounting for the relatively slow rise of the uranium concentration in each section of Figure 54. This suggests a possible advantage in collecting separately two fractions of eluents, the first containing most of the phosphate and sulfate from the resin with little of the uranium, and the second being high in uranium and low in phosphate.

Figure 56 shows that the chloride ion (after elution of the uranium) was readily removed by barren liquor, and that the volume of barren liquor required for this was only a small fraction of the volume resulting from the original saturation of the column unit.

FIGURE 53

ANION EXCHANGE SORPTION FROM SULFATE LZ LIQUOR

ELUTION OF SINGLE COLUMN

[redacted]

DWG. 18179

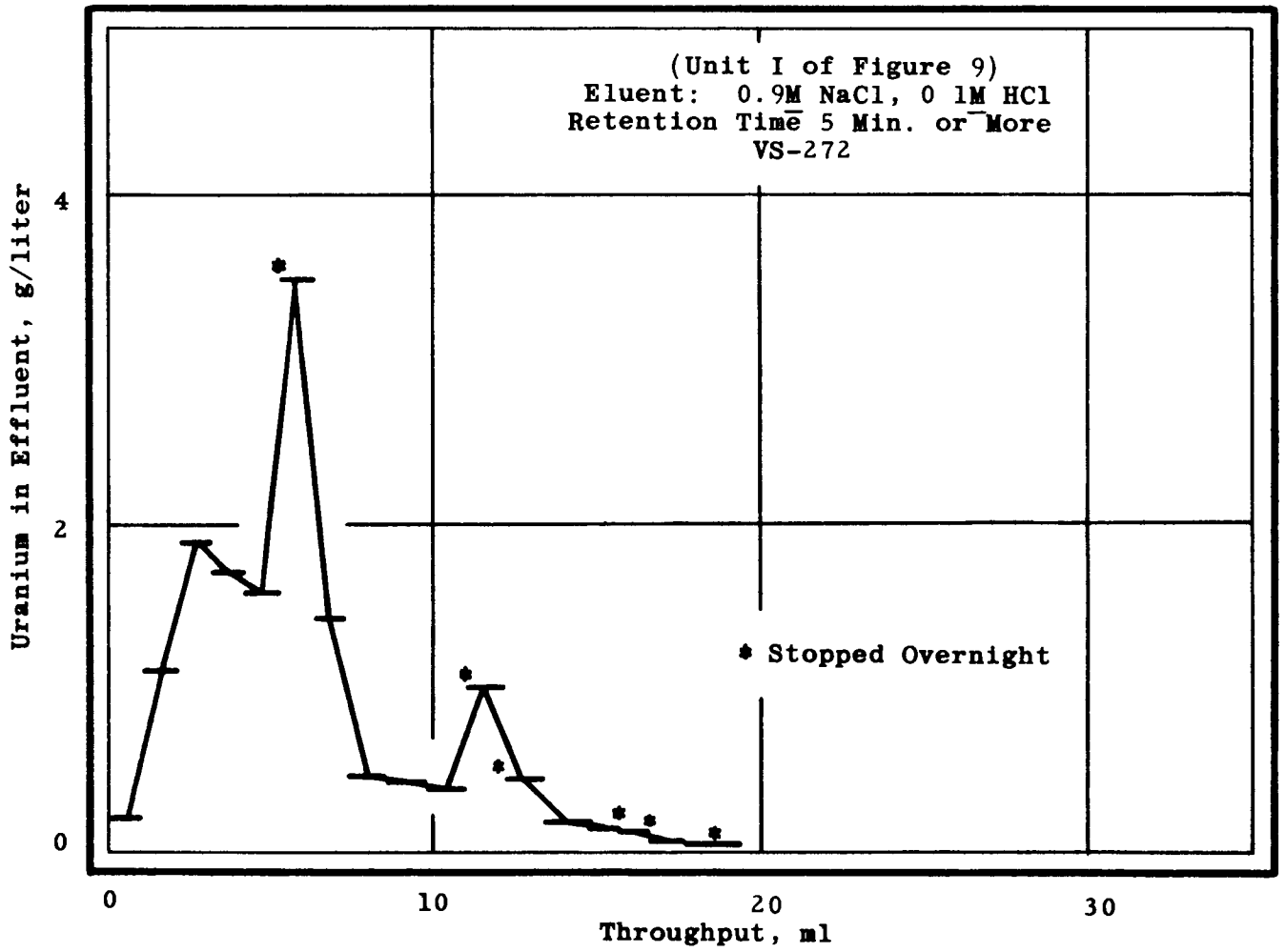
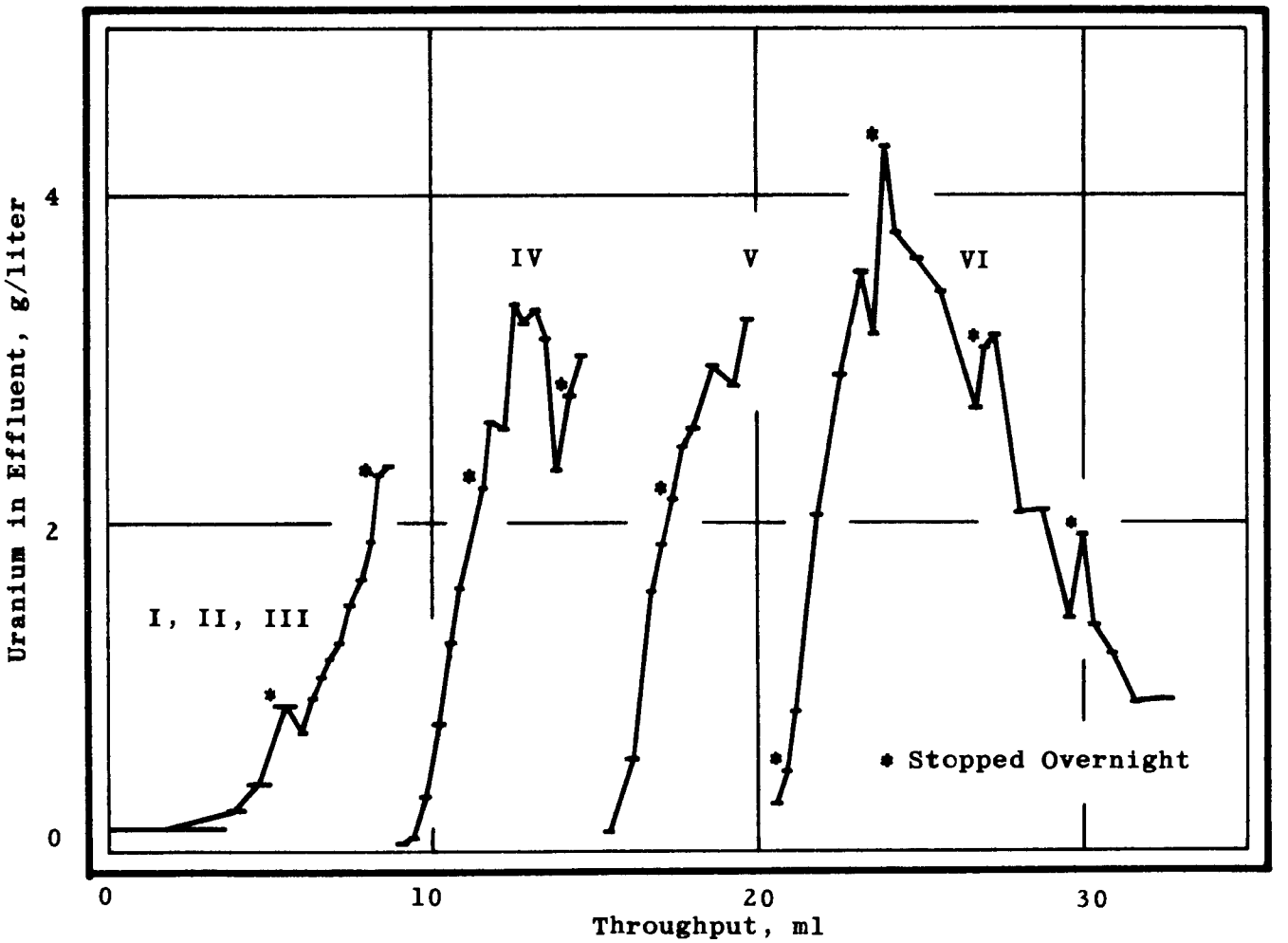


FIGURE 54

ANION EXCHANGE SORPTION FROM SULFATE LZ LIQUOR
ELUTION OF COLUMNS IN SERIES

Eluent 0.9M NaCl, 0.1M HCl
Intermittent Flow
VS-273

[redacted]
DWG. 18180



DWG. 18181

FIGURE 55

ANION EXCHANGE SORPTION FROM SULFATE LZ LIQUOR

RELATIVE ELUTION OF URANIUM, IRON, SULFATE, AND PHOSPHATE

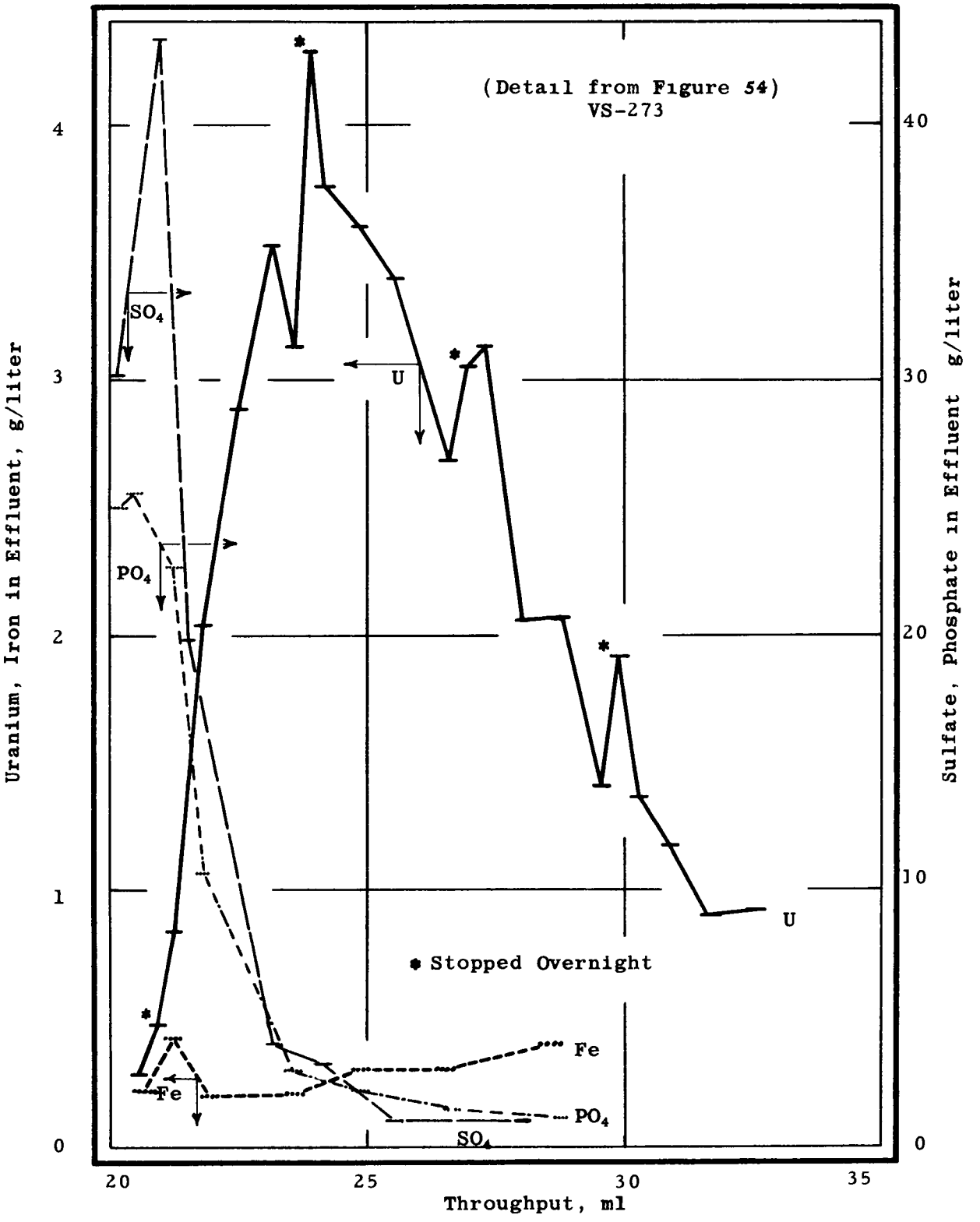


FIGURE 56

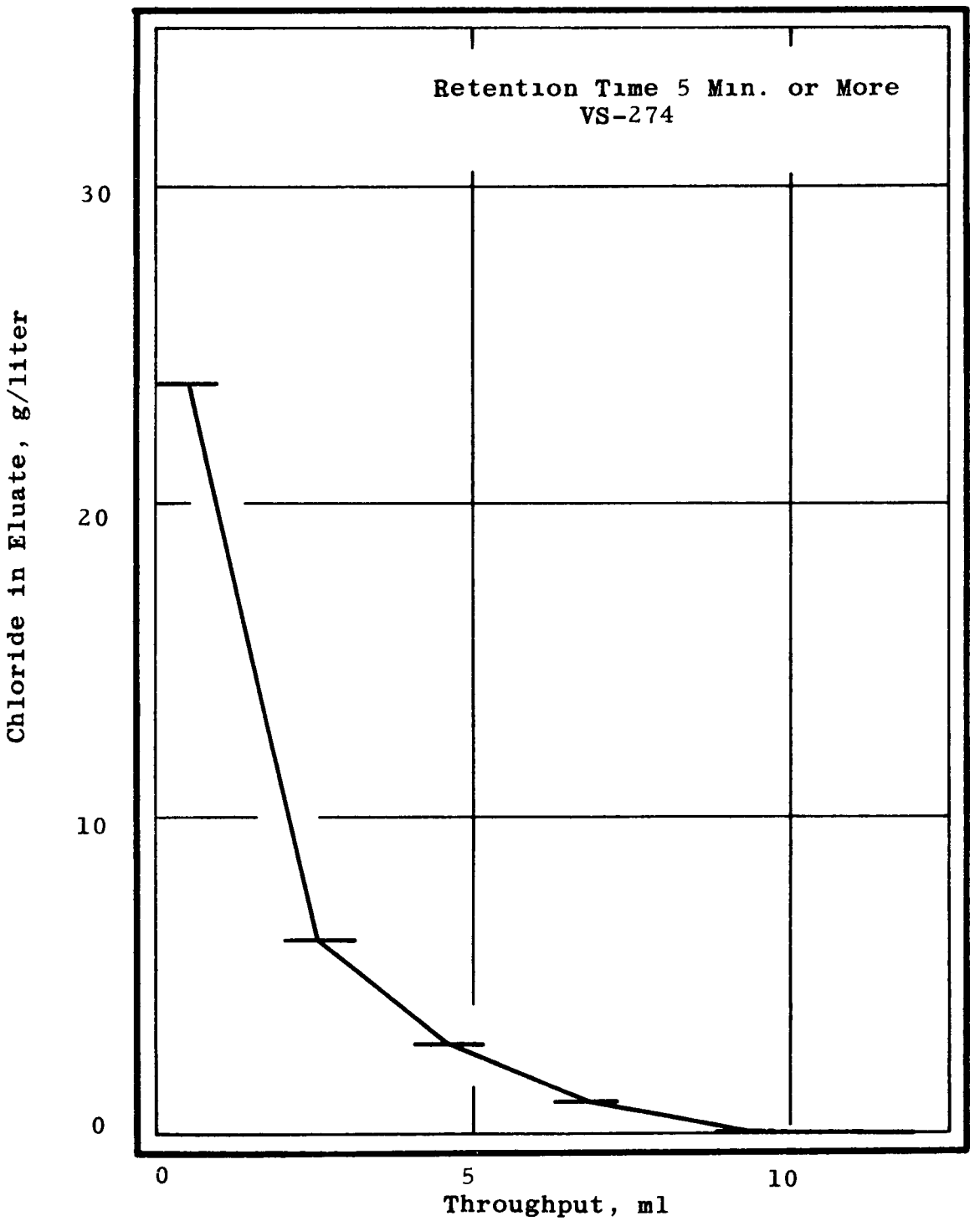
ANION EXCHANGE SORPTION FROM SULFATE LZ LIQUOR

REGENERATION OF ELUTED RESIN BY BARREN LIQUOR

(VS-268)

[redacted]

DWG. 18182



Recovery of Uranium from Sulfate Leach Liquor by Liquid-Liquid Extraction

A program is being pursued in this laboratory of the investigation and evaluation of a variety of reagents for use in the solvent extraction recovery of uranium and other metal ions from various types of aqueous solutions.(5a,b,c,d) Some of the organophosphorus compounds which have been examined showed considerable promise for recovery of uranium from such solutions as the LZ nitric acid and sulfuric acid leach liquors.

Only a few extraction tests were made from the low-acid LZ leach liquors. These were survey tests, and no attempt was made to carry them into as much detail as was done with the anion exchange sorption described above, since most of the available effort was still required in study of the leaching of uranium from the ores. It should also be pointed out that the extractions which are described below were made with one organophosphorus acid, while other reagents which have subsequently been found promising in the evaluation program were not tested with the low sulfate LZ liquor.

In a series of tests with one type of LZ nitrate-phosphate liquor, tri(2-ethylhexyl)phosphine oxide, di(2-ethylhexyl)phosphinic acid, butyl dibutylphosphinate, tetrabutyl ethylenediphosphonate, di(2-ethylhexyl)phosphoric acid, tributyl phosphate, and octylpyrophosphoric acid appeared promising.* The results obtained with these and other similar reagents in the evaluation program referred to above suggest that at least some of these reagents may be useful for uranium recovery from sulfuric acid leach liquors. With all these reagents, the extraction of uranyl sulfate was similar to that of uranyl nitrate from reagent solutions containing little excess anion. High concentrations of sulfate ion (e.g., one molar or more) interfered to some extent with the uranium extraction. Corresponding concentrations of phosphate ion interfered much more strongly than did the sulfate; hence, it is expected that the usefulness of a reagent in a sulfuric acid liquor as compared with a nitric acid liquor will depend mainly on the relative concentrations of phosphate in the two. The effectiveness of the phosphate in inhibiting uranium extraction may be decreased when the solution also contains a considerable concentration of aluminum, which forms complexes with the phosphate. The amount of sulfate left in solution and the amounts of phosphate and aluminum taken into solution will depend both on the amount of sulfuric acid needed for leaching and the amount of calcium in the ore, which have varied widely for the different ore samples examined.

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*These tests have been summarized in Memorandum Y-B34-3, and will be reported separately.

The concentrations of sulfate and phosphate in the low acid liquors have been typically in the range of 0.2 to 0.5 molar (cf. Table 9), which does not appear to be excessive.

Extraction tests from LZ sulfuric acid leach liquor BC-41 (see Table 9) with di(2-ethylhexyl)phosphinic acid showed the expected dependence on reagent concentration, and also a strong dependence on pH. Extraction coefficients of unity or better were obtained in single-stage tests from liquor at pH 1.8 by the reagent at 0.03M, and from liquor at pH 0.8 by reagent at about 0.1M.

In multi-stage cascade tests from liquor BC-41 adjusted to pH 2.0, with equal volumes of organic and aqueous, the stagewise percent extraction by 0.05M di(2-ethylhexyl)phosphinic acid dropped from 95 to 66% in six stages, and extraction by 0.2M reagent dropped from 99 to 95% in eight stages. The apparent extraction coefficients (organic/aqueous) for each stage were between 12 and 16 with the 0.05M reagent and between 120 and 160 with the 0.2M reagent. In each, the final "contaminant ratio" (weight ratio of iron plus aluminum to uranium) in the final organic solution was less than 0.5, as compared with about 50 in the head liquor, i.e., the purity of the extracted uranium with respect to these two principal contaminants was improved at least by a factor of 100.

Recovery of Uranium from Sulfate Leach Liquor by Precipitation

Hydrolytic titration curves for several LZ sulfuric acid leach liquors are shown in Figures 57 and 58, with the point at which precipitation started in each titration marked with an arrow. Aluminum phosphate appeared to be the principal component of all the precipitates. The pH for the start of precipitation varied considerably among different types of liquors, probably depending on the ratios of the components, especially aluminum and phosphate. In the group shown in Figure 58, low sulfate leaches of ore samples BC-1 and BC-5B at acid levels ranging from 220 to 900 lb. sulfuric acid per ton, precipitation began more uniformly, appearing in each titration at the first point checked above about pH 2.2. Some of the curves show an inflection around pH 6.5, indicating phosphoric acid still in solution, while the lack of the inflection in others show that most of the phosphate was removed in the precipitate, presumably because of higher aluminum content.

The compositions of two cakes precipitated from reduced sulfate liquor are shown in Table 13. In the first cake, the uranium precipitation was less complete, and the uranium grade of the cake was higher, than was found in most other precipitations made under similar conditions. The precipitation of the second

Table 12

SULFATE LEACH LIQUORS

DATA FOR TITRATION CURVES OF FIGURES 57, 58

	Leach Test No.	Ore	H_2SO_4 lb/ton	pH Before Washing	pH, Pregnant Liquor + Washings*
I.	LZ[illegible]-15-3	BC-1	565	1.6	1.5
II.	-15-4	BC-1	725	1.2	1.3
III.	-15-5	BC-1	900	0.9	1.1
IV.	-19-2	BC-5B	220	1.4	1.4
V.	-19-4	BC-5B	500	0.9	1.2

* Pregnant liquors diluted approximately x2 by washings.

Table 13

Composition of Phosphate Cakes

Precipitated from Reduced Sulfate Liquor

BC-41

Test No.:	BC-47	BC-55
	percent	
U_3O_8	3.6	2.2
CaO	.72	0
Al_2O_3	39.7	31.8
Fe_2O_3	6.8	.7
P_2O_5	44.4	48.3
SO_4		1.1
	95.2	84.1

DWG. 18183

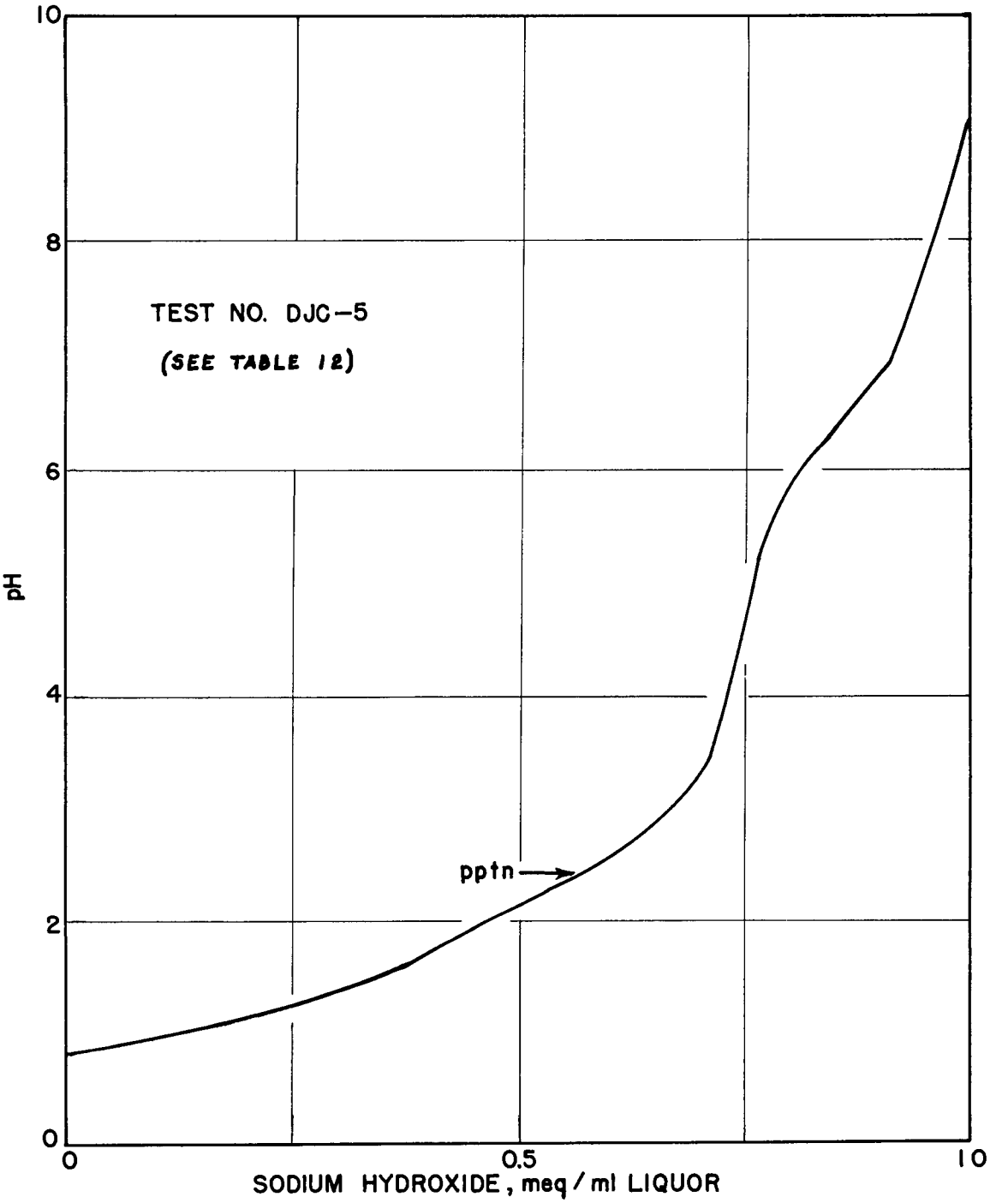
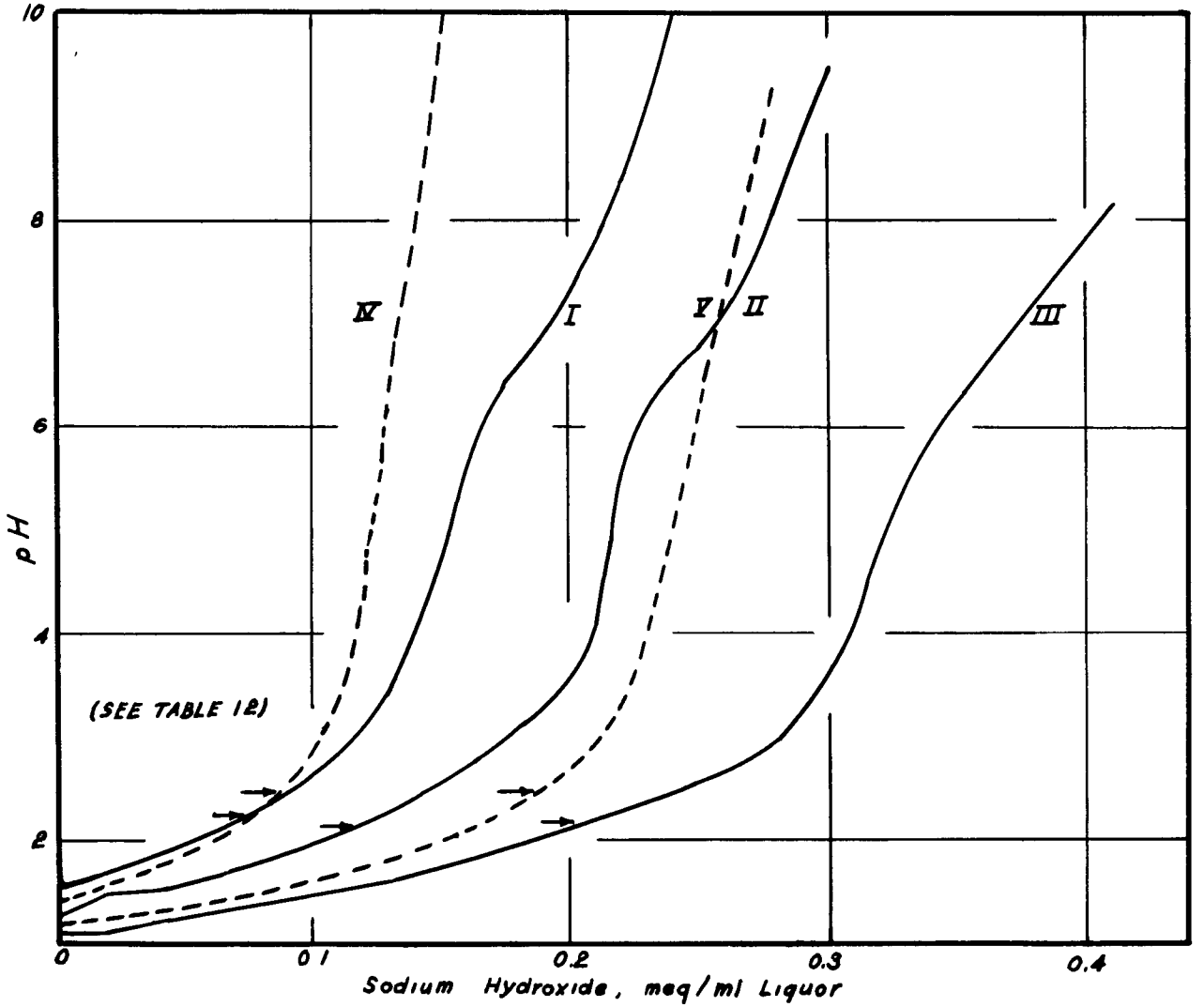


FIGURE 57. TITRATION OF SULFATE LEACH LIQUOR

BC – 32

[redacted]

DWG. 18184



TITRATION OF SULFATE LEACH LIQUORS

Figure 58

cake corresponded more closely to the usual results. However, the gross compositions of the two cakes were essentially similar.

In another test, summarized in Table 14 and Figure 59, the precipitation was carried out in steps by addition of increments of ammonium hydroxide to the reduced liquor, and a sample of the well-mixed slurry was taken at each step for filtrate analysis. The precipitate filtered from each sample was washed, dried, and weighed, but not analyzed. The compositions of the cumulative precipitate and of its increments were calculated by differences from the filtrate analyses. The gross composition was nearly constant throughout the precipitation. The uranium grade was slightly higher in the first increment than later, but not enough to indicate feasibility of fractional precipitation.

Attempts to get a useful fraction of the uranium precipitated at a good cake grade were continued with variations of pH and technique as shown in Table 15. Ammonia gas was used for most of these precipitations because it is less likely than aqueous hydroxides to cause excessive local precipitation. The best cake grade obtained in this series was 1.5%, with 20% recovery, and the best recovery was 72% with 0.3% cake grade.

Precipitation tests from reduced sulfate liquors are shown in Tables 16, 17, and 18. It was not possible to determine whether the uranium was reduced to uranous or remained uranyl. The best combinations of recovery and cake grade in these tests are better than the best from the unreduced liquor as described above, but they are still of the same order of magnitude. The better result of test No. BC-40 was not confirmed by test No. BC-42-2C, repeated under nearly the same conditions.

In two tests, bismuth nitrate was added to provide a bismuth phosphate carrier, giving essentially complete precipitation of uranium at both pH 0.8 and 1.8. Both cakes contained 0.5% uranium. The bismuth was not completely precipitated; hence, recycle of it would require an additional precipitation.

The effect of an oxidizing agent, sodium nitrate, was tested with the results shown in Table 19. The results were no better than from untreated solutions, and poorer than results from reduced solutions. Large variation of the nitrate caused very little change in the percent uranium precipitated.

None of the foregoing precipitation tests gave a cake which could be considered a uranium product without upgrading. Tests of upgrading of such cakes are shown in Table 20. For the primary precipitations, the liquors were reduced with metallic iron (plus zinc in Test No. BC-49) at 60-70°C, to final potentials

Table 14

Composition of Phosphate Cakes

Precipitated from Reduced Sulfate Liquor

BC-41

Stepwise Precipitation by NH_4OH

Calculated Compositions,[a] Cumulative

pH	U_3O_8	Al_2O_3	Fe_2O_3	P_2O_5	Cake Wt., g[b]
	Percent				
2.2	0.66	34	1	64	2.0
2.3	.52	35	2	63	8.7
2.6	.33	33	2	65	16.4
3.4	.33	35	2	64	21.9

Calculated Compositions[a] of Increments

1.4-2.2	0.66	34	1	64	2.0
2.2-2.3	.41	36	2	62	6.7
2.3-2.6	.11	30	2	68	7.7
2.6-3.4	.33	54	0	49	5.5

a) Calculated by differences from filtrate analyses of slurry aliquots.

b) Weights of cakes from slurry aliquots, dried at 110°C, calculated to basis of 1 liter head liquor.

DWG. 18185

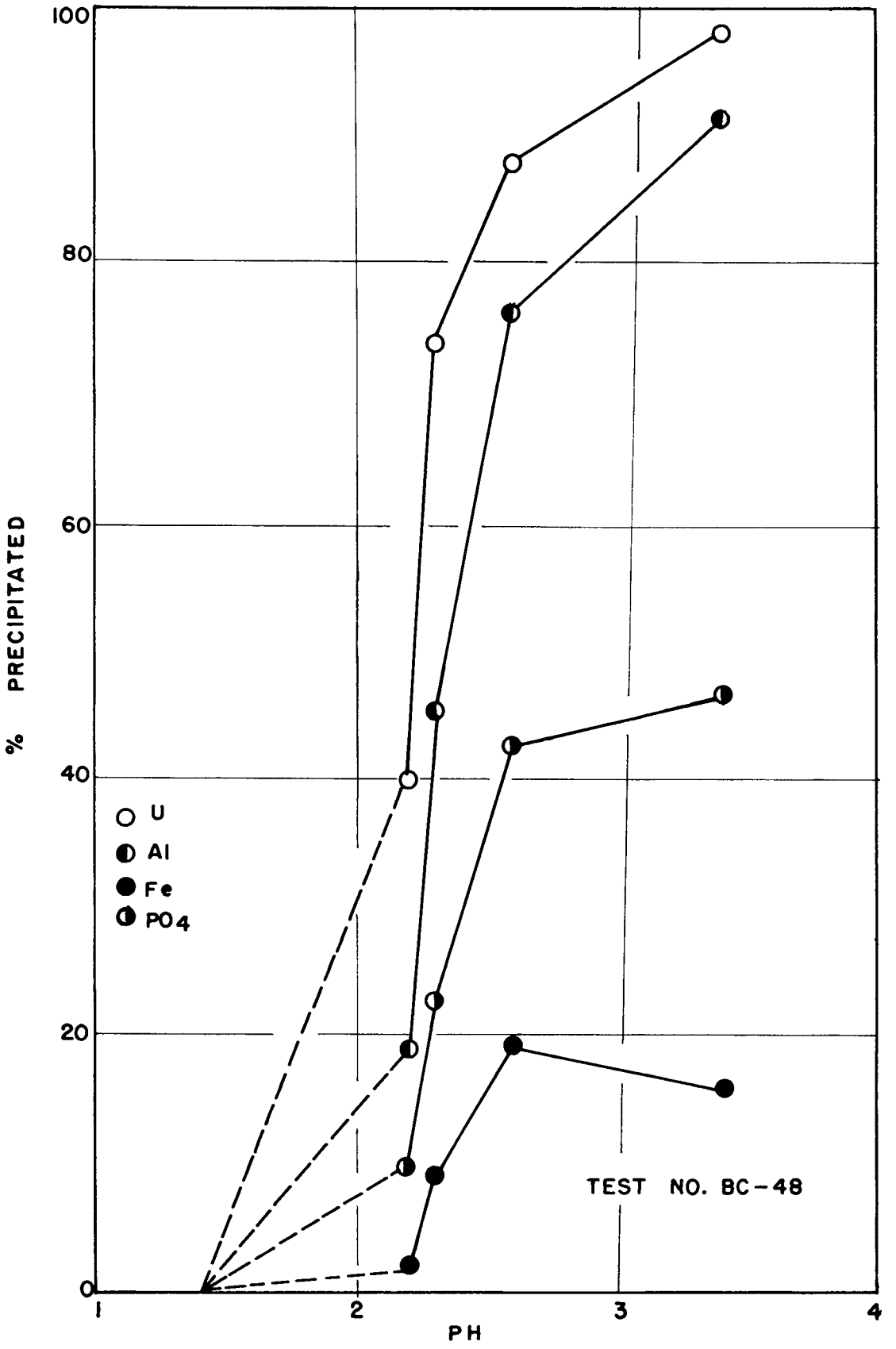


FIGURE 59. STEPWISE PRECIPITATION FROM REDUCED SULFATE LIQUOR BC-41

Table 15

FRACTIONAL PRECIPITATION FROM SULFATE LIQUOR

BC-32, 100 ml per test

Test No.	5% NaOH to pH-	Additional Base	Final pH	Cake Weight g[a]	% of U pptd[b]	Cake Grade, %[b]
BC-34-1	2.0	NH_3	2.37	0.38	38	0.6
-2	2.0	NH_4OH	2.13	.08	20	1.5
-3	2.2	none	2.22	.24	33	.8
-4	1.8	NH_3	2.28	.29	35	.7
-5	1.5	NH_3	2.18	.28	20	.4
-6	1.5[d]	NH_3	2.10	.25	12	.3
-7	2.0	NH_3	2.28[e]	.37	10	.2
-8	2.0	NH_3	2.32[e]	.48	30	.4
-9	2.0	NH_3	2.75[e]	1.59	72	.3

(a) Cakes dried at 110°C
(b) Calculated from filtrate analysis
(d) Two drops 30% H_2O_2 added
(e) Final pH after standing two days

Table 16

Fractional Precipitation from Reduced Sulfate Liquor

BC-32, 100 ml per test

Test No.	5% NaOH to pH-	Sodium Hydrosulfite g [a]	NH_3 to pH -	Cake Weight g [b]	% of U Pptd [c]	Cake Grade % [c]
BC-34-10	2.0	0.1	2.25[e]	0.16	55	2.1
-11	2.0	.1	2.68[e]	1.31	68	.3
-12	2.0	.1	2.55[e]	.85	12	.1
-13	2.0	.1	2.20[e]	.48	35	.4
-14	2.0	.1	2.17[d,e]	.18	45	1.5
BC-35-7	1.5	.04		None		
-8	1.5	.1		Very slight		
-9	1.5	.2		.13	75	3.5
-10	2.0	.04		None		
-11	2.0	.1		Very slight		
-12	2.0	.2		.19	82	2.6

a) Added as 2% solution.
b) Cakes dried at 110°C.
c) Calculated from filtrate analysis.
d) Heated to 60° for 10 minutes; NH_3 added to hot solution.
e) Final pH after standing two days.

Table 17

Fractional Precipitation from Reduced Sulfate Liquors

Reductant-Zinc Amalgam

Test No.	Head Liquor	Base	pH	Temperature pptn	Temperature filtn	% of U pptd[a]	Cake Grade[a] % U
BC-42-1A	BC-41	NH_4OH	2.2	Hot	RT	48	1
-1B	"	"	2.4	"	"	99	0.4
BC-43-1[b]	"	"	2.4	"	"	99	.6
BC-40-4	BC-32	"	2.7	RT	"	98	.9
-1	"	"	2.8	Hot	Hot	65	5
BC-42-1C	BC-41	"	2.9	Hot	RT	99	.3
BC-40-7A	BC-32	MgO	2.75	"	"	95	2
BC-44-1A	BC-41	"	2.8	RT	RT	94	1
-1B	"	"	3.25	"	"	98	.4
-1C	"	"	3.7	"	"	99	.3
BC-40-7B	BC-32	"	3.9	Hot	RT	99	.4
BC-44-2A	BC-41	$MgCO_3$	2.6	RT	RT	23	2
-2B	"	"	2.7	"	"	77	1
-2C	"	"	2.8	"	"	93	.9
-2D	"	"	2.9	"	"	63	.5

a) Calculated from filtrate analyses; cake grades based on weights of cakes dried at 110°C.

b) Reduced with iron instead of zinc.

Table 18

Fractional Precipitation of Reduced Sulfate Liquors

Reductant - Zinc Amalgam
Sodium Hydrosulfite Added
pH Adjusted with NH_4OH

Test No.	Head Liquor	Na_2SO_4 g/liter	pH	Temperature pptn	Temperature filtn	% of U pptd[a]	Cake Grade % U[a]
BC-40-3	BC-32	1	1.8	Hot	Hot	33	4
-5	"	1	2.4	RT	RT	73	9
BC-42-2A	BC-41	2	1.6	Hot	RT	18	18
-2B	"	2	2.2	"	"	71	2
-2C	"	2	2.4	"	"	99	.6
-2D	"	2	2.7	"	"	98	.4
-2E	"	2	3.1	"	"	99	-

a) Calculated from filtrate analyses; cake grades based on weights of cakes dried at 110°C.

Table 19

Precipitation from Oxidized Sulfate Liquor

BC-32, 100 ml per test
Pptd at pH 2.4 with 1:1 NH_4OH

Test No.	$NaNO_3$ Added g	NO_3 g/liter	Final pH	Cake Weight g[a]	% of U Pptd[b]	Cake Grade %[b]
BC-37-1	0	0	2.45	0.898	55	0.4
-2	0.68	5	2.50	1.122	62	.3
-3	1.36	10	2.47	1.066	62	.4
-4	2.72	20	2.48	1.256	68	.3
-5	5.44	40	2.41	1.421	68	.3

a) Cakes dried at 110°C.

b) Calculated from filtrate analysis.

Table 20

Upgrading of Phosphate Cakes Precipitated from Reduced Sulfate Liquors

Test No.	Primary Cake: Uranium Recovery	Primary Cake: Grade % U	Primary Cake: Uranium Balance	Upgrading Method	Secondary Cake: Uranium Recovery: % of Total U	Secondary Cake: Uranium Recovery: % of U in Primary Cake	Secondary Cake: Grade % U	Secondary Cake: Uranium Balance %
BC-45	(74)	(2)		NaOH Leach[a]	45	61	12	94
BC-46	(88)	(0.9)		NaOH Leach[a]	58	65	23	99
BC-49[b]	(62)	(0.6)		Double pptn.	57	92	7.8	134
BC-52	(76)	(1.5)		NaOH Leach[c]	41	54	22	83
						Secondary Leach		
BC-55-1	92	1.5	112	DEHP[d] Extn	2	2		67
-2				5% Na_2CO_3 Leach	65	71		76
BC-59-1a	(83)			5% Na_2CO_3 Leach	66	79		86
				10% Na_2CO_3	77	93		59
-2a	(97)			5% Na_2CO_3	83	86		85
				10% Na_2CO_3	91	94		64

a) Caustic leach at 80°C.
b) Primary precipitation with MgO; reprecipitation with NH_4OH.
c) Cake calcined at 800°C before caustic leach at R.T.
d) Di(2-ethyl hexyl) phosphinic acid, 0.1 M in CCl_4.

at -0.26v* or below, and precipitated at pH's from 2.2 to 2.7 except for BC-45 which was at pH 1.8. Magnesium oxide was used to raise the pH in BC-49, aqueous ammonium hydroxide in the others. The double precipitation in BC-49 consisted of complete dissolution of the primary cake with hydrochloric acid and hydrogen peroxide, reduction, and reprecipitation at pH 1.9. Again, it was not known whether the uranium itself was reduced, but its reduction was considered more likely in the second reduction than in the first because the phosphate concentration was lower. The lower pH and improved results in the second precipitation were possible both because the contamination was less in the second solution than in the original liquor, and because hydrochloric acid is more favorable than sulfuric for uranous phosphate precipitation.

The sodium hydroxide leaches in BC-45, -46, and -52 effectively dissolved aluminum and phosphate, decreasing the dry weight of the cakes from 2.4, 6.7, and 2.9g to 0.26, 0.18, and 0.11g, respectively. However, about half of the uranium content was dissolved from each into the caustic, presumably because of complexing by the high phosphate contents.

The other tests in Table 20 were attempts to redissolve the precipitated uranium without dissolution of a large fraction of the cake. Extraction by di(2-ethylhexyl)phosphinic acid (0.1M, in carbon tetrachloride) was hoped to provide specific leaching, but the uranium extraction was nil. No nitric acid was used in this test with the phosphinic acid; it is possible that under different conditions extraction with a complexing agent might provide satisfactory upgrading.

Most but not all of the precipitated uranium was recovered by sodium carbonate leaching. High concentration of carbonate was required so that its use would be feasible only if recycle or regeneration were possible.

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*Platinum-Saturated Calomel electrode system. The sign is that of the platinum electrode.

METHODS TO AVOID FILTRATION

Simultaneous leaching of the uranium and sorption of the dissolved uranium by anion exchange resin mixed with the pulp appeared promising for use with the low sulfate leach, in case the filtration of the pregnant liquor from the tailings should prove impracticable. Such resin-in-pulp leaching was previously suggested for LZ ores by workers at MIT.[2] It was expected that the resin-in-pulp sorption would be better in low sulfuric acid leaches than in leaches using greater acid quantities, for the same reasons that applied to the clarified liquors. The results were fairly well comparable with the results obtained from clarified low-sulfate liquors.

Slurry-liquid extraction similarly offers a means of avoiding filtration, and one which would probably be simpler in equipment and operation than would a resin-in-pulp process, if engineering tests proved it operable in the LZ slurries. In laboratory tests, extractions were obtained without serious emulsion formation when the phases were contacted without vigorous mixing. Extractions of uranium from the ore were similar to those obtained in simple acid leaching, and most of the dissolved uranium was extracted into the organic phase in a single stage.

Since ores difficult to filter from aqueous liquors might filter readily from some non-aqueous liquors, the difficulty of filtration might be avoided by organic leaching, or solid-liquid extraction without an aqueous phase. Such organic leaching of various ores has been studied elsewhere.[11,12] Survey tests have been made of organic leaching of several LZ ores with various acidic extraction agents. In some tests nitric or sulfuric acid was added. None of the tests completed to date showed uranium extractions as good as obtained in aqueous leaching.

Resin-in-Pulp Leaches

The use of resin-in-pulp leaching as a unit operation, and special types and forms of exchange resins for such use, have been reported elsewhere.[7,8] In the following tests, standard commercial resins in bead form were used, screened to 40-60 mesh to give ample margin in separation from the minus 200 mesh ore concentrates by means of 100 mesh screen. Much finer resin beads could have been used, with more precautions in the physical separations, which probably would have given more rapid equilibration in each stage but should not have materially changed the equilibrium results obtained.

The uranium recovery compared fairly well with that obtained by low-sulfuric acid leach and filtration, followed by anion exchange sorption from the clarified liquor. With the quantities of resin used in most of the tests, two resin stages were sufficient to extract most of the solubilized uranium, but with resulting low uranium loading on the resin. More stages with less resin per stage in countercurrent operation should give similar recovery and better loading.

Table 21 shows the results obtained over a range of acid quantities in leaching of ore BC-2. The lowest acid quantities solubilized only a small amount of the uranium; most of that which was solubilized was picked up in the first resin stage and most of the remainder in the second. With 500 lb. acid or more per ton, 75% of the uranium was dissolved. At 720 lb. acid per ton, the highest quantity tested in this series, less of the uranium was sorbed in the first stage, more in the second, and the aqueous phase after the two resin stages still contained about 5% of the solubilized uranium. These results are consistent with previous studies of sorption of uranium from sulfate and phosphate solutions,[6] which showed decreasing equilibrium sorption in the presence of increasing excess of sulfate or phosphate.

The effect of the quantity of resin present in a given amount of the slurry is shown in Table 22. These tests showed essentially constant results in two resin stages at all but the lowest quantity of resin tested. The results with the lowest quantity tested are shown through four stages in Table 23. The drop-off in these four stages is appreciable but not great, while the cumulative uranium pickup reached 50% (two-thirds of the solubilized uranium; cf. Table 21). These results also indicate that the first-stage loading of 6 mg uranium per meq of resin is about the maximum loading that could be expected in a countercurrent leach with this ore and acid quantity.

Table 24 shows nearly identical results obtained with three types of commercial resins, and appreciably better results with resins in the sulfate form than in the chloride form. The latter effect is to be expected from the sorption studies previously reported,[6a] and would be less important if the ratio of chloride ion to total slurry were decreased, as in a countercurrent operation.

Resin-in-pulp sorptions in constant pH leaches of several different ore samples are shown in Table 25. The acid consumptions and total uranium extractions in these leaches were shown in Figures 27 to 39.

Table 21

RESIN-IN-PULP LEACHES: QUANTITY OF ACID

20 g(d.b.) BC-2 Ore treated with acid for 6 hours at R. T. Two resin stages, each with 8 meq Dowex-2-SO_4 for 16 hours at R. T. Initial pulp density 20%, Final, 5-10%.

Test No.	lb H_2SO_4 per ton Ore	1st Resin Stage	2nd Resin Stage	Uranium Distribution, % [a] Slurry	Filtrate	Total U Dissolved	Tailings	Uranium Balance, %[b]
LZS-17	100	27	6	1		33	67	93
-18	200	53	5	1		58	42	105
-19	300	60	3	1		63	37	95
-23	310[c]	51	4	1		56	44	109
-2	400	69	5	2		76	24	102
-20	400	56	2	1		59	41	82
-21	470[c]	53	14	1		69	31	120
-4	500	65	8	1		75	25	105
-1	575	65	10	1		75	25	108
-5	600	61	13	2		76	24	104
-6	600	65	10	1		76	24	112
-22	720[c]	39	33	4		76	24	138

(a) Percent distribution based on total Uranium found in each test.
(b) Uranium balance based on head analysis.
(c) Leaches at about 10% pulp density instead of 20%.

Table 22

RESIN-IN-PULP LEACHES: QUANTITY OF RESIN

20 g(d.b.) BC-2 ore treated with acid (600 lb. H_2SO_4 per ton) for 6 hours at R. T. Two resin stages with Dowex-2-SO_4, each for 16 hours at R. T. Initial pulp density 20%; final, about 4%.

Test No.	meq Resin per Stage	Uranium Distribution, %[a] 1st Resin Stage	2nd Resin Stage	Slurry Filtrate	Total U Dissolved	Tailings	Uranium Balance, %[b]
LZS-16[c]	0.2	15	16	-	-	-	-
-7	3.6	63	8	2	72	28	111
-15	4.0	62	15	-	78	22	95
-5	7.2	61	13	2	76	24	104
-6	7.2	65	10	1	76	24	112
-8	10.9	66	4	1	71	29	107
-9	14.5	66	4	1	71	29	107
-10	18.1	66	4	1	70	30	105

(a) Percent distribution based on total uranium found in each test.

(b) Uranium balance based on head analysis.

(c) Test No. LZS-16 calculated to basis of 20 g ore. See Table 23.

Table 23

RESIN-IN-PULP LEACHES

Resin Loading

(Test No. LZS-16)

200 g(d.b.) BC-2 ore treated with acid (600 lb H_3SO_4 per ton) for 6 hours at R.T. Four resin stages, each with 2.0 meq Dowex-1-SO_4, at pH 1.5-1.6.

Resin Stage No.	Resin Contact Time, hours	Loading mgU/meq R	Uranium Pickup, %[a] per Stage	Uranium Pickup, %[a] cumulative
1	20	5.4	15	15
2	24	6.0	16	31
3	24	4.0	11	42
4	96	3.5	10	52

(a) Percent based on head analysis.

Table 24

RESIN-IN-PULP LEACHES: COMPARISON OF RESINS

20 g(d.b.) BC-2 ore treated with acid (600 lb. H_2SO_4 per ton) for 6 hours at R. T. Two resin stages, each with 4.0 meq resin for 16 hours at R. T. Initial pulp density 20%; final, about 3%.

Test No.	Resin Used	Uranium Distribution, %[a]					Uranium Balance, %[b]
		1st Resin Stage	2nd Resin Stage	Slurry Flitrate	Total U Dissolved	Tailings	
LZS-11	IRA-400-Cl	57	14	4	75	25	91
-12	Dowex-1-Cl	57	15	5	77	23	85
-13	Dowex-1-SO_4	66	12	-	79	21	93
-14	Dowex-2-Cl	54	15	6	76	24	93
-15	Dowex-2-SO_4	62	15	-	78	22	95

(a) Percent distribution based on total uranium found in each test.

(b) Uranium balance based on head analysis.

Table 25

CONSTANT pH SULFURIC ACID LEACHES

WITH RESIN IN PULP

20 g ore (dry basis)
10% pulp density
8 meq R_2SO_4 per stage
24 hours at R.T.

				Uranium Distribution, %[a]		
				Resin		Slurry
Test No.	Ore No.	pH	Resin	Stage 1	Stage 2	Filtrate
LZS-41	BC-0B1	1.0	Dowex-1	68	14	4
-40		1.5	-1	84	4	1
-39		2.0	-1	80	3	1
-32	BC-1	1.0	-2	47	10	3
-31		1.5	-2	27	3	2
-30		2.0	-2	47	2	1
-46	BC-2	1.0	-1	77[b]		3
-21		1.5	-2	64	17	2
-45		1.5	-1	68[b]		1
-23		2.0	-2	56	5	0.4
-26	BC-3	1.0	-2	43	12	2
-25		1.5	-2	29	12	0.7
-24		2.0	-2	33	3	0.6
-29	BC-4B	1.0	-2	27	3	4
-28		1.5	-2	23	5	2
-27		2.0	-2	24	3	0.5
-35	BC-5B	1.0	-2	64	10	4
-49		1.0	-1	60[b]		3
-34		1.5	-2	53	4	1
-48		1.5	-1	57[b]		1
-33		2.0	-2	42	7	0.4
-38	BC-6B	1.0	-1	49	9	2
-37		1.5	-1	44	4	2
-36		2.0	-1	36	15	2
-44	BC-7	1.0	-1	17[b]		5
-43		1.5	-1	17[b]		2
-42		2.0	-1	15[b]		1

a) "Percent Uranium Distribution" based on total uranium found in each test.

b) First and second stage resin batches combined for analysis.

Slurry-Liquid Extraction

When acidified LZ ore slurries and organic solvents diluted with petroleum ether or kerosene were mixed as vigorously as was permissible with clarified liquors, emulsions were formed which were presumably stabilized by the finely-divided solids. When violent mixing was avoided, extractions were made in laboratory equipment without serious formation of emulsions. This was accomplished in different tests by gentle mixing in a separatory funnel, by slow stirring of two liquid layers in a beaker, or by means of a small spray column giving large drop size. The aqueous slurry was the dispersed phase in the spray column.

Most of the slurry-liquid extraction tests were made with di(2-ethylhexyl)phosphinic acid in petroleum ether, from nitric acid slurries. In one test, ore BC-3 was digested with nitric acid (1000 pounds per ton), then extracted in three stages with 0.005M di(2-ethylhexyl)phosphinic acid in petroleum ether. The volume ratio of organic to aqueous was about 1:25 in each stage, and the contact time was 10 minutes. Analyses of the organic extracts, the final aqueous solution filtered from the extracted slurry, and the solid residue indicated about 80% of the uranium dissolved, and about 85% of the dissolved uranium extracted. The assumption that uranium dissolution was completed before the first extraction stage gives apparent extraction coefficients (organic/aqueous) for the three stages of about 35, 15, and 20.

In further tests with the same reagent, one phase was sampled at intervals in order to follow the rate of the extraction. The final results of these tests are shown in Table 26 The samples taken during the progress of the extraction indicated that the extraction into the organic phase was approaching equilibrium only in Tests BC-74 and BC-76. The dissolutions of uranium from the ore were similar to those obtained in direct leaches (Figure 10), and with sufficient contact time most of the dissolved uranium was extracted, even when the volume of the organic phase was very much smaller than that of the slurry.

The methods of contacting used in the foregoing tests were probably much slower than necessary, so that the times required were not more than relatively significant. Since uranium dissolution from the slurry and extraction into the organic phase both were encouraging, the potential value of slurry-liquid extraction would appear to depend on the effectiveness of mixing possible in process equipment, together with the effective life of the extraction reagent and the diluent used.

Table 26

EXTRACTION OF URANIUM FROM ACIDIFIED LZ SLURRY

BY DI(2-ETHYLHEXYL)PHOSPHINIC ACID IN PETROLEUM ETHER

Ore. BC-3 in 20% slurry.

Extractant: 0.05M

Test No.:	BC-63	BC-64	BC-66	BC-68[a]	BC-74	BC-75	BC-76
Method of Contact:	Slow stirring in two layers					Spray column	
Acid Used:	H_2SO_4	HNO_3					
Lb/acid/ton ore.	400	400	400	600	570	800	800
Digestion Time, hrs.:	0	0	16	16	22	24	24
Digestion Temp., °C:	--	--	R.T	R.T.	R.T.	70°	70°
Vol. Ratio, org/aq:	1.5	1.5	1.5	1.5	0.7	0.10	0.14
Extraction Time, hrs.:	5	5	4.5	5	25	3.5	8
U in Extract, mg/liter:	25	60	33	50	110	230	295
% of U Dissolved:[b]	34	37	48	47	59	75	78
% of U Extracted.[b]	16	31	28	32	54	42	71

a) Kerosene used instead of petroleum ether.

b) % Dissolved and % Extracted based on total uranium found in Tests BC-63 to -74, calculated by differences in Tests BC-75 and -76.

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APPENDIX

Phosphate Extractions in Low Acid Leaches for Uranium

In addition to the phosphate extractions which were presented in discussion of the wide-range acid leaching, phosphate was determined in many of the low acid leaches of several different ores. These data are not of direct significance to a process for uranium alone, but they may furnish information of some value to other processes, and hence are summarized in the following table.

[redacted]

PHOSPHATE EXTRACTIONS

IN LOW ACID LEACHES FOR URANIUM

Test No.	Ore, ORNL No.	Acid,*	lb./Ton	Pulp Density, %	Time, hrs.	Temp., °C	Final pH	Uranium Extracted, %	Phosphate Extracted, %
BC-82-1	BC-0	N	150	20	24	R.T.	2.2	26	19
-2			300				1.8	50	38
-3			450				1.6	69	51
-4			600				1.4	79	66
LZP-34-1	BC-0B4	N	349	10	24	R.T.	2.1	38	36
-2			538				1.8	60	52
-3			727				1.7	66	64
-4			916				1.5	80	75
-5			1135				1.0	85	80
-6			1494				0.5	90	86
LZD-15-9	BC-0B3	S	785	17	20	R.T.	1.2	76	71
-11							1.4	78	70
-10					6	80	1.1	66	32
-12							1.1	72	51
LZP-40-1	BC-2	N	388	16	24	R.T.	1.7	48	30
-2			582				1.2	69	43
-3			776				0.8	64	46
-4			970				0.5	72	50
-5			1166				0.3	76	55
-6			1359				0.1	81	60
LZP-44-1	BC-2	N	385	15	6	80	1.7	45	26
-2			572				1.4	58	36
-3			766				1.1	75	51
-4			957				0.8	80	60
-5			1155				0.7	82	67
-6			1342				0.5	92	78

PHOSPHATE EXTRACTIONS

IN LOW ACID LEACHES FOR URANIUM (Cont'd.)

Test No.	Ore, ORNL No.	Acid,*	lb./Ton	Pulp Density, %	Time, hrs.	Temp., °C	Final pH	Uranium Extracted, %	Phosphate Extracted, %
LZP-43-1	BC-2	N	394	15	24	80	1.6	36	18
-2			586				1.6	59	27
-3			784				1.3	77	52
-4			980				1.2	85	66
-5			1182				1.0	89	76
6			1374				0.7	92	83
LZD-12-1	BC-2	S	310	20	6	80	1.7	43	20
-2			310		24	R.T.	1.8	54	33
LZD-15-1	BC-2	S	616	19	20	R.T.	0.9	72	40
-2			616		6	80	0	73	42
LZP-39-1	BC-7	N	36	10	24	R.T.	1.8	7	0.6
-2			94				1.4	13	3
-3			194				1.1	17	2
-4			284				0.9	21	3
-5			523				0.5	19	3
-6			783				0.4	21	3
-7			1042				0.2	24	4
-8			1539				0	27	6
LZP-35-1	BC-7	S	36	10	24	R.T.	1.9	11	0.6
-2			90				1.5	16	1
-3			176				1.2	17	2
-4			270				1.0	19	3
-5			493				0.7	21	4
-6			737				0.5	20	5
-7			985				0.4	25	6
-8			1474				0.2	22	8
LZD-20-6	BC-7	S	101	10	6	80	1.5		3
-7			304				1.0		8
-8			696				0.5		20
-9			1104				0.4		35
-10			1493				0.4		52

PHOSPHATE EXTRACTIONS

IN LOW ACID LEACHES FOR URANIUM (Cont'd.)

Test No.	Ore, ORNL No.	Acid,*	lb. / Ton	Pulp Density, %	Time, hrs.	Temp., °C	Final pH	Uranium Extracted, %	Phosphate Extracted, %
LZD-20-1	BC-7	S	100	10	6	80	2.0	14	2
-2	(Calcined)		305				1.7	51	21
-3			696				1.6	83	76
-4			1100				1.1	95	98
-5			1496				0.6		98
LZD-14-4	BC-8	S	244	10	24	R.T.	0.9	15	1
-5			567				0.6	12	1
-6			1000				0.3	13	2
LZD-14-1	BC-8	S	250	10	6	80	1.0	24	5
-2			500				0.7	39	15
-3			1000				0.5	62	31
LZD-1-3	BC-8B	S	33	10	24	R.T.	2.1	7	0.7
-2			72				1.5	14	1
-1			254				0.9	20	2
LZD-19-4	BC-8B	S	100	10	6	80	1.3	17	3
-5			304				1.0	16	7
-6			706				0.6	24	21
LZD-19-1	BC-8B	S	100	10	6	80	2.1	23	2
-2	(Calcined)		311				2.0	40	11
-3			690				1.9	84	71
LZD-13-2	BC-9	S	31	30	24	R.T.	1.6	12	2
-1			60				1.0	29	3
LZD-15-15	BC-9B	S	46	28	20	R.T.	1.8	9	1
-16			46		6	80	1.8	19	1

PHOSPHATE EXTRACTIONS

IN LOW ACID LEACHES FOR URANIUM (Cont'd.)

Test No.	Ore, ORNL No.	Acid,*	lb. / Ton	Pulp Density, %	Time, hrs.	Temp., °C	Final pH	Uranium Extracted, %	Phosphate Extracted, %
LZD-13-4	BC-10	S	31	30	24	R.T.	1.5	20	2
-3			70				1.1	43	3
LZD-15-19	BC-10B	S	109	30	20	R.T.	1.3	16	6
-20			109		6	80	1.4	24	6
LZD-13-6	BC-11	S	33	30	24	R.T.	1.5	11	0.6
-5			93				0.9	16	2
LZD-15-23	BC-11B	S	30	28	20	R.T.	1.7	10	7
-24			30		6	80	1.7	18	7
LZD-13-8	BC-12	S	24	30	24	R.T.	1.4	4	0.7
-7			61				1.1	5	2
LZD-15-27	BC-12B	S	34	24	20	R.T.	1.7	5	0.8
-28			34		6	80	1.7	6	1
LZD-13-10	BC-13	S	155	30	24	R.T.	1.5	54	42
-9			251				1.0	83	52
LZD-13-12	BC-14	S	127	30	24	R.T.	1.4	8	14
-11			175				1.0	36	17

* N = nitric acid (100%).
S = sulfuric acid (100%).