UNCLASSIFIED

HW-62086

UC-10, Chemistry - Separation Process
for Plutonium and Uranium
(TID-4500, 15th Ed.)

REPROCESSING OF LOW-ENRICHMENT URANIUM-MOLYBDENUM ALLOY FUELS

By

W. W. Schulz and E. M. Duke

Chemical Development
Chemical Research and Development Operation

September 15, 1959

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

Work performed under Contract No. AT(45-1)-1350 between
the Atomic Energy Commission and General Electric Company

Printed by/for the U. S. Atomic Energy Commission

Printed in USA. Price $1.25. Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

UNCLASSIFIED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ABSTRACT

Procedures for the dissolution of uranium-molybdenum alloy fuels to prepare feed solutions for low-acid (Redox) type solvent extraction processing are presented. Uranium-molybdenum alloys can be dissolved in boiling ferric nitrate - nitric acid solutions to higher terminal uranium concentrations and lower terminal acidities without precipitation of uranyl molybdate than in nitric acid alone. Anion resin exchange studies indicate the presence of negatively charged iron-molybdenum complex ions in the solutions. The U-Mo alloys also dissolve more rapidly in ferric nitrate - nitric acid solutions than in nitric acid alone; dissolution rate data are given. Curves delineating free acid, uranium and iron(III) concentrations within which solutions stable towards solids formation can be prepared from U - 3 w/o and - 10 w/o Mo alloys are presented.

Stability during prolonged storage of uranium-molybdenum-ferric nitrate-nitric acid solutions is discussed. Data on the oxidation of plutonium in these solutions and on further neutralization of the solutions are presented. Fission product decontamination and product recovery obtained in solvent extraction studies similating the Redox process are discussed.

TABLE OF CONTENTS

	Page
I. INTRODUCTION	4
II. SUMMARY AND CONCLUSIONS	4
III. EXPERIMENTAL	5
A. Alloy Source and Description	5
B. Decladding Procedures	6
C. Dissolution of U - Mo Alloys	6
1. Dissolution in Nitric Acid	6
2. Dissolution in HNO_3-$Fe(NO_3)_3$	8
a. Dissolution Conditions	8
b. Dissolution Rates	12
c. Off-gas Composition	15
d. Corrosivity of HNO_3-$Fe(NO_3)_3$ Solutions	16
e. Stability of Dissolver Solutions During Prolonged Storage	16
D. Redox Processing of U - Mo Alloy Dissolver Solutions	19
1. Feed Preparation	19
a. Acidity Adjustment	19
b. Plutonium Oxidation	21
2. Solvent Extraction Behavior	23
E. Chemical Flowsheet	26
IV. ACKNOWLEDGMENT	26
APPENDIX A	28
APPENDIX B	32
LITERATURE CITED	36

REPROCESSING OF LOW-ENRICHMENT URANIUM-MOLYBDENUM ALLOY FUELS

I. INTRODUCTION

Several of the power reactors currently being designed and constructed utilize low enrichment (<5 per cent U^{235}) uranium in U-Mo alloys as fuels.[1] Special techniques are required in the dissolution of these low enrichment U-Mo alloys to obtain feed solutions having relatively high uranium concentration and which are stable toward precipitation at low acidity. This report discusses studies done at the Hanford Laboratories on the dissolution of such alloy fuels to prepare feed solutions suitable for processing by the Redox process. Stability of the feed solutions during long term storage and recovery and decontamination of uranium and recovery and decontamination of uranium and plutonium during Redox processing are also discussed.

II. SUMMARY AND CONCLUSIONS

Because of the limited solubility of uranyl molybdate, dissolution of U-Mo alloy cores in nitric acid alone does not appear practical for preparation of low-acid Redox process feeds.* The maximum uranium concentration attainable without precipitation of solids at a terminal acidity of 1 M HNO_3 is about 0.4 molar for U - 3 w/o Mo alloy and considerably less for ten per cent alloy. Even lower uranium concentrations are required for stability at lower acidities.

The solubility of uranyl molybdate is increased significantly in the presence of iron(III) nitrate. At 1.0 M $Fe(NO_3)_3$, for example, stable 1 M $UO_2(NO_3)_2$ - 0.1 M HNO_3 solutions can be prepared by nitric acid dissolution of U - 3 w/o Mo alloy. Anion exchange resin studies indicate that a negatively charged, iron-molybdenum complex ion is present in such solutions. Curves delineating acid and uranium concentrations where stable solutions can be prepared from U - 3 and -10 w/o Mo alloys at various iron(III) concentrations are presented.

---

* Note in proof - This statement refers to the case where U - 3 to 10 w/o Mo alloy cores are dissolved in solutions initially about 8 molar or less in nitric acid. Under such conditions the solubility of yellow uranyl molybdate limits the maximum terminal uranium concentration

(continued on page 26)

Dissolution rates of U - 3 and -9 w/o Mo alloys in 1 - 5 M HNO_3 - 0.5 to 1.0 M $Fe(NO_3)_3$ solutions are in the range 0.7 to 5.5 g/cm^2, hr. Iron(III) catalyzes the dissolution at low acidities. The off-gas from HNO_3 - $Fe(NO_3)_3$ dissolution of U - Mo alloys is mainly oxides of nitrogen; only traces (0 to 0.2 volume per cent) of hydrogen are evolved.

Solutions obtained by HNO_3 - $Fe(NO_3)_3$ dissolution of U - Mo alloys can be stored at room temperature for long periods of time without significant deposition of solids. Stability during storage is greater at higher acidities but is decreased as the storage temperature is increased.

Oxidation of plutonium in U - Mo alloy dissolver solutions to the hexavalent state can be accomplished readily by making such solutions 0.2 M $Na_2Cr_2O_7$ and allowing them to stand two weeks at room temperature. Alternatively, oxidation can be achieved by heating one to two hours at 90-95 C after dichromate addition.

Depending on iron(III) concentration, U - Mo alloy dissolver solutions may be adjusted to -0.3 to -0.7 M HNO_3 by addition of either sodium hydroxide or dibasic aluminum nitrate at room temperature. The resulting solutions constitute acceptable Redox process feeds, but, because of hydrolysis of iron(III), are more acidic than normal Redox process feeds. Gross beta and gamma decontamination factors obtained in mixer-settler runs with U - Mo alloy solutions adjusted to about maximum acid deficiency consistent with solution stability were about five times lower than those for normal Redox feeds after one solvent extraction cycle. Decontamination decreases at higher feed acidities. Molybdenum is not extracted from U - Mo alloy solutions under Redox process conditions.

III. EXPERIMENTAL

A. Alloy Source and Description

The majority of the experimental work was conducted with U - 3 w/o Mo alloy prepared at Hanford by dilution (with ingot uranium) of a nine per cent alloy obtained from Battelle Memorial Institute. One-eighth-inch sheets of the three per cent alloy were prepared by hot rolling at 800-850 C and

water quenching. A few experiments were performed with the nine per cent alloy and also with a ten per cent alloy obtained from the Nuclear Metals Division of the National Lead Company. In all cases alloy specimens were unclad and unirradiated.

B. Decladding Procedures

Stainless steel cladding may be removed satisfactorily from U - Mo alloy cores by treatment with boiling 4 M H_2SO_4 [Sulfex process].[2] Removal of aluminum cladding with 10 w/o NaOH - 20 w/o $NaNO_3$ is a well known procedure and will suffice for decladding aluminum clad U - Mo alloy fuels. Dissolution rates of unirradiated U - 3 w/o Mo alloy in boiling 10 w/o NaOH - 20 w/o $NaNO_3$ and in 4 M H_2SO_4 are 0.15 and 0.4 mg/cm^2 hr, respectively. The dissolution rate of U - 9 w/o Mo alloy in boiling 4 M H_2SO_4 has been reported[3] to be about 0.1 mg/cm^2, hr. These data indicate that stainless steel and aluminum cladding can be removed from U - Mo alloy fuel elements without significant loss of core material.

C. Dissolution of U - Mo Alloys

As previously stated, these studies were directed toward preparation of feed solutions satisfactory for subsequent processing by the Redox process. It was desired that the dissolver solutions contain as high an uranium concentration as possible up to one molar, that the solutions be stable towards solids precipitation during long storage periods between dissolution and solvent extraction processing, that the solutions be stable at the low acidities[4,5] appropriate to Redox processing, and that the solutions be compatible with 300 series stainless steel equipment during storage after dissolution and during solvent extraction processing.

1. Dissolution in Nitric Acid

Flocculent, yellow precipitates believed to be a form of uranyl molybdate were obtained when U - 3 and - 10 w/o Mo alloys were dissolved in nitric acid. Although the composition of these yellow solids was approximately the same in all cases, changes in dissolution conditions markedly affected the amount of solids produced. Data in Table I indicate the solubility of the precipitate to be a function of both terminal acidity and terminal molybdenum concentration (or terminal uranium concentration

TABLE I

SOLIDS FORMATION IN HNO_3 DISSOLUTION OF U - Mo ALLOYS

Conditions: Specimens of U - 3 and 10 w/o Mo alloy completely dissolved at boiling temperature in HNO_3 solutions. Resulting solutions were allowed to stand 24 hours at room temperature. Solids were then isolated, washed, dried two hours at 110 C, weighed and analyzed.

Alloy, w/o Mo	Dissolvent HNO_3, M	Terminal Solution U, M	Terminal Solution HNO_3, M	Solids Weight Per Cent*	Solids Volume Per Cent**	Solids Analysis U, w/o	Solids Analysis Mo, w/o
3	4.3	0.94	0.24	8.76	32.4	43.9	33.6
3	5.3	0.98	1.18	8.01	28.4	37.8	--
3	6.3	1.00	2.29	3.07	18.3	38.3	--
3	3.2	0.75	0.50	8.87	31.1	43.4	27.2
3	4.2	0.74	1.29	7.59	13.5	--	--
3	4.7	0.75	1.84	6.06	25.0	38.4	26.5
3	5.2	0.77	2.44	3.23	11.3	43.5	29.7
3	4.7	0.67	1.86	3.43	9.3	44.0	31.1
3	5.7	0.64	2.99	0.03	0.01	--	--
10	3.3	0.66	0.46	30.1	42.7	41.3	31.9
10	4.3	0.67	1.66	27.5	65.8	44.8	32.3
10	5.3	0.69	2.39	26.9	64.8	42.2	31.8

* Calculated as weight per cent of initial alloy charge.

** Determined after allowing slurry to stand 24 hours at room temperature.

for a given alloy composition). The three per cent alloy can be dissolved to a terminal uranium concentration of about 0.4 molar without precipitation of solids provided terminal acidity is about one molar. Dissolution of ten per cent alloy to the same uranium concentration or of three per cent alloy to higher uranium concentrations requires an even higher terminal acidity to avoid solids formation.

Nitric acid solutions of U - Mo alloys appear to be slightly more stable with respect to solids formation at 25-30 C than at boiling temperature. Thus, when dissolver solutions are cooled, some neutralization of free acidity with either dibasic aluminum nitrate (diban) or with sodium hydroxide is possible. However, even at 25 C terminal acidities in the range 1 - 2 molar are required for stability at 0.5 M $UO_2(NO_3)_2$ for U - 3 w/o Mo alloy solutions. These acidities are higher than desired for Redox process feeds.

Precipitation of large amounts of solids in plant-scale processing of U - Mo alloy cores is objectionable for several reasons. The presence of solids complicates the problem of maintaining adequate nuclear safety in processing equipment. Processing time cycles would be greatly lengthened by the need to make solid-liquid separations in critically safe centrifuges. Additional processing steps and equipment would be required to recover uranium and plutonium from the solid material. In this latter connection the uranyl molybdate precipitate is soluble in 0.5 M Na_2CO_3 and can be metathesized to sodium diuranate and molybdate solutions by treatment with sodium hydroxide.

2. Dissolution in HNO_3-$Fe(NO_3)_3$ Solutions

a. Dissolution Conditions

Uranium-molybdenum alloys can be dissolved in boiling HNO_3-$Fe(NO_3)_3$ solutions to higher terminal uranium concentrations and lower terminal acidities without solids formation than in nitric acid alone. The action of iron(III) nitrate in preventing precipitation of uranyl molybdate is illustrated by the data shown in Figures 1 and 2. These data were

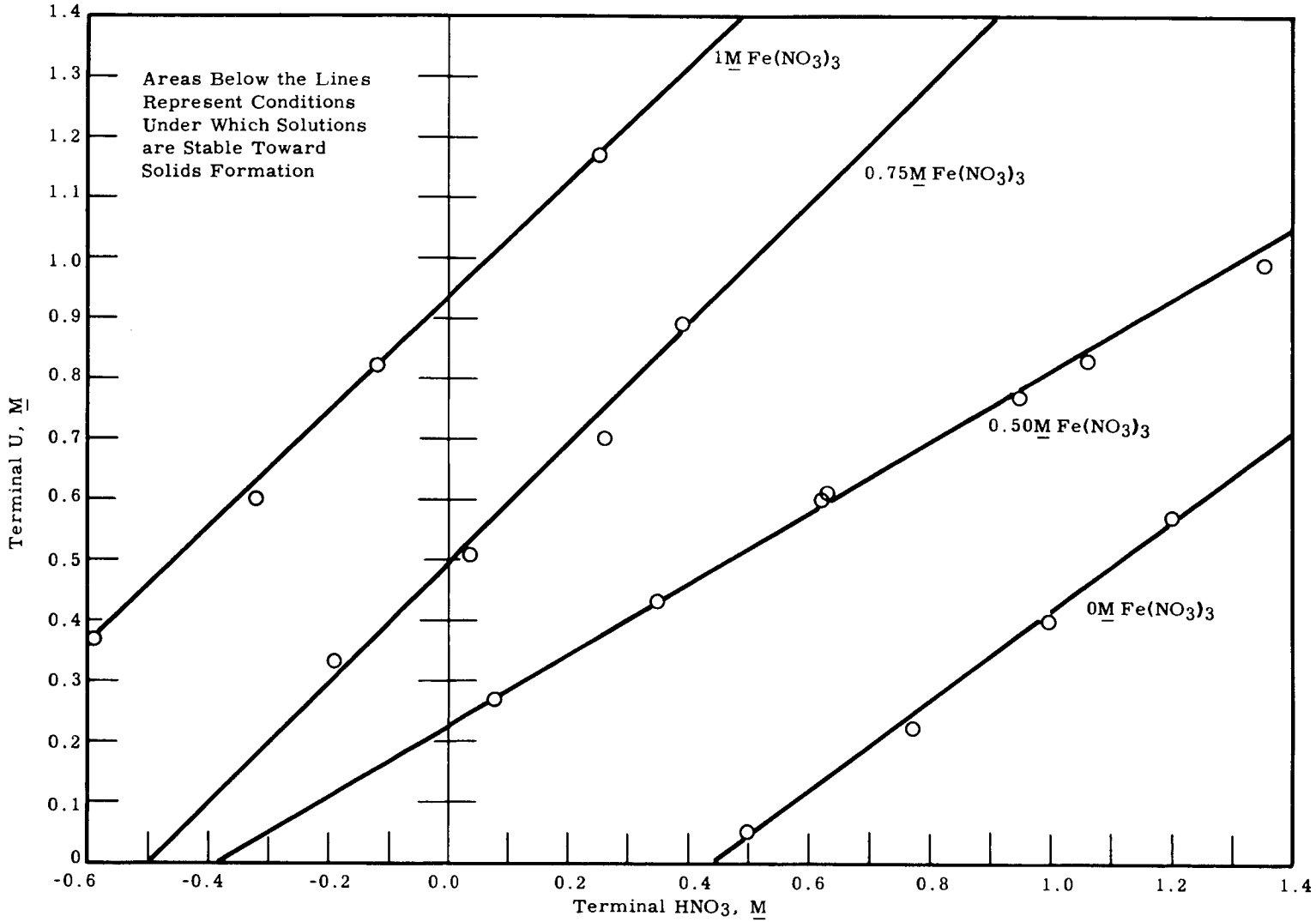

FIGURE 1

Stability Relations for Dissolution of U - 3 w/o Mo Alloy in HNO_3-$Fe(NO_3)_3$ Solutions

AEC-GE RICHLAND, WASH.

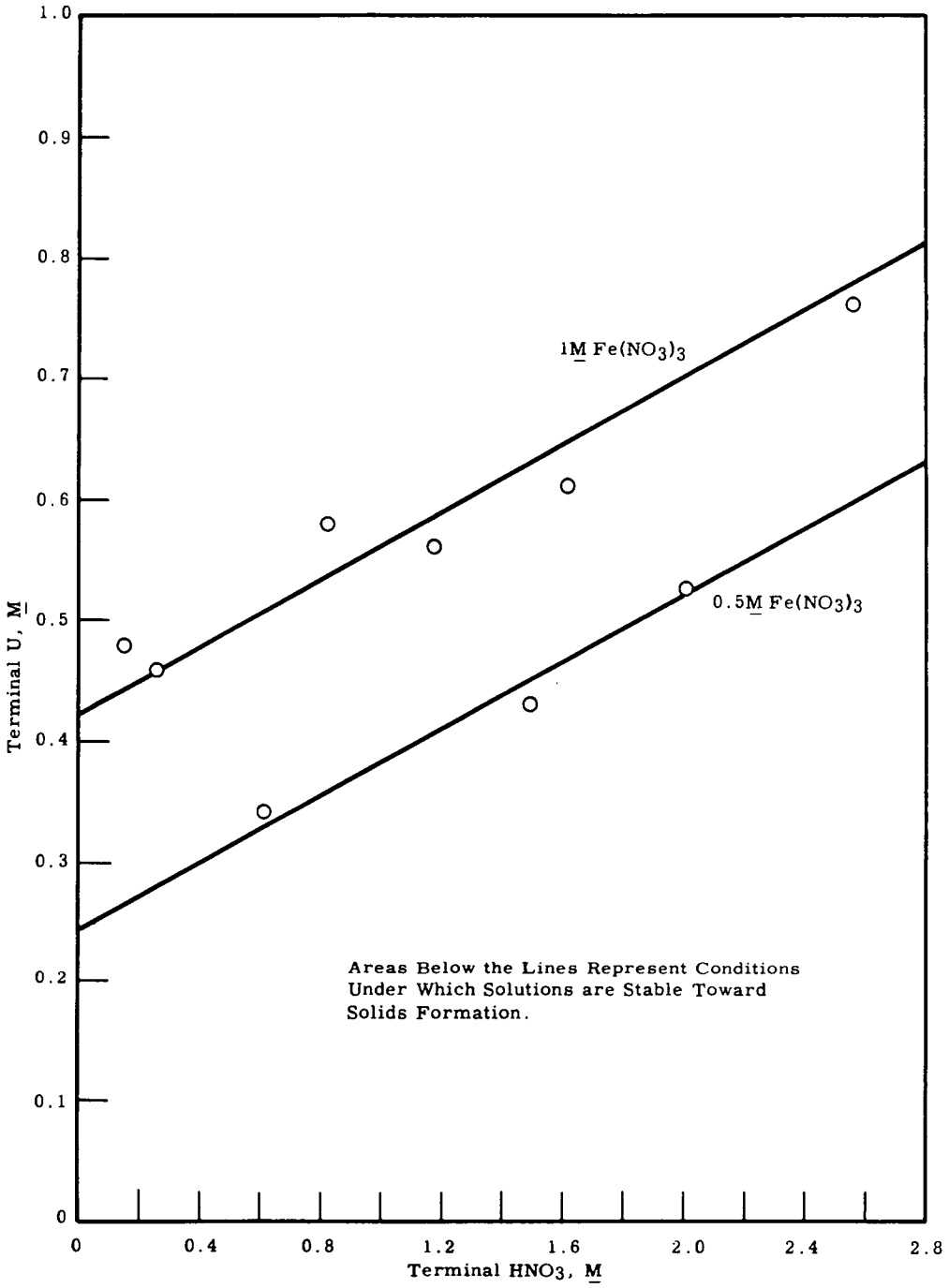

FIGURE 2

Stability Relations for Dissolution of
U - 10 w/o Mo Alloy in HNO_3-$Fe(NO_3)_3$ Solutions

obtained in experiments in which excess U - Mo alloy was dissolved in 100 ml of boiling HNO_3-$Fe(NO_3)_3$ solution until the first traces of precipitate were apparent. Uranium concentrations of the resulting solutions were determined from the weight of unreacted alloy. Acidities were determined by potentiometric titration with sodium hydroxide after addition of oxalate ion to prevent interference from hydrolysis of iron(III) and uranium(VI) ions.

The area below each of the curves in Figures 1 and 2 represents the concentration region where solutions stable with respect to precipitation of uranyl molybdate can be prepared. As is the case for dissolution in nitric acid alone the solubility of the precipitate at any particular iron(III) concentration is a function of terminal acidity and molybdenum concentration. The effect of molybdenum concentration is very apparent when data for three and ten per cent alloys are compared. The slope of the curve for the three per cent alloy at 0.5 molar iron(III), although out of line with that for the other curves for this alloy, was verified in duplicate experiments.

Some "gray zone" is associated with each curve. This arises from errors in judgment in deciding when solids were present in the boiling solutions and from errors associated with the determination of free nitric acid concentrations in the presence of large concentrations of hydrolyzable iron(III) and uranium(VI) ions. Data presented elsewhere in this report indicate, however, that the "gray zone" is not large.

The increased solubility of uranyl molybdate in the presence of iron(III) is ascribed tentatively to the formation of a soluble iron-molybdenum complex ion. Evidence to support this belief is presented in Appendix A. Russian workers have also observed that iron(III) inhibits precipitation of uranyl molybdate. These investigators report[6] that the presence of as little as 6 g/l $Fe(NO_3)_3$ is sufficient to prevent solids formation when U - 9 w/o Mo alloy is dissolved in nitric acid to yield solutions containing 5 M HNO_3 and 0.3-0.5 M $UO_2(NO_3)_2$.

Technical grade iron(III) nitrate (75 per cent solution) for use in processing U - Mo alloy cores can be purchased from Allied Chemical Corporation in 30-60 ton lots at $9.04 cwt. This material has not been

evaluated in laboratory experiments. Alternatively, satisfactory HNO_3-$Fe(NO_3)_3$ dissolvents can be prepared by dissolving 1020 steel in nitric acid. Data relative to this latter process are presented in Appendix B.

b. Dissolution Rates

Instantaneous dissolution rates of U - 3 and - 9 w/o Mo alloys in boiling HNO_3-$Fe(NO_3)_3$ solutions are presented in Figure 3. The technique used to obtain these data was similar to that described by Burns and Holm[7] and by Moore, et al.[8] Under comparable conditions three and nine per cent alloys dissolve at about the same rate. Dissolution rates of the three per cent alloy in the absence of iron(III) nitrate are factors of 5 to 20 higher than rates of ingot uranium metal at corresponding nitric acid concentrations.[8] It is evident also that iron(III) nitrate catalyzes the nitric acid dissolution of U - Mo alloys, particularly at low acidities.

The mechanism whereby dissolution rates are increased in the presence of iron(III) nitrate is not known with certainty. At low acidities iron(III) itself appears to be a catalyst. Dissolution rates of three per cent alloy in boiling 1.0 M $Fe(NO_3)_3$ and in boiling 0.28 M HNO_3, 2.37 M $NaNO_3$ are 1.14 and 0.001 g/cm^2, hr, respectively. These solutions have about the same pH (0.2) and nitrate ion concentration, yet the rate in 1.0 M $Fe(NO_3)_3$ is over 1000 times greater than that in the $NaNO_3$-HNO_3 solution.

Iron(III) apparently becomes less effective in its action as acidity increases, and increases in dissolution rates may be correlated with increases in total nitrate ion concentration (Figure 4). At nitrate ion concentrations greater than about 3.5 molar, rates for three per cent alloy in nitric acid solutions fall on the same curve as those for both the three and nine per cent alloys in HNO_3-$Fe(NO_3)_3$ solutions. Below 3.5 molar nitrate ion (a region of lower acidity for a constant iron(III) nitrate concentration) rates with iron(III) present are greater than those in nitric acid alone.

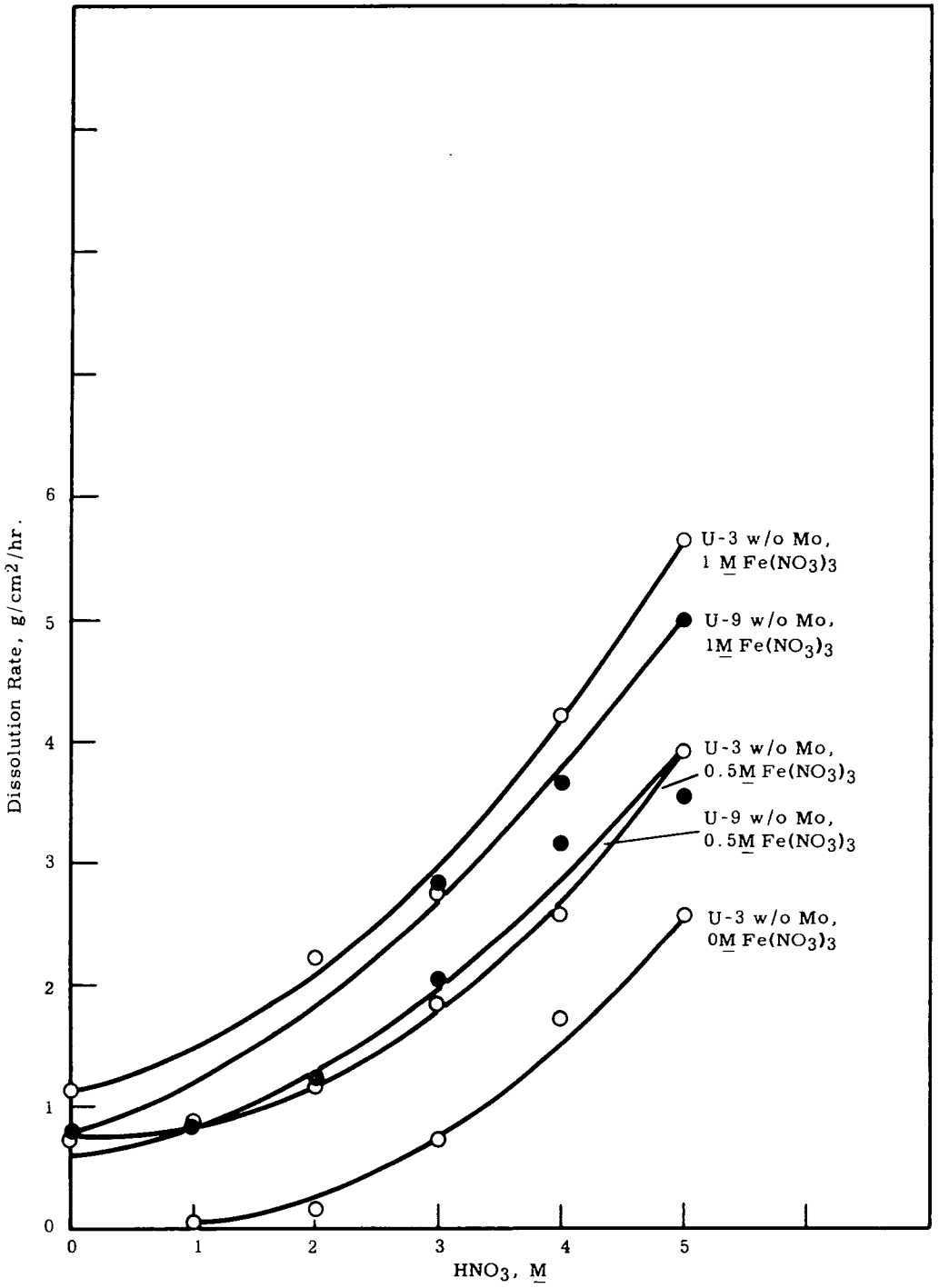

FIGURE 3

Instantaneous Dissolution Rates of U - Mo Alloys in Boiling HNO_3-$Fe(NO_3)_3$ Solutions

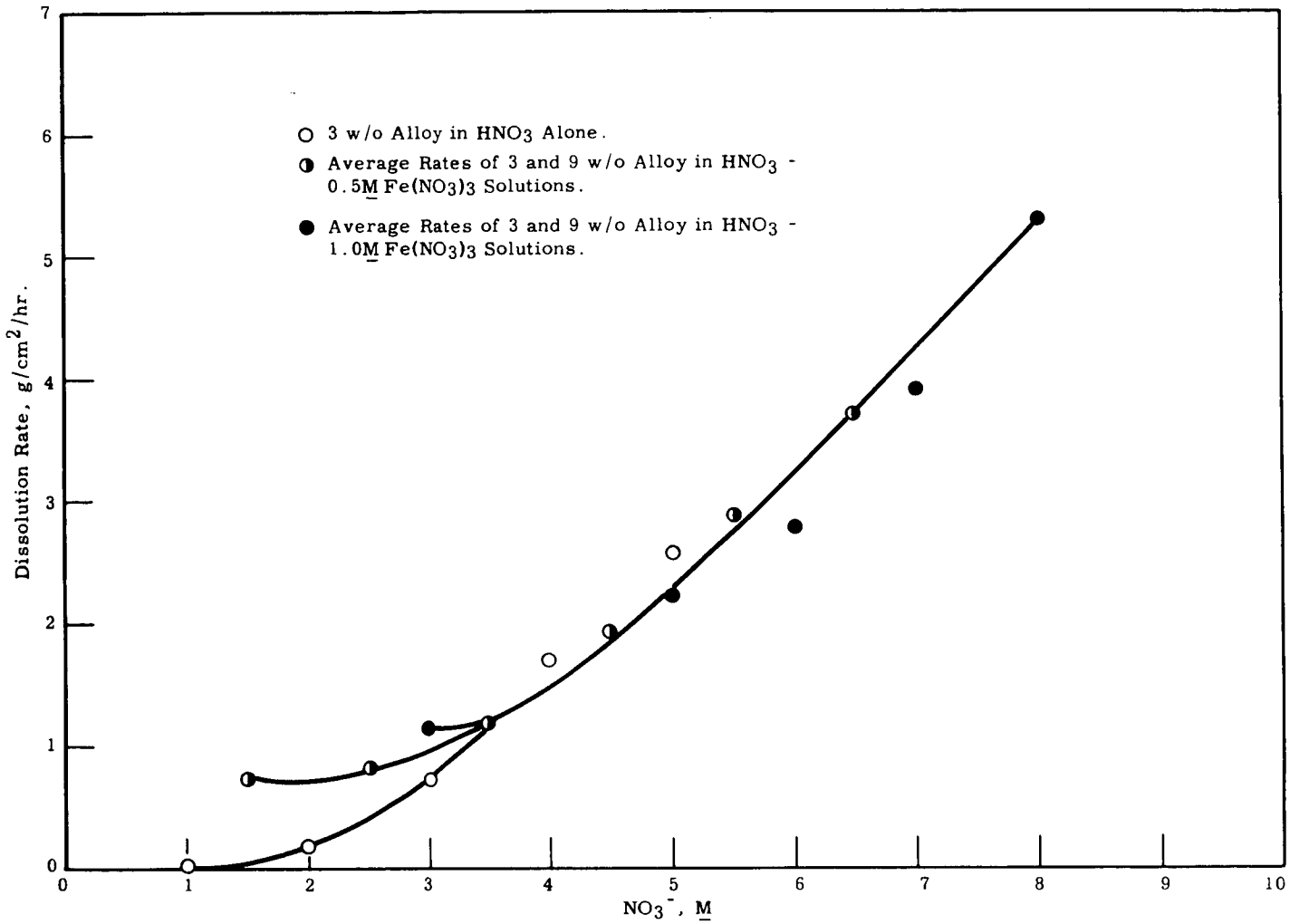

FIGURE 4

Instantaneous Dissolution Rates of U - Mo Alloys in HNO_3-$Fe(NO_3)_3$ Solutions As Function of Total Nitrate Ion Concentration

AEC-GE RICHLAND, WASH.

c. Off-gas Composition

Samples of gas evolved at various times during complete dissolution of three and nine per cent alloys in boiling HNO_3-$Fe(NO_3)_3$ solutions were collected by displacement of air in U - tubes. The three per cent alloy was dissolved in 5 M HNO_3-1 M $Fe(NO_3)_3$ to yield a solution of the composition 1.0 M $UO_2(NO_3)_2$ - 1.0 M $Fe(NO_3)_3$ - 0.25 M HNO_3. The ten per cent alloy was dissolved in 2 M HNO_3- 1 M $Fe(NO_3)_3$ to produce a solution of the composition 0.4 M $UO_2(NO_3)_2$ - 1.0 M $Fe(NO_3)_3$ - 0.25 M HNO_3. In both dissolvings samples of gas were collected 7 and 47 minutes after dissolution started. Samples were analyzed by a combination of mass spectrographic and titration methods two to three days after being collected. Gas composition at the time of analysis is given in Table II.

TABLE II

OFF-GAS COMPOSITION DURING DISSOLUTION OF U-Mo ALLOYS IN HNO_3-$Fe(NO_3)_3$ SOLUTIONS

	U - 3 w/o Mo Alloy Volume Per Cent		U - 10 w/o Mo Alloy Volume Per Cent	
Component	Sample 1	Sample 2	Sample 1	Sample 2
NO	61.6	71.7	70.0	72.0
NO_2	31.2	21.4	25.0	21.7
N_2O	0.26	0.36	0.12	0.50
H_2	0.05	0.19	*	*
H_2O	0.28	0.30	*	*
N_2	5.13	4.56	3.83	5.09
O_2	0.55	0.79	0.19	0.17
A	0.10	0.10	0.01	0.01
CO_2	0.86	0.69	0.88	0.57

* Not detected

Because of incomplete displacement by the incoming gas a slight amount of air was present in each sample. Neglecting the components of air (O_2, N_2, A, and CO_2), the off-gas is essentially oxides of nitrogen

plus traces of water vapor and hydrogen. Nitric oxide makes up the bulk of the nitrogen oxides as would be expected for the acidity range traversed during dissolution. The amounts of hydrogen evolved are below the lower limit required for formation of explosive hydrogen-air-nitrogen oxide mixtures.[9] An inert atmosphere should not be required for safe dissolution of U - Mo alloys.

d. Corrosivity of HNO_3-$Fe(NO_3)_3$ Solutions

R. Maness[10] has measured the corrosivity of HNO_3-$Fe(NO_3)_3$ to various materials of construction including 304-L stainless steel, vacuum-melted Hastelloy F and Ni-o-nel. He finds that corrosion is severe in nitric acid solutions containing 1.0 M $Fe(NO_3)_3$ and suggests that dissolution of U - Mo alloy cores in nitric acid solutions containing more than 0.7 - 0.8 M $Fe(NO_3)_3$ will require incremental addition of iron(III) nitrate and/or nitric acid.

e. Stability of U - Mo Alloy Dissolver Solutions During Prolonged Storage

In certain cases dissolver solutions prepared from U - Mo alloy fuels by dissolution in HNO-$Fe(NO_3)_3$ solutions might be stored for as long as six months before subsequent processing steps were carried out. Reasons for desiring that these solutions be stable with respect to precipitation of solids throughout the entire storage period have been mentioned earlier.

Stability data as a function of solution composition and storage time and temperature for dissolver solutions prepared from three per cent alloy are presented in Table III. Solutions were prepared by complete dissolution of alloy specimens in boiling HNO_3-$Fe(NO_3)_3$ solutions. After cooling to room temperature the solutions were centrifuged and any solids present were isolated, washed, dried and weighed. Separate portions of the centrifuged solutions were allowed to stand at room temperature and at 50 C. Solutions were filtered at regular time intervals through medium porosity sintered glass filters to determine solids content.

TABLE III

STABILITY OF U - 3 w/o Mo ALLOY DISSOLVER SOLUTIONS ON PROLONGED STORAGE

Conditions: 25 ml portions of solutions of composition indicated stored at 25 C and 50C. Solutions filtered at times indicated to determine solids content.

$UO_2(NO_3)_2$ M	$Fe(NO_3)_3$ M	HNO_3 M	Solids on Dissolution w/o *	mg Solids Deposited During 0-2 weeks 25 C	0-2 weeks 50 C	2-12 weeks 25 C	2-12 weeks 50 C	12-18 weeks 25 C	12-18 weeks 50 C	Total mg Solids Deposited 18 weeks 25 C	Total mg Solids Deposited 18 weeks 50 C
1.0	1.0	0.24	0.028	4.7	132.2	0.4	89.0	0.0	2.5	5.1	224.7
0.97	1.0	0.38	0.046	6.7	160.9	0.2	48.4	0.0	0.4	6.9	169.7
1.03	1.0	0.62	0.00	0.6	8.5	0.3	0.2	0.0	0.6	0.9	9.3
1.05	1.0	0.95	0.006	2.9	9.6	0.6	0.8	0.0	0.8	3.5	11.2
				0-1 weeks 25 C	0-1 weeks 50 C	1-3 weeks 25 C	1-3 weeks 50 C	3-6 weeks 25 C	3-6 weeks 50 C	Total Solids - 6 weeks 25 C	Total Solids - 6 weeks 50 C
** 1.03	0.75	0.44	0.037	3.0	88.8	0.0	20.6	0.0	18.0	3.0	127.4
1.05	0.75	0.84	0.00	2.4	12.1	0.0	5.7	0.0	5.7	2.4	23.5
1.05	0.75	1.22	0.00	1.5	2.8	0.0	0.1	0.0	0.0	1.5	2.9
1.04	0.75	1.68	0.00	1.7	4.7	0.0	0.0	0.4	0.5	2.1	5.2
0.83	0.75	0.30	0.00	1.0	14.2	0.0	0.2	0.0	0.0	1.0	14.4
0.83	0.75	0.84	0.00	1.0	0.4	0.0	0.0	0.0	0.0	1.0	0.4
0.82	0.75	1.10	0.00	1.0	1.7	0.0	0.4	0.0	0.0	1.0	2.1
0.83	0.75	1.34	0.00	0.0	2.4	0.0	1.6	0.0	0.0	0.0	4.0
0.84	0.50	0.80	0.45	0.0	9.1	0.0	1.5	0.0	97.5	0.0	108.1
0.83	0.50	1.03	0.00	0.6	66.1	0.0	11.7	0.0	4.9	0.6	82.7
0.83	0.50	1.60	0.00	0.7	1.1	0.0	0.0	0.0	0.2	0.7	1.3
0.83	0.50	1.75	0.00	0.0	3.9	0.0	0.1	0.0	0.0	0.0	4.0

* Calculated as weight per cent initial alloy charge.

** Data from this experiment used in calculations discussed in text, page 18.

The stability curves in Figure 1 were used to select dissolution conditions for these experiments. With one exception the amount of solids produced during dissolution was less than 0.05 weight per cent of the initial alloy charge. The validity of the stability curves is thus established.

Uranium-molybdenum alloy dissolver solutions are considerably more stable at 25 C than at 50 C on prolonged storage. Of the total amount of solids deposited at the lower temperature almost all deposited prior to the first filtration. The solids deposited during the initial storage period at 25 C are thought to represent finely divided material present at the termination of dissolution and not removed by centrifugation prior to storage. Indeed, solutions filtered prior to storage at 25 C contained almost no solids after storing one to two weeks. Although again greater in the initial storage period, some deposition of solids occurred in most cases during each of the storage periods at 50 C. Evidently the iron-molybdenum complex is less stable at higher temperatures.

Data in Table III also show stability on prolonged storage to be greater at higher dissolver solution acidities. Thus solids deposition could be eliminated or at least reduced by storage at acidities greater than those required for stability during dissolution. This procedure would not appear to be required for solutions stored at 25 C, however. For example, calculations based on the data for the solution denoted with a double asterik in Table III show that about 0.7 pound of solids would be produced during dissolution of one ton of U - 3 w/o Mo alloy. An additional pound of solids would deposit during storage of the resulting dissolver solution at room temperature. Assuming the solids to contain 42 weight per cent uranium (Table I) the total amount of solids produced would correspond to an uranium loss of only about 0.04 per cent.

Some evidence was obtained to indicate that stability during storage at both 25 and 50 C was increased when solutions were made 0.2 $\underline{M}$ $Na_2Cr_2O_7$ prior to storage. The presence of sodium dichromate during storage serves also to oxidize plutonium to the hexavalent state, see page 22.

D. Redox Processing of U - Mo Alloy Dissolver Solutions

1. Feed Preparation

a. Acidity Adjustment

Depending on dissolution and storage conditions, solutions obtained by $Fe(NO_3)_3$-HNO_3 dissolution of U - Mo alloys may be expected to contain 0.2 to 1.0 M HNO_3. Preparation of desired low-acid Redox process feeds from these solutions requires further adjustment of acidity.

In preliminary experiments U - Mo alloy solutions were adjusted to various acidities by addition of either sodium hydroxide or diban at room temperature. Depending on iron(III) concentration, acidities in the range -0.4 to -0.7 M HNO_3 could be attained before precipitation of reddish-brown solids occurred. Analysis of the solid material indicated it to be iron(III) hydroxide rather than uranyl molybdate or sodium diuranate.

Table IV lists the results of further neutralization studies. Solution compositions (except for the absence of molybdenum) were selected as typical of those that might be obtained as Redox feeds from U - Mo alloy solutions. Solutions were prepared from stock solutions of reagent grade iron(III) nitrate, sodium dichromate, aluminum nitrate and uranyl nitrate. Sodium hydroxide was added to adjust solutions to desired acidities. Solutions were allowed to stand seven days at room temperature and inspected each day for clarity; those which contained no solid material after seven days were considered stable. In all cases where solids were formed, these were reddish-brown in color and were presumed to be iron(III) hydroxide.

The acid deficiency to which the solutions listed in Table IV could be adjusted without solids formation was determined primarily by iron(III) concentrations. For example, at 1.0 M $Fe(NO_3)_3$ stable solutions were obtained at -0.6 to -0.7 M HNO_3 irrespective of aluminum, uranium, and total nitrate ion concentrations. Similar behavior but at lower acid deficiencies was noted at 0.5 and 0.75 M $Fe(NO_3)_3$.

TABLE IV

STABILITY OF NEUTRALIZED, SYNTHETIC U-Mo ALLOY SOLUTIONS

Composition[1]				Stable[2]		Unstable[4]	
$UO_2(NO_3)_2$ M	$Al(NO_3)_3$ M	$Fe(NO_3)_3$ M	NO_3^- M	HNO_3 M	pH[3]	HNO_3 M	pH[3]
1.0	0.50	1.0	6.50	-0.6	<0	-0.7	0.2
1.0	0.50	0.75	5.75	-0.5	<0	-0.6	<0
1.0	0.50	0.50	5.00	-0.4	0.15	-0.5	--
1.0	0.25	1.0	5.75	-0.6	<0	-0.7	<0
1.0	0.25	0.75	5.00	-0.5	0.08	-0.6	0.29
1.0	0.25	0.50	4.25	-0.3	0.05	-0.4	--
0.75	0.50	1.0	6.00	-0.6	<0	-0.7	<0
0.75	0.50	0.75	5.25	-0.5	0.01	-0.6	0.19
0.75	0.50	0.50	4.50	-0.35	0.30	-0.46	--
0.75	0.25	1.0	5.25	-0.7	0.05	-0.8	0.20
0.75	0.25	0.75	4.50	-0.5	0.30	-0.6	--
0.75	0.25	0.50	3.75	-0.3	0.38	-0.4	0.50
0.50	0.50	1.0	5.50	-0.6	<0	-0.7	0.05
0.50	0.50	0.75	4.75	-0.5	0.30	-0.6	--
0.50	0.50	0.50	4.00	-0.3	0.35	-0.4	--
0.50	0.25	1.0	4.75	-0.7	0.20	-0.8	0.30
0.50	0.25	0.75	4.00	-0.4	0.20	-0.5	--
0.50	0.25	0.50	3.25	-0.3	0.55	-0.4	--

(1) All solutions were 0.1 M $Na_2Cr_2O_7$ also.

(2) Solutions were free from solids after standing seven days at room temperature.

(3) pH measured with Beckman Model H pH Meter with machine buffered both at pH 1 and pH 4.

(4) Solutions contained solids after standing less than seven days at room temperature.

Several additional experiments with U - Mo alloy solutions were made to check the stability data listed in Table IV. Agreement was excellent in all cases. It is believed, therefore, that the data given in Table IV can be used for predicting the stability of neutralized U - Mo alloy solutions.

Stability data in Table IV are also valid for the case where diban rather than sodium hydroxide is used to neutralize acid. Diban is preferable to sodium hydroxide in that neutralization of acid and addition of salting strength for the extraction operation are accomplished simultaneously. Localized precipitation of iron and uranium is also avoided when diban is used.

The pH of neutralized, stable U - Mo alloy solutions range from less than zero to about 0. 5 (see Table IV). In contrast, normal first cycle Redox feed solutions are made -0. 2 M HNO_3 and have a pH of about 1. 0. Hence, even though U - Mo alloy solutions can be made -0. 3 to -0. 7 M HNO_3, hydrolysis of iron(III) makes them more acidic than normal Redox feeds. This higher acidity results in decreased fission product decontamination in subsequent solvent extraction (see page 24).

b. Plutonium Oxidation

Plutonium in U - Mo alloy dissolver solutions will be present principally (> 90 per cent) as plutonium(IV). This was demonstrated in experiments in which Fe HNO_3-$Fe(NO_3)_3$ dissolvents were spiked with plutonium(IV) prior to dissolution of U - Mo alloy specimens. The plutonium(IV) was not oxidized during the dissolving. Oxidation of plutonium in these solutions to plutonium(VI) will be required for first cycle extraction in the Redox process.

Oxidation of plutonium in U - Mo alloy dissolver solutions may be achieved conveniently by making such solutions 0. 2 M $Na_2Cr_2O_7$ prior to storage in stainless steel tanks. Data in Table V for solutions of various compositions derived from both three and ten per cent alloy indicate 99. 8 to 99. 9 per cent oxidation after two weeks storage at room temperature.

Alternatively, U - Mo alloy solutions may be stored without prior addition of sodium dichromate. In this case, rapid oxidation of plutonium prior to processing can be accomplished by making feed solutions 0. 1 to 0. 2 M $Na_2Cr_2O_7$ and heating two to four hours at temperatures in the range 95 C to boiling. In a typical experiment a portion of U - 3 w/o Mo alloy dissolver solution of the composition 0. 95 M $UO_2(NO_3)_2$ - 1. 08 M $Fe(NO_3)_3$ - 0. 16 M HNO_3 was made 0. 5 g/l Pu(IV) and 0. 2 M $Na_2Cr_2O_7$ and

TABLE V

OXIDATION OF PLUTONIUM IN U - Mo ALLOY DISSOLVER SOLUTIONS

Conditions: Portions of U - 3 and - 10 w/o Mo alloy dissolver solutions made 0.1 g/l Pu(IV) and 0.2 M $Na_2Cr_2O_7$ and allowed to stand two weeks at 25 to 29 C.

Alloy w/o Mo	Solution Composition $UO_2(NO_3)_2$ M	$Fe(NO_3)_3$ M	HNO_3 M	Per Cent Pu(VI)
3	0.98	0.73	1.30	99.8
3	0.97	0.73	1.00	99.8
3	0.97	0.73	0.77	99.8
3	0.77	0.73	0.95	99.9
3	0.75	0.71	0.70	99.8
3	0.76	0.72	0.30	99.9
10	0.38	0.72	1.86	99.9
10	0.38	0.72	1.11	99.9
10	0.31	0.77	0.65	99.9
10	0.28	0.71	0.52	99.9

heated two hours at 95 C. After 30, 60 and 120 minutes 98.9, 99.9 and 99.9 per cent, respectively, of the plutonium was present as plutonium(VI).

Acidity during plutonium oxidation at elevated temperatures should be kept as low as possible to minimize corrosion of stainless steel process equipment. However, acidity during the oxidation step should be higher than that which might be desired or attained at room temperature for feeds to the solvent extraction battery (See page 20). If not, precipitation of uranyl molybdate may occur when solutions are heated at 95 C. The minimum acidity possible for stability during plutonium oxidation appears to be determined primarily by the iron to molybdenum mole ratio. Solutions derived from three per cent alloy in which the Fe/Mo mole ratio was 12

or greater have been heated at -0.4 M HNO_3 for two hours at 95 C without precipitation of solids. Solutions from ten per cent alloy in which the Fe/Mo mole ratio was 9 or higher could be heated at acidities as low as -0.2 M HNO_3 without solids formation. In plant scale operations oxidations at 0.0 M HNO_3 might be preferred to insure a safety factor. Data obtained by Maness[10] indicate corrosion rates of stainless steel 304 L during plutonium oxidation to be acceptably low at this acidity.

2. Solvent Extraction Behavior

Continuous countercurrent solvent extraction studies with U - Mo alloy dissolver solutions were made with a 12-stage miniature mixer-settler of the type described by Alter, et al.[11] Experiments were designed to evaluate effects of feed composition on fission product decontamination, uranium and plutonium recovery, and molybdenum extraction. Results with feeds prepared from U - Mo alloy dissolver solutions were compared with those for standard Redox process feeds.

Uranium-molybdenum dissolver solutions obtained by complete dissolution of alloy specimens in HNO_3 - $Fe(NO_3)_3$ solutions were neutralized to about zero molar acid by addition of diban, made 0.2 g/l Pu(IV), and spiked with standard Redox process dissolver solution. The solutions were then made 0.2 M $Na_2Cr_2O_7$ and heated two hours at 90-95 C to oxidize plutonium to the hexavalent state. After cooling to room temperature the solutions were adjusted to final feed acidity by addition of diban. Standard Redox process feeds of the composition suggested by Schneider[12] for use with low-enriched material were prepared in a similar fashion from reagent grade chemicals.

Solvent extraction runs were of three hours duration; end stream analyses indicated equilibrium was attained after about one hour. Waste losses and decontamination factors were calculated from analyses of effluent streams produced in the third hour of operation. Molybdenum in organic effuents was determined spectroscopically. Standard wet chemical and radiochemical procedures were used in all other analyses. Detailed run data are given in Table VI. Operating conditions for these runs were

TABLE VI

SOLVENT EXTRACTION OF U - Mo ALLOY SOLUTIONS - MIXER-SETTLER RUNS

Run No.	Feed Composition(1)					Org. Product		Decontamination Factors				Waste losses, Per Cent	
	HNO_3 M	$UO_2(NO_3)_2$ M	$Al(NO_3)_3$ M	$Fe(NO_3)_3$ M	Mo M	HNO_3 M	Mo ppm U(2)	Gross Gamma	Gross Beta	Zr-Nb	Ru	U	Pu
1(3)	-0.2	0.75	1.3	0.0	0.0	0.03	0	1320	1690	> 3000	140	0.080	0.17
2	0.0	0.80	0.36	0.89	0.061	0.19	5	29	41	91	5	0.019	0.013
3	-0.3	0.77	0.30	0.85	0.059	0.15	0	45	115	1800	9	0.18	0.14
4	-0.5	0.78	0.35	0.89	0.060	0.05	0	190	260	> 3000	35	0.40	0.38
5	-0.5	0.75	0.61	0.83	0.058	0.06	<5	290	370	> 3000	20	0.018	0.063
6(4)	-0.3	0.40	0.80	0.60	0.11	0.05	0	125	165	1540	20	0.036	0.52

(1) All feeds also 0.2 M $Na_2Cr_2O_7$, 0.2 g/l Pu, ca. 6×10^{10} c/m/gal gross beta, ca. $3 \times 10^5 \mu c$/gal gross gamma.

(2) Parts per million parts of uranium.

(3) Standard Redox process feeds; data from four runs averaged.

(4) This run with solution prepared from U - 10 w/o Mo alloy; all others with three per cent alloy solution.

AEC-GE RICHLAND, WASH.

as follows:

Extraction Stages	- 7
Scrub Stages	- 5
Extract	- Redox plant undistilled, neutral hexone
Scrub Composiiton	- 1.3 M $Al(NO_3)_3$ - 0.01 M $Na_2Cr_2O_7$ - (-0.2) M HNO_3
Flow Ratios Feed/Scrub/Extractant	- 1.0/0.22/2.1

The following conclusions were drawn from the mixer-settler run data:

(a) At about the maximum acid-deficiency consistent with feed stability (Runs 4 and 5) gross gamma and beta decontamination factors for U - Mo alloy solutions were lower than those for standard feeds by factors of about six and five, respectively. Radioruthenium decontamination limited over-all decontamination at this acidity. At higher acidities increased extraction of zirconium and niobium, as well as of ruthenium, resulted in decreased decontamination.

(b) In most cases plutonium and uranium recoveries from U - Mo alloy solutions were comparable to those obtained with standard feeds.

(c) Molybdenum is not extracted from U - Mo alloy solutions under Redox process conditions.

Other observations made during these runs and listed without additional comment included the following:

(a) Operation stability was excellent throughout. Precipitation of solids during mixer-settler operation or in feed solutions did not occur in any run. Aqueous raffinates from feeds -0.3 molar or higher in nitric acid were stable at least 24 hours at room temperature.

(b) Extraction or entrainment of dichromate ion, sometimes observed when feed acidity is high, did not occur in these runs.

(c) In all cases oxidation of plutonium in feed solutions was 99.0 - 99.9 per cent complete after two hours heating at 90-95 C.

E. Chemical Flowsheet

A chemical flowsheet for the preparation of Redox process feedstock from U - 3 w/o Mo alloy is shown in Figure 5. For dissolution with an up-draft condenser it was assumed that 4.3 moles of nitric acid were required to dissolve one mole of uranium. Less nitric acid would be required, of course, with a down-draft condenser. Appropriate adjustments in terminal uranium and/or terminal acidity would be required also for dissolution of alloys of higher or lower molybdenum content.

IV. ACKNOWLDGEMENT

Grateful acknowledgement is made to D. G. Bouse, M. M. Darby, and L. C. Neil for their cooperation and assistance in obtaining the experimental data.

(contd. from page 4) attainable without precipitation of solids. However, results obtained recently at both ORNL and at the Hanford Laboratories have demonstrated that a large fraction of the molybdenum content of U - 3 to 10 w/o Mo alloys is precipitated as a white solid when such alloys are dissolved in concentrated (12-15 M) nitric acid solutions. This solid has tentatively been identified as hydrated MoO_3 and after washing contains less than 0.1 w/o U. Preliminary results indicate that the solutions resulting from dissolution of U - 3 w/o Mo alloy in concentrated nitric acid can be adjusted to 0 to - 0.2 M HNO_3 without precipitation of uranyl molybdate. This method of reprocessing U - Mo alloy cores requires a solid-liquid separation step but otherwise appears feasible as a means of preparing low-acid Redox feeds by dissolution in nitric acid alone.

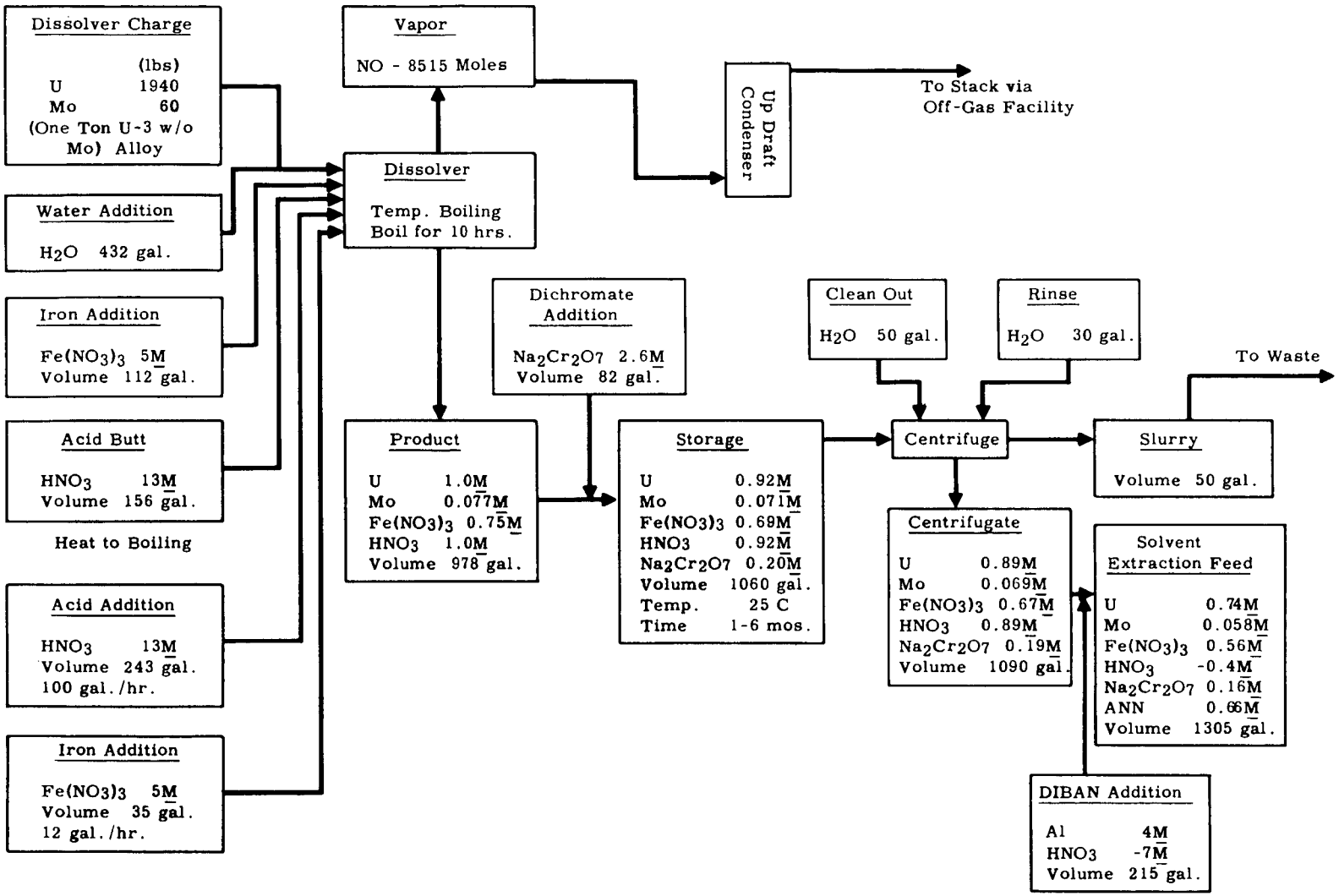

FIGURE 5

Chemical Flowsheet for Preparation of Redox Process Feed from U - 3 w/o Mo Alloy Fuel

AEC-GE RICHLAND, WASH.

APPENDIX A

MOLYBDENUM CHEMISTRY IN $Fe(NO_3)_3$-HNO_3-$UO_2(NO_3)_2$ SYSTEMS

1. Qualitative Observations

Several experiments of a qualitative nature were performed to elucidate chemistry involved in the reaction between iron(III) and molybdate ions. These included:

a. Demonstration that the precipitate obtained when iron(III) nitrate is added to a water solution of ammonium paramolybdate is soluble in excess iron(III) nitrate or chloride solution.

b. Demonstration that solutions containing as much as 0.15 molar molybdenum could be prepared by dissolution of molybdenum metal in boiling 1 M $Fe(NO_3)_3$.

c. Demonstration that solutions obtained as in (b) give a blue color with a glacial acetic acid solution of benzidine. Formation of the blue color is characteristic of molybdenum contained in a heteropoly acid[13] and does not occur with acid solutions containing molybdate ions.

These observations led to the hypothesis that a negatively charged iron-molybdenum complex ion is formed when molybdenum metal or U - Mo alloys are dissolved in $Fe(NO_3)_3$ - HNO_3 solutions. In this connection, some 50 years ago Rosenheim[14] and others[15, 16] prepared compounds which Rosenheim formulated as $R_9[Fe(MoO_4)_6]$ where R is potassium or ammonium. Baker and co-workers[17, 18] have recently restudied 6-molybdo heteropoly anions containing tervalent aluminum, chormium, iron, and cobalt as central atoms. Results obtained by these latter workers suggest that $[XO_6Mo_6O_{15}]^{3-}$ where XO_6 is an octahedral group containing the central atom is a reasonable formula for these anions rather than $[X^{+3}(MoO_4)_6]^{9-}$ given in older notation.

2. Anion Resin Experiments

Anion exchange resin studies were made to test for the presence of the postulated complex ion. The experimental procedure was as follows: Five or ten g portions of air-dried, 50-100 mesh, Dowex 1, X-2 (2 per cent cross linked) anion resin in the nitrate form were contacted ten minutes at room temperature with five to ten ml of solutions prepared by dissolving either molybdenum metal or U - 3 w/o Mo alloy in $Fe(NO_3)_3$ - HNO_3 solutions. After equilibration the mixture was centrifuged and the supernatant liquid removed. The resin was then batch washed 10 to 12 times with successive 20 ml portions of distilled water until iron(III) could not be detected in the wash liquid (KCNS test). The resin was then contacted five to seven times with successive 10 ml portions of 4 M HNO_3 to elute any adsorbed iron and molybdenum. Iron and molybdenum concentrations of each of the successive elution solutions were determined spectrophotometrically. The o-phenanthroline procedure[19] was used to determine iron. The thiocyanate-stannous chloride procedure outlined by Sandell[20] was used to determine molybdenum.

Duplicate experiments (Runs 2 and 3) were performed with a solution obtained by dissolving 0.72 g of molybdenum metal (200 mesh powder, 99.8 per cent pure, from Fisher Scientific Co.) in 49 ml of boiling 1 M $Fe(NO_3)_3$. The molybdenum concentration of the final solution as determined by the CNS - $SnCl_2$ method was 0.146 molar. One experiment (Run 4) was performed with a solution of the composition 0.16 M HNO_3 - 0.95 M $UO_2(NO_3)_2$ - 1.05 M $Fe(NO_3)_3$ - 0.0722 M Mo (0.0744 M Mo calculated) prepared by complete dissolution of an U - 3 w/o Mo alloy specimen in boiling 1.0 M $Fe(NO_3)_3$ - 4.1 M HNO_3 solution. A control experiment (Run 1) with 1.0 M $Fe(NO_3)_3$ was also performed. Analytical data for these experiments are shown in Table VII.

In the absence of molybdenum (Run 1) only very small amounts of iron were retained on the washed resin. This result is the expected one since one would predict normally only very little, if any, adsorption of

TABLE VII

ANION RESIN EXPERIMENTS WITH Mo $Fe(NO_3)_3$-HNO_3-$UO_2(NO_3)_2$ SOLUTIONS

Conditions: See text.

Solution Description	Run 1 Vol ml	Run 1 mg Fe	Run 2 Vol ml	Run 2 mg Fe	Run 2 mg Mo	Run 3 Vol ml	Run 3 mg Fe	Run 3 mg Mo	Run 4* Vol ml	Run 4* mg Fe	Run 4* mg Mo
Solution before Adsorption	--	--	10.0	--	140.	10.0	--	140.	10.0	--	71.5
Solution after Adsorption	--	--	10.0	--	123.	10.0	--	119.	10.0	--	54.5
First Elution Solution	13.5	0.027	13.4	1.09	8.79	13.1	1.19	10.01	16.9	0.15	5.81
Second Elution Solution	10.0	0.002	9.3	0.31	3.70	9.4	0.28	4.29	10.2	0.05	1.85
Third Elution Solution	9.2	0.002	9.3	0.14	2.16	10.0	0.10	2.58	9.6	0.03	1.14
Fourth Elution Solution	9.8	0.002	10.0	0.06	1.33	9.8	0.04	1.35	9.8	0.01	0.82
Fifth Elution Solution	9.6	0.002	9.5	0.02	0.71	9.9	0.02	0.72	9.8	<0.03	0.57
Sixth Elution Solution	--	--	--	--	--	10.1	0.03	0.42	10.0	<0.03	0.47
Seventh Elution Solution	--	--	--	--	--	10.1	0.003	0.23	10.0	<0.03	0.32
Total mg Fe and Mo in Elutions 1 - 7	0.035			1.62	16.69		1.66	19.60		0.24	10.98
Millimoles Fe and Mo in Elutions 1 - 7	--			0.0290	0.174		0.0297	0.204		0.0043	0.114
Mole Ratio Mo/Fe in Elutions 1 - 7	--			6.00			6.9			26.5	

* 5 g resin used in this run; 10 g resin used in all other runs.

positively charged iron(III) on an anion resin. Conversely and significantly, appreciable amounts of iron were eluted from the washed resin after contact of the resin with solutions containing both iron and molybdenum. This latter result is considered important evidence for the existence of the hypothesized complex ion.

The Mo/Fe mole ratio of about six in the composite elution solutions in Runs 2 and 3 together with the work of Baker cited earlier suggest that the ionic species adsorbed on the resin and possibly that existing in solution is $[FeO_6Mo_6O_{15}]^{-3}$. The agreement between the results of Runs 2 and 3 is remarkable in view of the low distribution coefficient of the complex to the resin in the presence of so much competing nitrate ion and of the difficulties experienced in analyzing for low concentrations of iron and molybdenum.

The Mo/Fe mole ratio in Run 4 was considerably higher than that found in Runs 2 and 3. The significance of the higher ratio is not clear. It may be that part of the molybdenum adsorbed on the resin was associated with uranium in some manner. Elution solutions were not analyzed for uranium. The results do indicate, however, the presence of a negatively charged, iron-molybdenum complex ion in solutions produced by HNO_3 - $Fe(NO_3)_3$ dissolutions of U - Mo alloys.

APPENDIX B

PREPARATION OF HNO_3 - $Fe(NO_3)_3$ DISSOLVENTS BY DISSOLUTION OF 1020 STEEL IN HNO_3

1. Dissolution Rates of 1020 Steel in Nitric Acid

Coupons of 1020 steel of the nominal composition 99.12 to 99.43 w/o Fe - 0.18 to 0.23 w/o C - 0.30 to 0.50 w/o Mn - 0.04 w/o P - 0.05 w/o S were used to determine instantaneous dissolution rates in boiling HNO_3 - $Fe(NO_3)_3$ solutions. The procedure used was similar to that used for determining dissolution rates of U - Mo alloys.[7,8] Results are shown in Figure 6.

In the absence of dissolved iron, maximum dissolution rate occurs at about 8 M HNO_3, the steel apparently passivates at higher acidities. Dissolution rates fall off as the iron(III) concentration builds up. However, even at 1.0 M $Fe(NO_3)_3$ the rate in 2 M HNO_3 is greater than 2 g/cm^2 hr. Complete dissolution of large amounts of 1020 steel thus can be accomplished in very short time cycles. Indeed, the reaction is so vigorous that some form of control (low dissolution temperature or incremental acid addition) may be required to limit the off-gas evolution rate.

Investigations to specify an optimum material of construction for a dissolver vessel have not been made. Titanium certainly should suffice, but less expensive materials probably could be found. Plastic lined vessels might be satisfactory at low dissolution temperatures.

2. Off-Gas Composition

Samples of the gas evolved during nitric acid dissolution of 1020 steel were collected for two different sets of dissolving conditions. In one case a 13 g coupon of 1020 steel was completely dissolved in boiling 9 M HNO_3 to yield a solution of the composition 1 M $Fe(NO_3)_3$ - 5 M HNO_3. Dissolution was complete in 15 minutes without application of heat. Two samples, (1) and (2), were collected. In the other experiment a

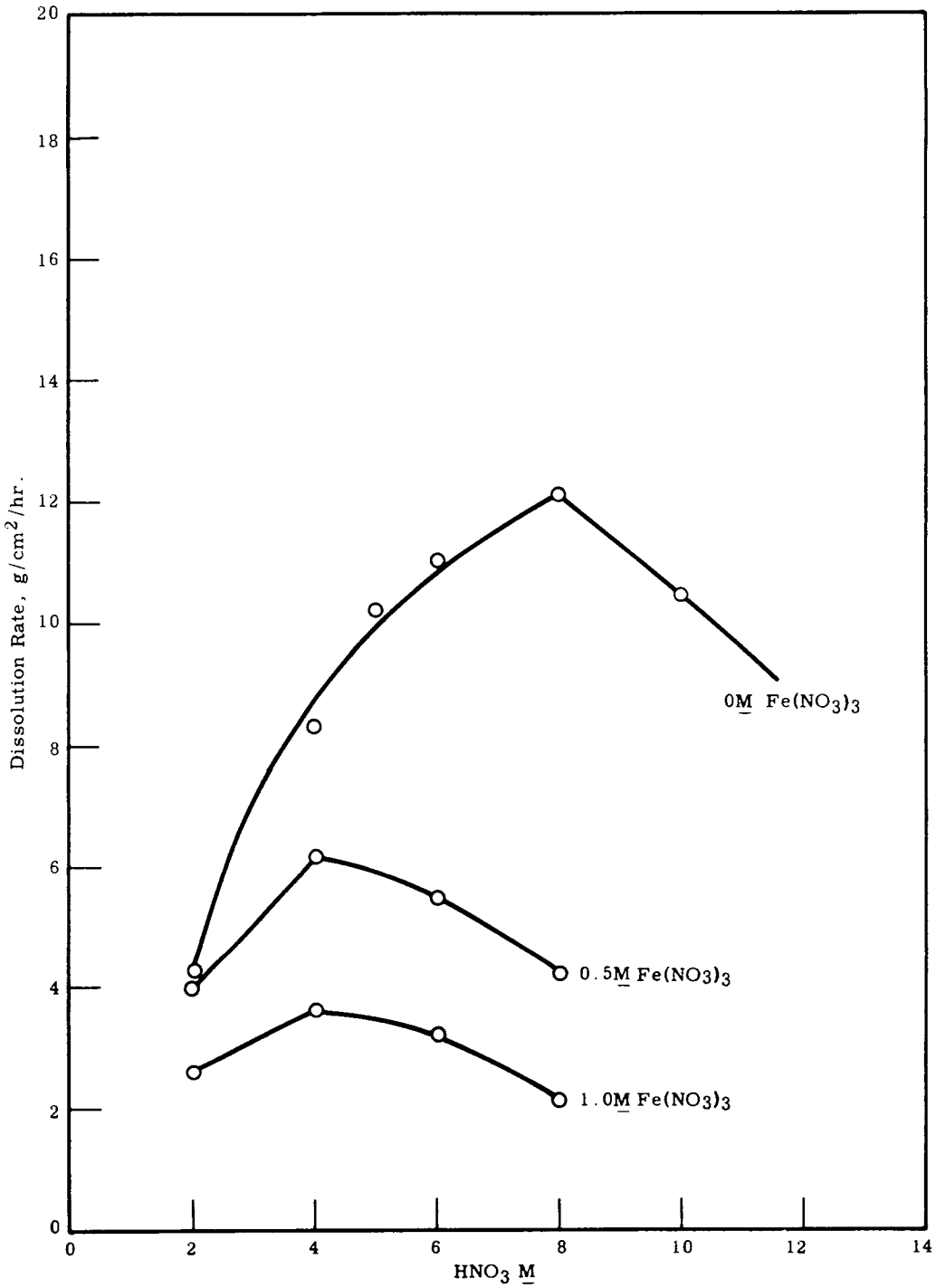

FIGURE 6

Instantaneous Dissolution Rates of 1020 Steel in Boiling HNO_3-$Fe(NO_3)_3$ Solutions

12 g coupon was completely dissolved in boiling 10 M HNO_3 to produce a solution of the composition 2.36 M $Fe(NO_3)_3$ - 0.95 M HNO_3. Dissolution required 30 minutes; one sample, (3), of gas was collected. Neglecting the components of air (N_2, O_2, A, and CO_2) the off-gas in both cases was essentially oxides of nitrogen (Table VIII). The amount of hydrogen evolved was far below that required for formation of explosive gas mixtures.[9]

TABLE VIII

OFF-GAS COMPOSITION FOR DISSOLUTION 1020 STEEL IN HNO_3 SOLUTIONS

Component	Volume Per Cent		
	Sample 1	Sample 2	Sample 3
NO	50.9	47.5	36.2
NO_2	36.0	36.0	47.0
N_2O	0.6	0.4	2.9
H_2	0.15	0.1	0.1
N_2	11.8	9.2	12.3
O_2	0.2	0.3	0.3
A	0.1	0.1	0.1
CO_2	0.1	0.7	0.1

3. Application of 1020 Steel Solutions in Processing U - Mo Alloy Cores

a. Dissolution U - Mo Alloy

A solution of the composition 5.8 M HNO_3 - 1.1 M $Fe(NO_3)_3$ prepared by dissolution of 1020 steel was used to dissolve a 20 g piece of U - 3 w/o Mo alloy. Complete dissolution to about 0.9 M $UO_2(NO_3)_2$ - 1.0 M $Fe(NO_3)_3$ - 0.19 M HNO_3 was achieved readily. Only trace amounts, less than 0.01 per cent of the initial alloy weight, of yellow solids were produced. In all respects dissolution behavior was comparable to that with dissolvents prepared from reagent grade iron(III) nitrate.

b. Redox-Type Batch Extraction Studies

Diban (4.17 M Al, - 7.68 M HNO_3) and 3 M $Na_2Cr_2O_7$ were added to a portion of the dissolver solution (produced as described above) to give a Redox fed solution of the approximate composition 0.9 M $UO_2(NO_3)_2$ - 1 M $Fe(NO_3)_3$ - 0.40 M $Al(NO_3)_3$ -(- 0.5) M HNO_3 - 0.2 M $Na_2Cr_2O_7$. A portion of this solution was contacted at room temperature with a double volume portion of undistilled, plant hexone. After phase separation the organic phase was again contacted with a fresh portion of the aqueous feed in the same volume ratio. The organic phase was then contacted twice with fresh one-fifth volume portions of a scrub solution of the composition 1.3 M $Al(NO_3)_3$ - (-0.2) M HNO_3 - 0.01 M $Na_2Cr_2O_7$. Finally, the scrubbed organic solution was stripped three times with one-sixth its volume of 0.01 M $Na_2Cr_2O_7$. Strips were composited.

Spectroscopic analysis of the organic phase after the second extraction contact, of the aqueous phase from the second scrub contact, and of the composite strip solution showed 20, 20, and 0 parts Mo per million parts U, respectively. These results are in excellent agreement with those obtained for extraction of U - Mo alloy dissolver solutions prepared with dissolvents made from reagent grade iron(III) nitrate. They demonstrate that dissolvents prepared from 1020 steel do not contain constituents which increase extraction of molybdenum into hexone.

LITERATURE CITED

1. Kelley, V. P. Fuel Element Data for Non-Production Nuclear Reactors, HW-58725 REV 4. August, 1959.
2. Flanary, J. R. et al. Development of the Sulfex Process for Decladding Stainless-Steel-Clad Power Reactor Fuel Elements with Sulfuric Acid, ORNL-2461. March, 1959.
3. Swanson, J. L., Hanford Laboratories Operation. Private Communication.
4. Culler, F. L. "Reprocessing of Reactor Fuel and Blanket Materials by Solvent Extraction", Paper 822, First Int'l. Conf. on Peaceful Uses of Atomic Energy, Geneva, 9: 464-483. New York: U. N. Pub., 1956.
5. Culler, F. L. and F. R. Bruce. "The Processing of Uranium-Aluminum Reactor Fuel Elements", First Int'l. Conf. on Peaceful Uses of Atomic Energy, Geneva, 9: 484-491. New York: U. N. Pub., 1956.
6. Shevchenko, V. B., M. S. Povitsky, and A. S. Solovkin. "Some Peculiarities in Treating Irradiated Fuel Elements at the First Atomic Station in the USSR", Paper 2182, 2nd Int'l. Conf. on Peaceful Uses of Atomic Energy. July, 1958.
7. Burns, R. E. and C. H. Holm. Nitric Acid Dissolution of Uranium-Aluminum Alloy, HW-18414. August, 1952.
8. Moore, R. L., W. W. Schulz, and S. J. Walter. Phosphate Catalysis in Nitric Acid Dissolution of Uranium Metal, HW-28995. July, 1953. (SECRET).
9. Scott, F. E. and M. G. Zabetakis. Flammability of Hydrogen-Air-Nitrogen Oxide Mixtures, U. S. Bureau of Mines Report No. 3507. Pittsburgh: 1956.
10. Maness, R. F. Power Reactor Fuels Reprocessing - Progress Report on Corrosion Aspects, HW-61662. September, 1959.
11. Alter, H. W., J. W. Codding and H. S. Jennings. "Miniature Mixer Settler for Continuous Counter Current Solvent Extraction", Anal. Chem. 26: 1357. August, 1954.
12. Schneider, K. J., Hanford Laboratories Operation. Private Communication.
13. Feigl, F., Chemistry of Specific, Selective, and Sensitive Reactions, 336-37. New York: Academic Press, 1949.
14. Rosenheim, A. and H. Schwer. "Uber Neunbasiche Heteropolysauren", Zeit. Anorg. Chem., 89: 224. August, 1914.
15. Hall, R. D. "Combinations of the Sesquioxides with the Acid Molybdates", J. Am. Chem. Soc. 29: 692. May, 1907.

16. Mellor, J. W. A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. XI: 603. New York: Longmans, Green & Co., 1948.

17. Baker, L. C. W., B. Loev and T. P. McCutcheon. "Hydrogen Cycle Cation Exchange for Heteropoly Acids and Salts", J. Am. Chem. Soc. 72: 2374. June, 1950.

18. Baker, L. C. W., G. Foster, W. Tan, F. Scholnick, and T. P. McCutcheon. "Some Heteropoly 6-Molybdate Anions: Their Formulas, Strengths of Their Free Acids and Structural Considerations", J. Am. Chem. Soc. 77: 2136. April, 1955.

19. Fortune, W. B. and M. G. Mellon. "Determination of Iron with o-phenanthroline", Ind. Eng. Chem. Anal. Ed. 10: 60. February, 1938.

20. Sandell, E. Colorimetric Determination of Traces of Metals, 2nd Ed., 455-459. New York: Interscience Publishers, Inc., 1950.

UC-10, Chemistry - Separation Process
for Plutonium and Uranium
(TID-4500, 15th Ed.)

INTERNAL DISTRIBUTION

Copy Number	
1	G. J. Alkire
2	R. G. Barns
3	L. P. Bupp
4	R. E. Burns
5	V. R. Cooper
6	E. M. Duke
7	J. B. Fecht
8	C. B. Foster
9	C. T. Groswith
10	K. M. Harmon
11	M. K. Harmon
12	O. F. Hill
13	E. R. Irish
14	D. W. Pearce
15	A. M. Platt
16	W. H. Reas
17	C. A. Rohrmann
18	W. W. Schulz
19	H. P. Shaw
20	R. J. Sloat
21	R. E. Tomlinson
22	M. T. Walling
23	L. L. Zahn
24	300 Files
25	Records Center
26 - 35	Extra
36 - 39	G. E. Technical Data Center, Schenectady, N. Y.

EXTERNAL DISTRIBUTION

Copy Number	
1	Aberdeen Proving Ground
1	Aerojet-General, San Ramon (IOO-880)
1	Air Technical Intelligence Center
2	ANP Project Office, Convair, Fort Worth
1	Alco Products, Inc.
1	Allis-Chalmers Manufacturing Company
10	Argonne National Laboratory
2	Army Chemical Center
1	AEC Scientific Representative, Belgium
1	AEC Scientific Representative, Japan
3	Atomic Energy Commission, Washington
3	Atomics International
1	Babcock and Wilcox Company (NYOO-1940)
2	Battelle Memorial Institute
1	Bettis Plant
1	Brookhaven National Laboratory
1	Carnegie Institute of Technology
2	Chicago Operations Office
1	Chicago Patent Group
1	Combustion Engineering, Inc.
1	Convair-General Dynamics Corporation, San Diego
1	Defence Research Member
2	Department of the Army, G-2
1	Dow Chemical Company (Rocky Flats)
4	duPont Company, Aiken
1	duPont Company, Wilmington
1	Frankford Arsenal
1	Goodyear Atomic Corporation
1	Iowa State College
1	Knolls Atomic Power Laboratory
2	Los Alamos Scientific Laboratory
1	Mallinckrodt Chemical Works
1	Maritime Administration
1	Martin Company
1	Mound Laboratory
1	National Bureau of Standards (Library)
1	National Lead Company of Ohio
3	Naval Research Laboratory
1	New Brunswick Area Office
2	New York Operations Office

EXTERNAL DISTRIBUTION (contd.)

Copy Number	
1	Nuclear Development Corporation of America
1	Nuclear Metals, Inc.
1	Oak Ridge Institute of Nuclear Studies
10	Office of Naval Research
1	Office of Ordnance Research
1	Patent Branch, Washington
6	Phillips Petroleum Company (NRTS)
1	Power Reactor Development Company
2	Pratt and Whitney Aircraft Divison
2	Public Health Service
1	Sylvania Electric Products, Inc.
1	Tennessee Valley Authority
3	Union Carbide Nuclear Company (ORGDP)
4	Union Carbide Nuclear Company (ORNL)
1	Union Carbide Nuclear Company (Paducah Plant)
1	U. S. Geological Survey, Denver
1	U S. Geological Survey, Washington
1	U. S. Naval Ordnance Laboratory
1	U. S. Naval Postgraduate School
1	U. S. Patent Office
2	University of California, Berkeley
2	University of California, Livermore
1	University of Puerto Rico
1	University of Utah
1	Westinghouse Electric Corporation (Schafer)
1	Yankee Atomic Electric Company
325	Technical Information Service Extension
75	Office of Technical Services, Washington