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PROCESS FOR DISSOLUTION OF BORAX IV REACTOR FUEL: LABORATORY DEVELOPMENT

L. M. Ferris

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
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ABSTRACT

Flowsheets are presented for the dissolution of Borax IV reactor fuel (6.35% $UO_{2.3}$-ThO_2 pellets encased in 1% nickel-aluminum alloy and bonded with lead). In the preferred method the aluminum is dissolved first in boiling 2 M NaOH—1.78 M $NaNO_3$, with a uranium loss of ~0.07%. The lead and nickel are then dissolved in boiling 1.5 M HNO_3, with uranium losses of <0.2%. The oxide core is dissolved in two successive digestions with boiling 13 M HNO_3—0.04 M NaF—0.1 M $Al(NO_3)_3$ to produce a solution 0.6 M in thorium and 0.04 M in uranium. Dissolution of only the aluminum in sodium hydroxide or sodium hydroxide—sodium nitrate solution prior to core dissolution is unattractive since the rate of core dissolution is lowered greatly if lead is present and a product solution containing greater than 0.2 M thorium is unattainable owing to the low solubility of lead nitrate in nitric acid—thorium nitrate solutions.

Simultaneous dissolution of aluminum and lead in mercury-catalyzed nitric acid appears costly since a mercury concentration of at least 0.5 M is required to ensure an adequate dissolution rate.

The solubility of lead nitrate in nitric acid and nitric acid—thorium nitrate solutions was determined.

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1.0 INTRODUCTION

Various aqueous methods for dissolution of Borax IV reactor fuel which were investigated are discussed in this report. This fuel is unique in that the heat-transfer bond between the 6.35% $UO_{2.3}$—93.65% ThO_2 pelleted core and the 1% nickel-aluminum (M-388) alloy cladding is metallic lead.[1-3] Since the fuel contains thorium, it will be reprocessed at ORNL under the Laboratory's interim reprocessing commitment. Direct total dissolution of the fuel in nitric acid—hydrofluoric acid solutions is impractical because of solubility limitations stemming from the high (Pb + Al)/Th mole ratio in the fuel. It was therefore concluded that decladding of the fuel prior to core dissolution was mandatory. Data presented in this report include reaction rates for decladding methods, necessary solubility determinations, and the results of several laboratory-scale flowsheet demonstration experiments with simulated unirradiated fuel.

Chemical and x-ray analyses for this program were made by the groups of G. R. Wilson, W. R. Laing, and R. L. Sherman of the ORNL Analytical Chemistry Division.

2.0 FLOWSHEET FOR TWO-STEP DECLADDING

A flowsheet in which the aluminum cladding and lead bond are dissolved in separate steps is shown in Fig. 1. The composition of the fuel charge is that given by Ullmann.[1] Initially the aluminum cladding is dissolved in 2 hr in the equivalent of boiling 2 M NaOH—1.78 M $NaNO_3$. In actual plant operation, water and 3.6 M $NaNO_3$ are first added to the dissolver; then the appropriate amount of 18.8 M NaOH is added continuously to effect the dissolution. The NaOH/Al mole ratio is 1.65.[4] Less than 0.07% of the uranium is lost to this waste solution.

Next, the lead bond and nickel residue are dissolved in 2 hr in boiling 1.5 M HNO_3 (HNO_3/Pb mole ratio of 4), which results in an additional uranium loss of less than 0.2%. After a water wash, the core is dissolved in two successive digestions with boiling 13 M HNO_3—0.04 M NaF—0.1 M $Al(NO_3)_3$. With pellets whose density is about 80% of theoretical, 93% of the core is dissolved in the first, 5-hr, contact with a 200% excess of dissolvent. The residue is then dissolved in about 1/3 volume of fresh dissolvent. The dissolution time for the actual fuel may be considerably longer since these pellets are about 93% of theoretical density. Recent studies have shown that the rate of dissolution of ThO_2-UO_2 pellets decreases with increasing density.[5] These solutions are combined with a water wash to produce a solution containing 0.6 M thorium, 0.039 M uranium, and 8.0 M HNO_3. After feed adjustment, the uranium and thorium are decontaminated by solvent extraction.

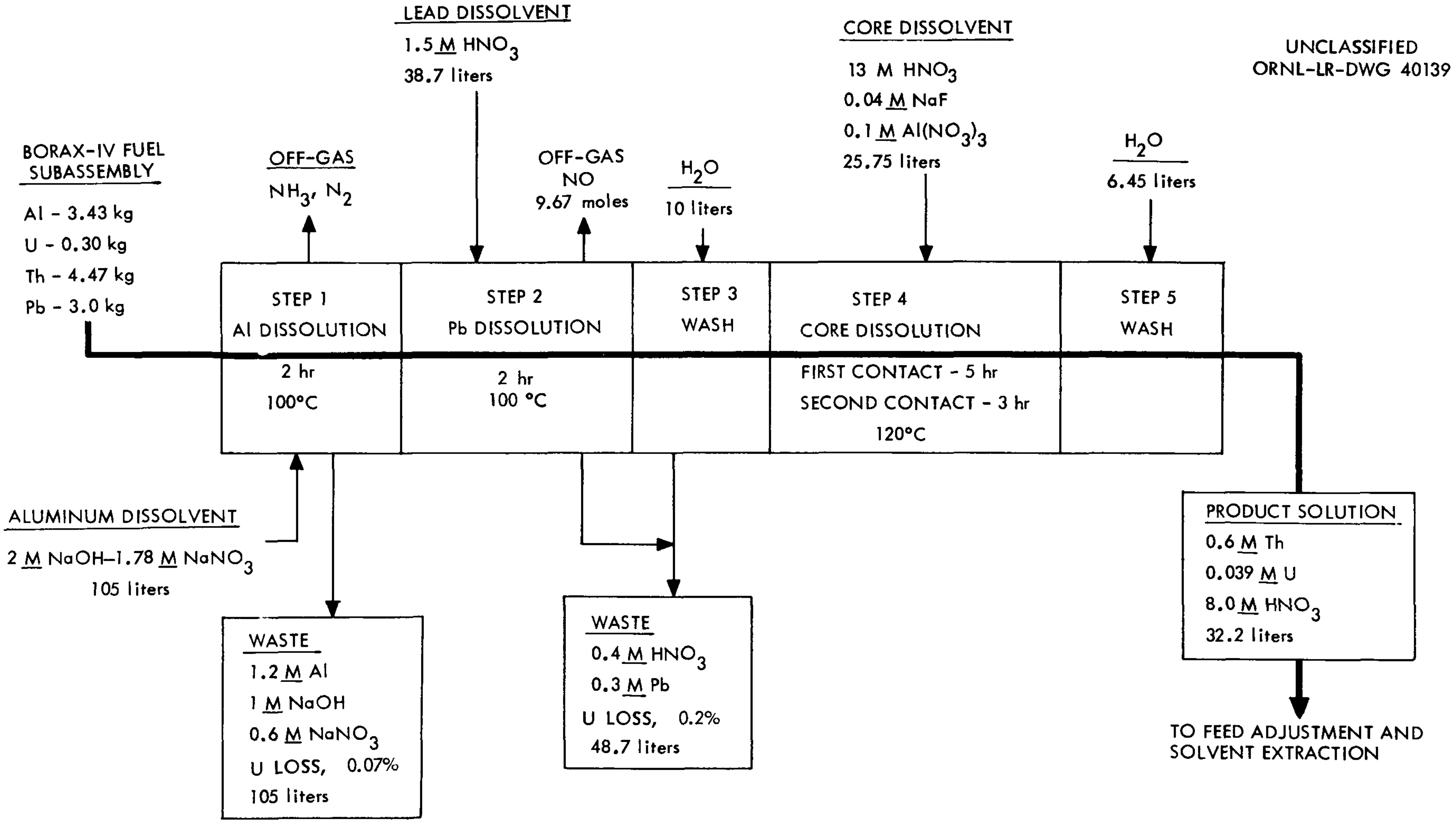

Fig. 1. Flowsheet for the two-step dissolution of Borax-IV fuel.

3.0 DATA OBTAINED IN DEVELOPMENT OF TWO-STEP DECLADDING FLOWSHEET

3.1 Dissolution of M-388 Alloy in Sodium Hydroxide and Sodium Hydroxide—Sodium Nitrate Solutions

M-388 alloy (1% nickel-99% aluminum), the cladding material of the Borax IV fuel, dissolved in boiling sodium hydroxide and sodium hydroxide—sodium nitrate solutions at essentially the same rate as pure aluminum. Rate constants in 3 M NaOH, 2 M NaOH—1.78 M $NaNO_3$, and 4 M NaOH—3.56 M $NaNO_3$ averaged 5.63×10^{-4} liter min^{-1} cm^{-2} (Table 1). The rate constant for aluminum dissolution in 3-4 M NaOH was 2.04×10^{-4} liter min^{-1} cm^{-2}, which compares favorably with the value 2.6×10^{-4} reported by Wymer and Blanco.[6] The relatively large scatter in the values of the rate constant is to be expected since the metallurgical treatment of the specimens affects the rate of reaction.[6]

Exposure of 1% nickel-99% aluminum alloy for 100 hr under static conditions to deionized water at 300°C had no effect on its dissolution in boiling 2 M NaOH—1.78 M $NaNO_3$. Under flowsheet conditions, a piece of autoclaved alloy dissolved at an average rate of 8.0 mg min^{-1} cm^{-2} to yield a solution containing 1.5 M aluminum. Under the same conditions type 2S aluminum dissolved at an average rate of 8.2 mg min^{-1} cm^{-2}.

Table 1. Dissolution of M-388 Alloy and Aluminum in Boiling Solutions of Sodium Hydroxide and Sodium Hydroxide—Sodium Nitrate

Metal	Solution	Rate Constant, liters min^{-1} cm^{-2}
M-388 alloy (1% nickel—99% aluminum)	2 M NaOH-1.78 M $NaNO_3$	5×10^{-4}
		8.4×10^{-4}
		14.5×10^{-4}
	4 M NaOH-3.56 M $NaNO_3$	4.13×10^{-4}
		4.30×10^{-4}
		3.99×10^{-4}
	3 M NaOH	2.29×10^{-4}
		2.40×10^{-4}
		5.63×10^{-4} (avg)
Al	3-4 M NaOH	2.04×10^{-4}
	NaOH	2.6×10^{-4} (Ref. 6)

Aluminum dissolves in aqueous sodium hydroxide according to the equation

$$Al + NaOH + H_2O \longrightarrow NaAlO_2 + 3/2H_2$$

The rate expression for the dissolution given by Wymer and Blanco[6] is

$$\frac{-dN_{OH}}{dt} = \frac{kS}{V} M_{OH}$$

where N = number of moles
S = surface area of the metal, cm^2
V = volume of solution, liters
k = rate constant, liter min^{-1} cm^{-2}
M_{OH} = molarity of NaOH
t = time, min

If the initial rate of evolution of hydrogen is used as a measure of the reaction rate, k is given by

$$k = \frac{2/3 \frac{dN_{H_2}}{dt} V^o}{S^o N^o_{OH}}$$

where the superscript zeros refer to the respective quantities at zero time.

3.2 Dissolution of Lead in Dilute Nitric Acid

Only dilute nitric acid was considered as a dissolvent for the lead bond to avoid high uranium and thorium losses in this step and to minimize waste volumes. In boiling 0.5 to 2 M HNO_3, lead dissolved at rates of 3-19 mg min^{-1} cm^{-2} (Table 2). Initial rates of dissolution (10 min exposure) of 0.04-cm-thick lead foil increased with increasing acid excess at each nitric acid concentration; at fixed HNO_3/Pb mole ratios, the rate also increased with increasing nitric acid concentration. In some cases, after the 10-min immersion test, the lead specimen was returned to the acid and completely dissolved. Analyses of the resulting

Table 2. Initial Rates of Dissolution of Lead Foil in Dilute Nitric Acid

Dissolution time: 10 min
Temperature: boiling point

HNO_3 Conc., M	Initial HNO_3/Pb Mole Ratio	Rate, mg min^{-1} cm^{-2}
0.5	2	3.1
	3	3.3
	4	3.3
	6	3.7
1.0	2	7.7
	3	9.3
	4	9.5
	6	12.2
1.5	2	11.0
	3	13.2
	4	16.5
	6	17.8
2.0	2	13.1
	3	15.9
	4	19.5
	6	-

solutions showed an average of 2.61 moles of nitric acid consumed per mole of lead (Table 3). This indicates that lead is dissolved approximately according to the reaction

$$3Pb + 8HNO_3 \longrightarrow 3Pb(NO_3)_2 + 4H_2O + 2NO$$

in which 2.67 moles of nitric acid is consumed for each mole of lead dissolved. Lead did not dissolve appreciably in 2-6 M NaOH or sodium hydroxide—sodium nitrate solutions.

Table 3. Consumption of Nitric Acid in the Dissolution of Lead in Nitric Acid

Initial HNO_3 Conc., M	Moles HNO_3 Per Mole of Pb	Initial HNO_3 Conc., M	Moles HNO_3 Per Mole of Pb
0.5	2.59	1.5	2.54
	2.61		2.79
1.0	2.53	2.0	2.64
	2.58		2.61
			2.61 (avg)

The solubility of lead nitrate in nitric acid decreased rapidly with increasing acid concentration (Fig. 2) at temperatures from 26 to 80°C (see appendix). For example, at 26°C the solubility decreased from 1.5 to 0.007 M as the nitric acid concentration increased from 0 to 12 M. Where data could be compared, agreement with the results of other workers was excellent.[7-9] As expected, the solubility increased with increasing temperature.

3.3 Core Dissolution

The core of the Borax IV fuel consists of air-fired 6.35% UO_2—93.65% ThO_2 pellets which are about 93% of theoretical density. Pellets used in this study were prepared at ANL and were only 83% of theoretical density. Chemical and thermogravimetric analyses showed that the uranium was present as UO_3. These pellets dissolved in 13 M HNO_3—0.04 M NaF—0.1 M $Al(NO_3)_3$ at essentially the same rate as the ThO_2-U_3O_8 pellets used in the dissolution studies of Bond[10] and of Ferris and Kibbey.[11] In a 200% excess of the boiling dissolvent, about 93% of the pellets dissolved in 5 hr. The remainder was dissolved in a 3-hr digestion with 1/3 volume of fresh dissolvent.

3.4 Flowsheet Demonstration Experiments: Two-step Decladding

Four laboratory-scale flowsheet experiments were made on the two-step decladding procedure (Fig. 1). Uranium losses during aluminum dissolution were less than 0.07% (Table 4). In three runs the pellets were in contact with the decladding solution at all times, while in the fourth run (B-11) an intact fuel pin was used. No difference in uranium loss was noted. Dissolution of the 0.04-cm-thick lead foil used in the experiments was complete in 1 hr in boiling 1.5 M HNO_3 with an attendant uranium loss of less than 0.2% (Table 4). In each case dissolution of the core was essentially complete under flowsheet conditions.

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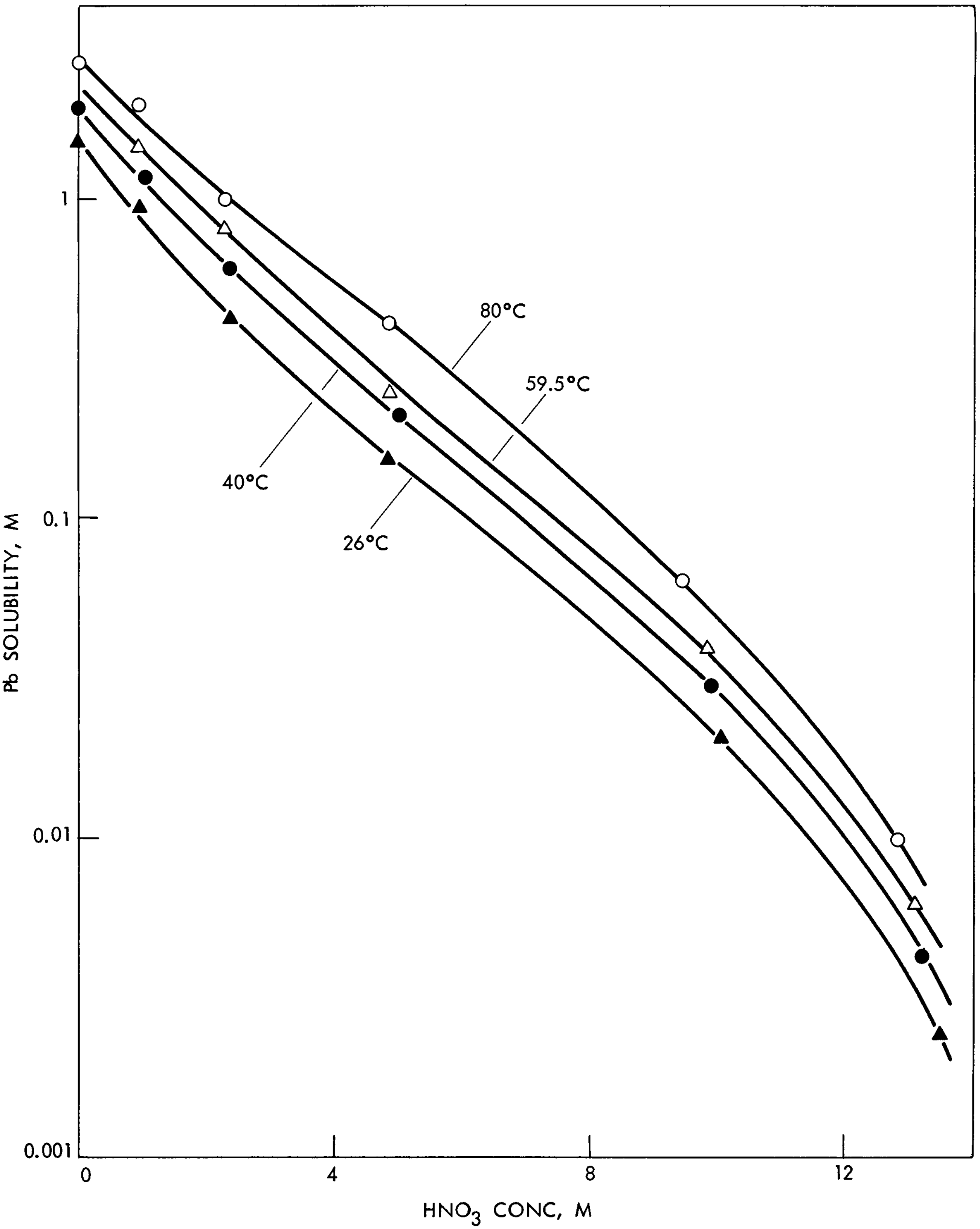

Fig. 2. Solubility of $Pb(NO_3)_2$ in nitric acid at various temperatures.

Nickel from the cladding remained after the aluminum dissolution step as a fine powder. No explosions were encountered in dissolving the nickel powder in boiling 0.5 to 8 M HNO_3. Experience has shown that the most hazardous situation exists when the powder is allowed to dry completely, e.g. after washing with acetone. In one such case the dry powder ignited spontaneously.

4.0 ALTERNATIVE FLOWSHEETS

4.1 Simultaneous Dissolution of Lead Bond and Core

The Borax IV fuel can be dissolved in nitric acid—sodium fluoride—aluminum nitrate solutions after removal of the aluminum cladding with sodium hydroxide or sodium hydroxide—sodium nitrate solutions (Fig. 3). However, dissolution of only the aluminum prior to core dissolution presents two problems: (1) The rate at which the core pellets dissolve in a 200% excess of 13 M HNO_3—0.04 M NaF—0.1 M $Al(NO_3)_3$ is much lower at the high Pb/Th mole ratio (0.77) in the fuel; and (2) because of the low solubility of lead nitrate in nitric acid—thorium nitrate solutions (Fig. 4), the thorium concentration in the solvent extraction feed solution is limited to 0.1-0.2 M. Not only does the solubility of lead nitrate decrease with increasing nitric acid concentration, but it also decreases with increasing thorium concentration.

Table 4. Dissolution of Borax IV Fuel by the Two-step Decladding Flowsheet

Aluminum dissolution in 2 M NaOH—1.78 M $NaNO_3$; 2 hr
Lead dissolution in 1.5 M HNO_3; 1 hr
Core dissolution in 13 M HNO_3—0.04 M NaF—0.1 M $Al(NO_3)_3$

Run No.	Losses in Al Dissolution, %		Losses in Pb Dissolution, %		Core Dissolved, %		
					First Digestion		
	U	Th	U	Th	U	Th	Over-all
B-8	0.028	0.004	0.088	0.0003	95.8	96.1	98.4
B-9	0.032	0.004	0.083	0.030	91.2	94.8	98.8
B-10	0.063	0.006	0.16	0.010	94.8	101	100
B-11	0.022	0.006	0.061	0.007	87.5	88.5	99.5

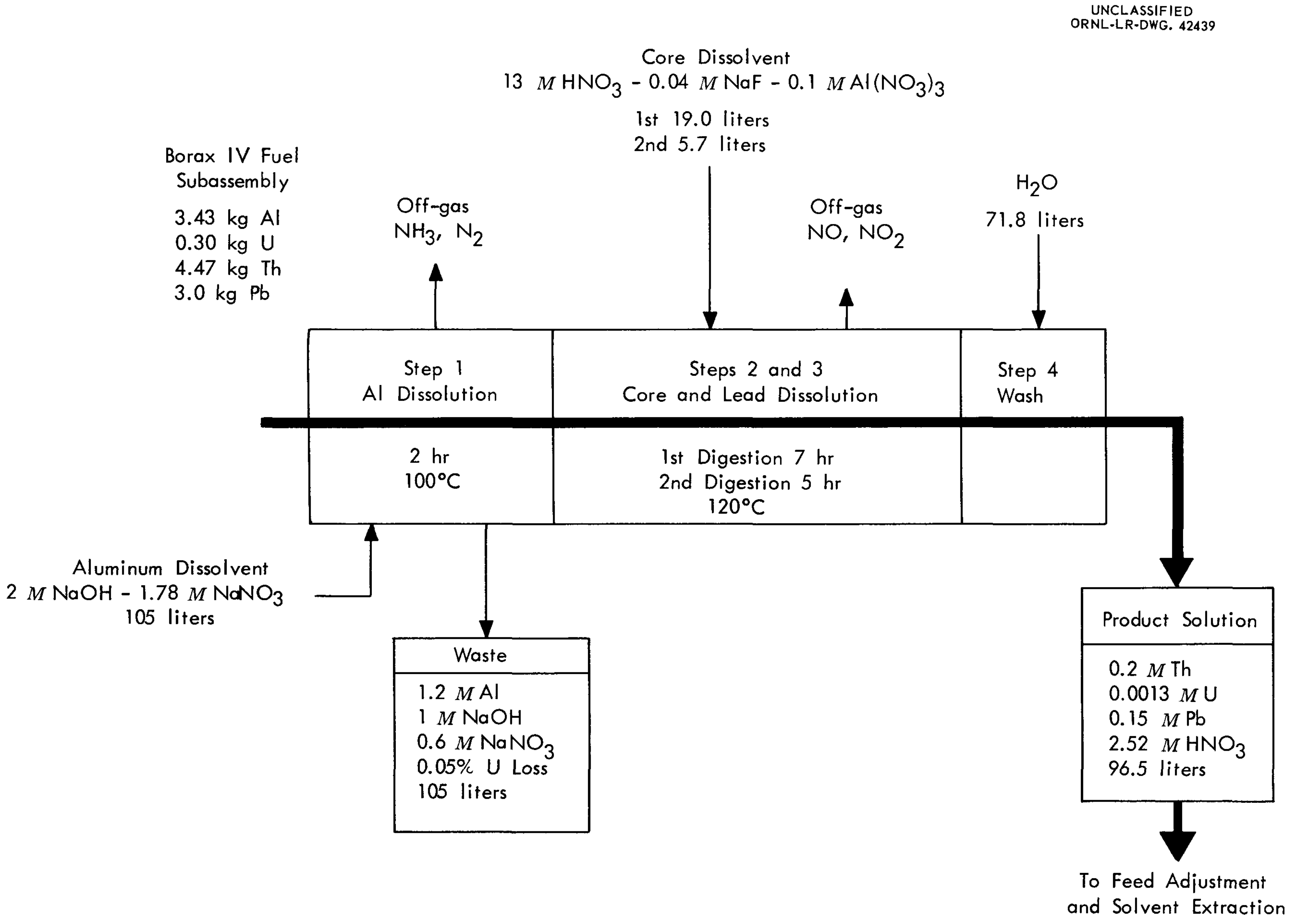

Fig. 3. Flowsheet for dissolution of Borax IV reactor fuel core after decladding with sodium hydroxide-sodium nitrate solution.

Table 5. Dissolution of Borax Fuel Core after Decladding with Sodium Hydroxide or Sodium Hydroxide—Sodium Nitrate

Run No.	Decladding Solution	Decladding Time, hr	Losses in Decladding, %		Core Dissolved, %			
					1st Digestion		2nd Digestion	
			U	Th	U	Th	U	Th
B-1	3 M NaOH	2	0.048	0.033	68.1	68.7	31.9	31.3
B-3	2 M NaOH— 1.78 M $NaNO_3$	2	0.014	0.020	75.8	68.6	24.2	31.4
B-4	3 M NaOH	2	0.019	0.25	74.9	78.4	25.1	21.6

In the three flowsheet experiments where the aluminum was dissolved in either 3 M NaOH or 2 M NaOH—1.78 M $NaNO_3$ prior to core dissolution, uranium losses were less than 0.05% (Table 5). The presence of lead during core dissolution resulted in only about 70% of the pellets being dissolved in 7 hr whereas about 93% was dissolved in only 5 hr in the absence of lead (Table 5). In run B-1 the lead nitrate precipitate from the core dissolver solution was removed by filtration. About 5.4% of the uranium was found in the precipitate.

4.2 Decladding with Mercury-catalyzed Nitric Acid

The M-388 alloy cladding and the lead bond can be dissolved simultaneously in mercury-catalyzed nitric acid prior to core dissolution. This technique does not appear attractive, however, since a mercury concentration of about 0.5 M is required to ensure a suitable rate of dissolution of aluminum when lead is present (Fig. 5). This mercury concentration is about 100 times higher than that normally required for dissolution of aluminum. In these experiments, 0.95-cm-dia 2.5-cm-high right cylinders of aluminum were digested with boiling 4 M HNO_3 (4 moles of HNO_3 per mole of aluminum) in the presence of lead (8.77 moles of aluminum per mole of lead). In general, the rate of dissolution of aluminum increased with increasing mercury concentration, but in no case was dissolution as rapid as when no lead was present (compare upper and lower curves in Fig. 5).

A single experiment was performed in which simulated Borax IV fuel was declad with boiling 4 M HNO_3—0.5 M $Hg(NO_3)_2$. The tentative flowsheet for this method is shown in Fig. 6. Both the aluminum and lead were completely dissolved at the end of 2 hr, but, on cooling, a large amount of precipitate formed. The precipitate, which was not dissolved when the decladding solution was diluted with an equal volume of water, contained about 40% of the aluminum and 50% of the lead. The uranium loss to the supernatant was 0.17%. Dissolution of the core pellets was complete under flowsheet conditions.

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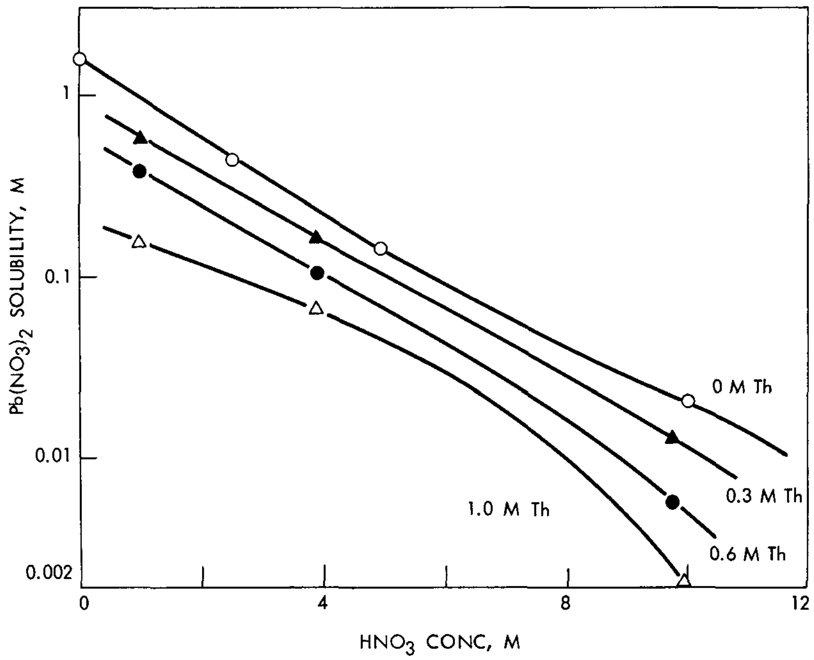

Fig. 4. Solubility at 25°C of $Pb(NO_3)_2$ in nitric acid—thorium nitrate solutions as a function of nitric acid and thorium nitrate concentrations.

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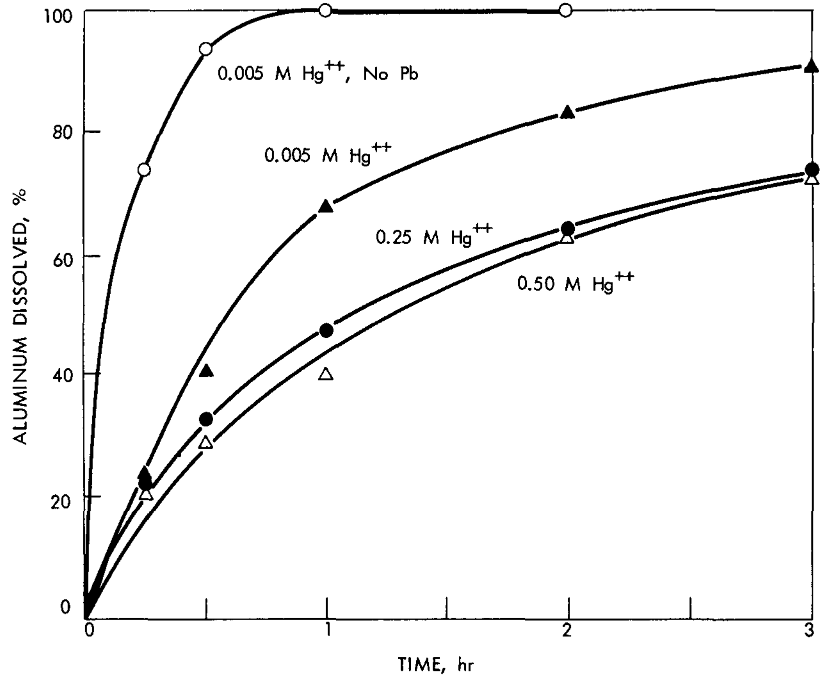

Fig. 5. Effect of mercury concentration on rate of dissolution of aluminum in boiling 4 M HNO_3 in the presence of lead. Al/Pb mole ratio = 8.77; HNO_3/Al mole ratio = 4.0. Aluminum specimens were 0.95-cm-dia 2.5-cm-high right cylinders.

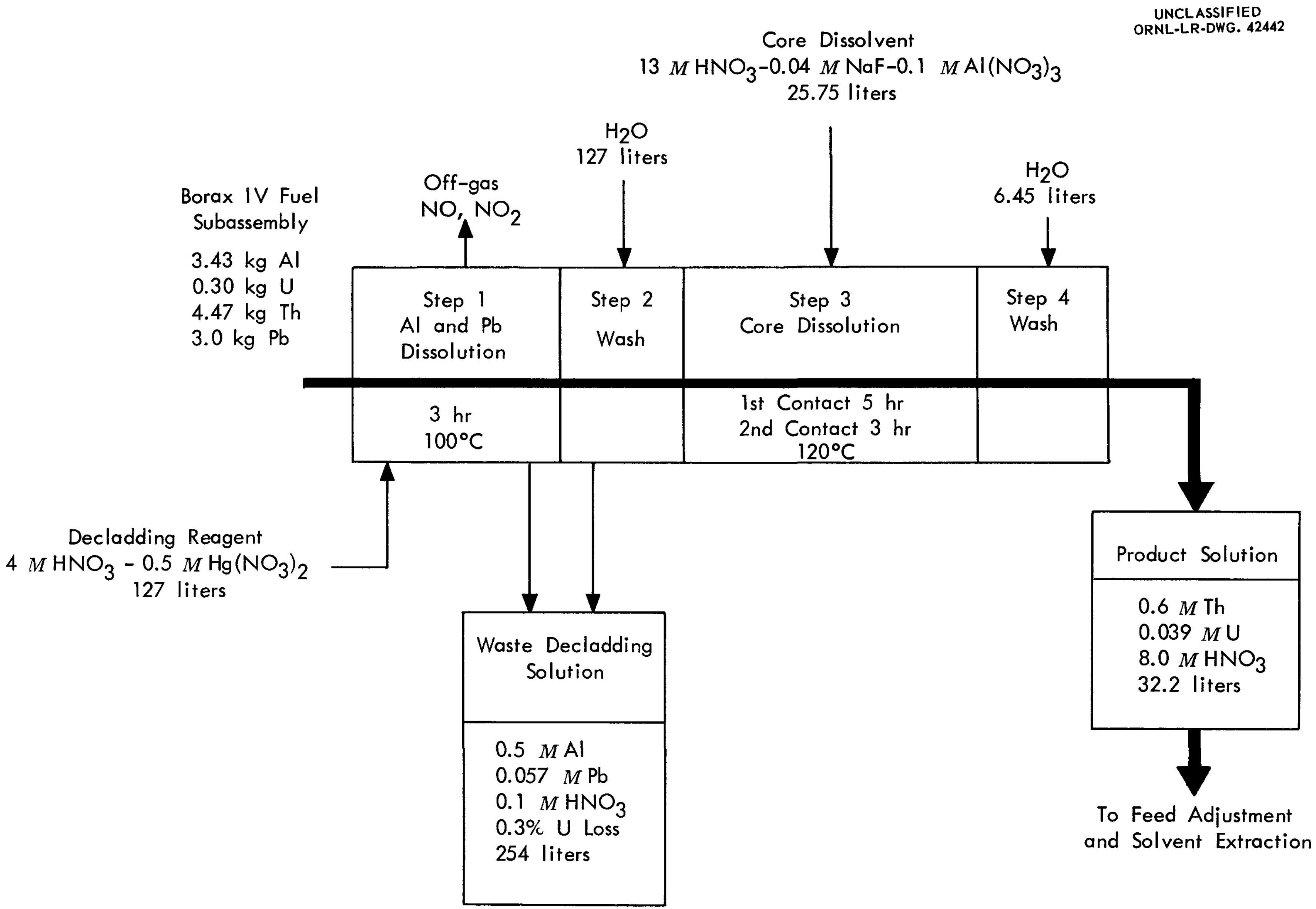

Fig. 6. Flowsheet for dissolution of Borax IV reactor fuel core after decladding with 4 M HNO_3 - 0.5 M $Hg(NO_3)_2$.

Five flowsheet experiments were performed in which prototype Borax IV fuel elements were declad with either 4 or 8 M HNO_3 containing 0.005 M Hg^{++}. The use of either 4 or 8 M HNO_3, with a HNO_3/Al mole ratio of 8 instead of 4, decreased the time required for total dissolution of the clad and bond from about 40 to about 20 hr (Table 6). Losses to the decladding solution were about 0.25 and 0.6% with HNO_3/Al mole ratios of 4 and 8, respectively. Since integral fuel specimens were not used in four of the experiments, both aluminum and lead were equally accessible to attack by the nitric acid. The lead dissolved almost immediately, and its presence in solution retarded the rate at which the aluminum dissolved even with a large excess of acid present. It was therefore conceivable that lead would not interfere with dissolution of the aluminum cladding in nitric acid containing a small (0.005 M) amount of mercury if the fuel specimens were fully intact. This concept was tested in Run B-12 with intact fuel, in which about 90% of the aluminum dissolved rapidly until lead was exposed. At this point, dissolution of the aluminum virtually ceased. In an actual processing facility, a high mercury concentration would be required in the event that a ruptured fuel element was present.

Table 6. Decladding of Simulated Borax IV Fuel with Nitric Acid Containing 0.005 M $Hg(NO_3)_2$

Fuel charge: 30 g of 6.35% UO_3--93.65% ThO_2 pellets; 16.6 g Pb; 19.1 g Al

Run No.	HNO_3 Conc., M	Moles HNO_3 per Mole Al	Time Required to Completely Dissolve Al, hr	Losses to Decladding Solution, % U	Losses to Decladding Solution, % Th	Core Dissolved in 1st, 7-hr, Digestion, % U	Core Dissolved in 1st, 7-hr, Digestion, % Th
B-2	4	4	42	0.21	0.058	93.3	93.5
B-5	4	4	38.1	0.25	0.063	98.2	98.4
B-6	8	8.5	23.2	0.60	0.10	98.0	98.6
B-7	4	8.5	21	0.60	0.11	97.6	98.2
B-12	4	4.25	2[a]	0.11	0.008	94.7	96.4

[a] Intact fuel specimen used. About 90% of the aluminum dissolved rapidly until lead was exposed to the solution; then dissolution virtually ceased.

Removal of both aluminum and lead in the decladding step allowed normal dissolution of the core in boiling 13 M HNO_3--0.04 M NaF--0.04 M $Al(NO_3)_3$. In the first, 7-hr, digestion, 92-98% of the core dissolved

(Table 6), as expected from previous rate data.[10,11]

5.0 FUTURE WORK

Since the Borax IV fuel is the only one of its type, there appears to be little incentive in developing an economical long-range processing method. If uranium losses of the order of 0.5% can be tolerated in the processing of this fuel, the simplest scheme may be the use of mercury-catalyzed nitric acid as the decladding reagent if the cost of the mercury is not prohibitive. A cursory cost estimate by Ullmann[12] indicated that the cost of enough mercury to ensure rapid dissolution would be prohibitively high for a long-range process, but might not be intolerable for interim pilot plant work. He estimated that $11,000 worth of mercury would be required to process the Borax IV core. Unless radiation markedly increases the uranium losses, the fuel could be processed by the two-step decladding method with a uranium loss of about 0.1%. This technique also avoids the use of large quantities of mercury. A more detailed cost estimate will be required before a choice between the two-step decladding method and use of mercury-catalyzed nitric acid can be made.

Further work on both the two-step decladding method and the use of mercury-catalyzed nitric acid for decladding seems warranted. The solubility of lead nitrate in nitric acid-mercury nitrate solutions has not yet been determined, and methods for recovering traces of uranium from such solutions may need to be devised. Corrosion of stainless steel and titanium by nitric acid solutions containing up to 0.5 $\underline{M}$ $Hg(NO_3)_2$ must be determined, and more detailed information on the effect of the mercuric ion concentration on the rate of core dissolution is desirable. More information on off-gases and feed adjustment is needed. Whether or not cross-contamination of solutions has any adverse effect on the processes should be determined.

No further work is planned on the process where only the aluminum is dissolved in caustic prior to simultaneous dissolution of the lead bond and core.

6.0 REFERENCES

1. J. W. Ullmann, ORNL, "Borax IV Data Sheet," Sept. 17, 1958.

2. J. H. Handwerk, C. L. Hoenig, and R. C. Lied, "Manufacture of the ThO_2-UO_2 Ceramic Fuel Pellets for Borax IV," ANL-5678 (August 1957).

3. D. K. Walker, R. A. Noland, F. D. McCusig, and C. C. Stone, "Borax IV Reactor: Manufacture of Fuel and Blanket Elements," ANL-5721 (March 1958).

4. R. E. Blanco in "Symposium on the Reprocessing of Irradiated Fuels," Brussels, Sept. 19, 1957, TID-7534, p. 24.

5. L. M. Ferris in "Monthly Progress Report for July 1959, Chemical Development Section B," ORNL-CF-59-8-6, p. 8.

6. R. G. Wymer and R. E. Blanco, "Uranium-Aluminum Alloy Dissolution," Ind. Eng. Chem., 49: 59 (1957).

7. H. G. Denham and J. O. Kidson, J. Chem. Soc., 1931: p. 1575.

8. A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," 3rd ed., Vol. I, Van Nostrand, New York, 1940, p. 1401.

9. A. A. Kazantsev, Nauch. Trudy Moskov Tekhnol. Inst. Legkoi Prom., 1956, No. 7: 326.

10. W. D. Bond, "Dissolution of Sintered Thorium-Uranium Oxide Fuel in Nitric Acid—Fluoride Solutions," ORNL-2519 (Oct. 28, 1958).

11. L. M. Ferris and A. H. Kibbey, "Laboratory Development of the Sulfex Process for the Dissolution of Consolidated Edison Power Reactor Fuel," ORNL-2714 (Oct. 16, 1959).

12. J. W. Ullmann, ORNL, personal communication, August 1959.

13. F. A. A. Schreinemakers, Z. phys. Chem., 23: 417 (1897).

14. S. Glasstone and R. N. Saunders, J. Chem. Soc., 123: 2134 (1923).

NOTEBOOK REFERENCES

L. M. Ferris, Classified Notebook 5845.

J. F. Land, Unclassified Notebook A-1682.

7.0 APPENDIX

7.1 The System Lead Nitrate—Nitric Acid—Water

Phase equilibria in the system lead oxide—nitrogen pentoxide—water where investigated at 25 and 50°C by Denham and Kidson.[7] Additional study of the solubility of lead nitrate in nitric acid at temperatures below 50°C was done by Kazantsev.[9] Similar solubility determinations in this laboratory extended the range of measurement to 80°C.

An excess of solid lead nitrate was added to a series of nitric acid solutions ranging in concentration from 0 to 15 M. The stoppered Pyrex flasks containing the solutions were kept in a constant-temperature bath for several days with periodic shaking to ensure equilibrium. In each case the temperature was constant to within 0.1°C. Samples of the liquid phase at each temperature were removed for density measurement and chemical analysis. At 80°C the wet residue was also analyzed to allow determination of the equilibrium solid phase by the method of Schreinemakers.[13] At 25°C the solid phase was identified by x-ray analysis.

Isotherms were obtained at 26, 40, 59.5, and 80°C (Table 7 and Fig. 7). At 26°C, the only temperature where data can be readily compared to those of Denham and Kidson,[7] the isotherm obtained is about that expected. Solubilities of lead nitrate in water obtained in this study at various temperatures are in excellent agreement with previously reported values.[7-9,14] As expected,[7] the solid phase at equilibrium was lead nitrate.

Table 7. The System $Pb(NO_3)_2$ - HNO_3-H_2O at 26, 40, 59.5, and 80°C

Temp., °C	Composition of Saturated Solution, wt %		Density of Saturated Solution, g/cm^3	Solid Phase At Equilibrium
	$Pb(NO_3)_2$	HNO_3		
26	37.41	0	1.434	$Pb(NO_3)_2$
	24.75	4.93	1.253	
	12.22	12.96	1.162	
	4.26	25.99	1.183	
	0.53	50.26	1.266	
	0.06	63.84	1.333	
	0.008	71.35	1.387	
40	42.16	0	1.516	$Pb(NO_3)_2$
	29.24	4.78	1.350	
	16.46	12.23	1.224	
	5.86	26.37	1.201	
	0.78	48.94	1.278	
	0.10	61.98	1.345	
59.5	33.77	4.04	1.443	$Pb(NO_3)_2$
	20.82	11.39	1.284	
	1.01	49.08	1.268	
	0.15	62.40	1.323	
	0.03	70.54	1.360	
80	52.45	0	1.692	$Pb(NO_3)_2$
	43.41	3.92	1.528	
	24.15	10.72	1.352	
	11.17	25.54	1.209	
	1.70	48.55	1.233	
	0.25	62.65	1.290	
	0.05	70.71	1.321	

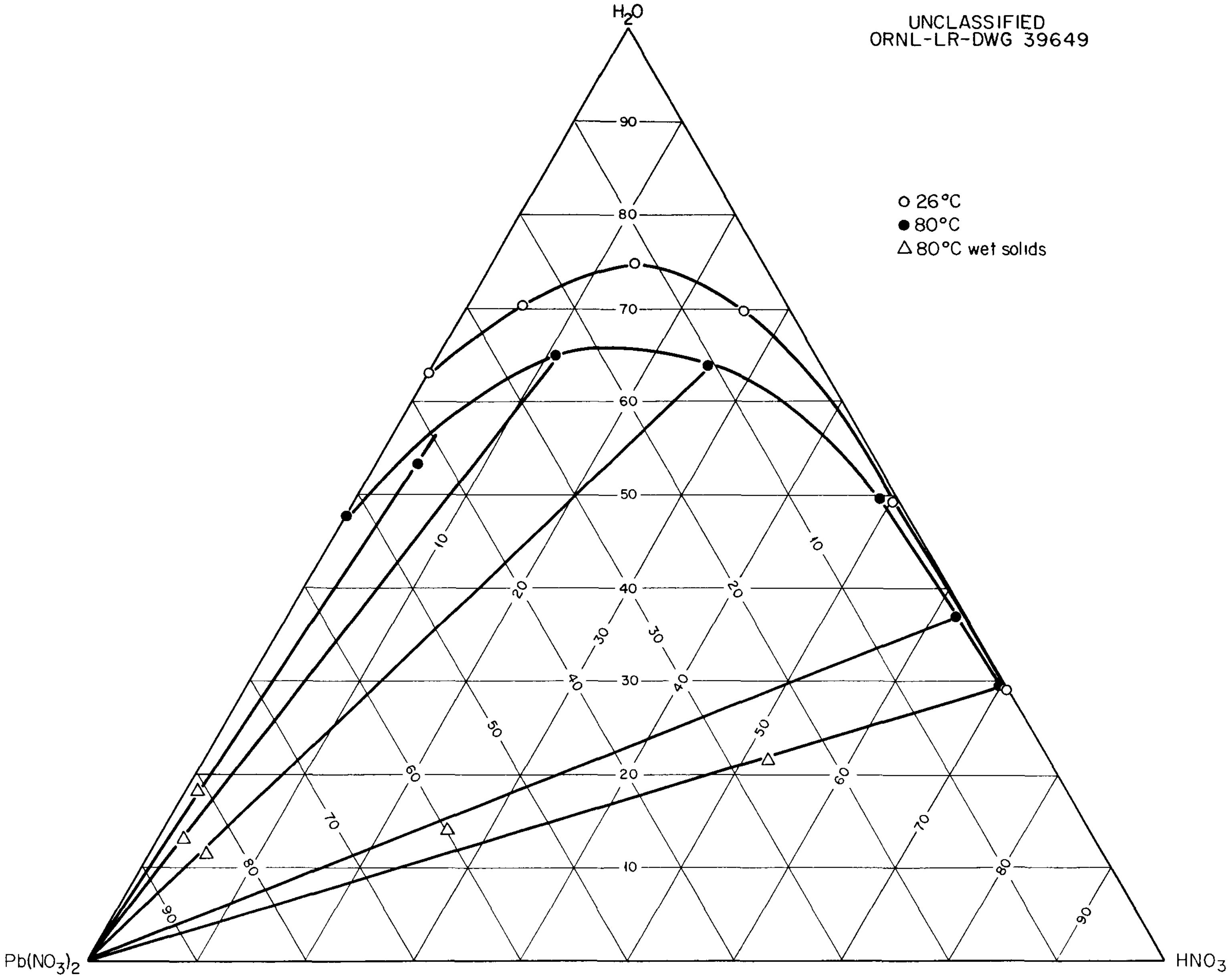

Fig 7 The system $Pb(NO_3)_2 - HNO_3 - H_2O$ at 26 and 80°C

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