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THE SEALED-REFLUX DISSOLUTION SYSTEM

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ABSTRACT

A simplified pressurized acid system, called the sealed-reflux dissolution system, was designed to dissolve various refractory materials. In this system, the sample and acid solution are heated to 150 to 200°C at 0.3 to 0.8 MPa (50 to 115 psi). Although this temperature and pressure are lower than that attained in sealed-tube methods, the sealed-reflux system has been effective in dissolving high-fired PuO_2 and irradiated fuels with as much as 12.5% burnup.

I. INTRODUCTION

Reliable chemical analysis requires quantitative dissolution of the sample, a process that is material dependent. Refractory materials usually are dissolved by acid treatment, by fusions, or in a sealed, pressurized acid system. High-fired fuels and high-burnup fuels are usually difficult to dissolve completely in acids at atmospheric pressure, and fusions tend to contaminate the sample with fluxes and reaction products from the container. A sealed-tube dissolution method, which produces a solution relatively free from contamination, has been proved effective for dissolving refractory oxides and other difficultly soluble materials.¹⁻⁶ The sealed-reflux dissolution system⁷ described in this report is applicable to oxide and nitride materials or small (< 100-mg) metallic samples soluble in $\text{HCl-HNO}_3\text{-HF}$ mixtures at temperatures up to 200°C. This method is not directly applicable to large (> 100-mg) metallic samples or to samples containing large quantities of organic materials because of the high pressures developed by reaction-product gases. However, it is effective in dissolving small quantities of residues from these and other materials left after normal acid treatment in an open container.

The sealed-reflux dissolution system operates at a temperature of 150 to 200°C and a pressure of 0.3 to 0.8 MPa (50 to 115 psi), and does not require an external compensating pressure as does the sealed-tube system.⁴ An advantage of the sealed-reflux system is the release of pressures above approximately 1 MPa without loss of sample, essentially eliminating the possibility of the tube rupturing because of high-pressure surges.

The sealed-reflux system is normally used with either of two acid mixtures: A (2 ml 12 M HCl , 1 drop 15 M HNO_3 , and 1 drop 0.4 M HF) heated to 150°C, which develops a pressure of 0.8 MPa, or B (2 ml 15 M HNO_3 , 0.4 ml 12 M HCl , and 1 drop 0.4 M HF) heated to 200°C, which develops a pressure of 0.3 MPa in the recommended size tube.

Caution: Although the possibility of a tube rupturing under pressure is small, we recommend that a safety shield be used inside the glove box and that the tubes not be handled at temperatures > 80°C. All plutonium materials should be processed in suitable glove boxes, and the operator should wear approved protective clothing.

II. APPARATUS AND REAGENTS

A. Apparatus

Centrifuge: clinical or equivalent.

Funnel: aluminum, to fit 8-mm-bore, fused-silica tube.

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Heating block: aluminum, with dimensions as shown in Fig. 1.

Hose clamp: worm drive, Aero seal No. GS4 or equivalent, 5.6- to 15.9-mm adjustable opening.

Hot plate: capable of heating to 300°C.

Laboratory equipment: including balances, beakers, centrifuge tubes, polyethylene containers, watch-glasses, etc.

Pinch clamps: size No. 18, for spherical ball and socket glass joints, modified by closing the opening in one side of the clamp.

Polyethylene stoppers: size 00, hollow, cut off at 8-mm length, with a rubber stopper insert.

Pyrovane: Honeywell or equivalent, to control temperature to $\pm 5^\circ\text{C}$ in the range 0 to 300°C.

Rubber stoppers: size 0000.

Rubber tubing: for cushion, 9.5-mm i.d., 3.1-mm wall thickness.

Thermocouple: Chromel-Alumel or equivalent.

Tubes: fused-silica, heavy-wall, approximately 8-mm-bore, 2-mm wall thickness, 300-mm-long, with a test-tube-type seal at one end, and prepared as follows. An approximately 9.5-mm-long section of rubber tubing is fitted around the open end of the tube, flush with the end. A hose clamp is

extruded tubing is trimmed so its dimensions do not exceed the clamp's dimensions or extend beyond the tube opening. See Fig. 2.

B. Reagents

Hydrochloric Acid: 12 M, reagent grade.

Hydrofluoric Acid: 27 M, reagent grade.

Hydrofluoric Acid: 0.4 M, prepared by diluting 1.5 ml 27 M HF, reagent grade, to 100 ml with double-distilled water.

Hydrofluoric Acid: 1.3 M, prepared by diluting 4.8 ml 27 M HF, reagent grade, to 100 ml with double-distilled water.

Nitric Acid: 15 M, reagent grade.

Water: double-distilled.

III. RECOMMENDED PROCEDURE

1. A 0.1-g sample of an oxide or nitride fuel, which does not contain organic materials, is accurately weighed, transferred into a fused-silica tube (see Apparatus) using an aluminum foil boat or

Fig. 1. Heating block for sealed-reflux dissolution system.

Fig. 2. Sealed-reflux dissolution tube and accessories.

funnel, and dissolved as described in Steps 7 - 11.

2. Samples containing metals or organic materials are accurately weighed, then reacted in a covered beaker with HNO_3 , HCl , HF , or mixtures of these acids. The solution is centrifuged and decanted into a 100-ml volumetric flask or other suitable container and saved. (If desired, samples containing organic materials can be ignited at 800°C in air and then dissolved as oxide samples.)

3. The residue, containing less than 100 mg of material, is quantitatively washed with water into a fused-silica tube (see Apparatus).

4. The tube and water are heated to approximately 85°C , and the slurry is evaporated to dryness using an air stream directed on the liquid's surface.

5. For residues remaining after acid treatment of thorium-, neptunium-, and plutonium-metal materials, irradiated (U-Pu) oxide fuel, or large (>200-mg) quantities of oxide and nitride fuels, acid mixture A (2 ml 12 M HCl , 1 drop 15 M HNO_3 , and 1 drop 0.4 M HF) is added. The tube is then sealed with a No. 0000 rubber stopper, clamped, and heated as described in Step 8.

6. For residues remaining after acid treatment of uranium materials or large (>200-mg) quantities of nitride fuel materials, acid mixture B (2 ml 15 M HNO_3 , 0.4 ml 12 M HCl , and 1 drop 0.4 M HF) is added. The tube is then sealed with a cut-off (approximately 8-mm-long) No. 60 hollow polyethylene stopper with a rubber stopper insert, clamped, and heated as described in Step 8.

7. For 0.1-g samples of nitride fuel materials or high-fired oxides of plutonium, neptunium, and thorium, acid mixture A (2 ml 12 M HCl , 1 drop 15 M HNO_3 , and 1 drop 0.4 M HF) is added. The tube is then sealed with a No. 0000 rubber stopper, clamped, and heated as described in Step 8.

[Note: The recommended conditions for dissolving specific types of samples as given in Steps 5, 6, and 7 are generally applicable. Success with either the HCl system (mixture A) or the HNO_3 system (mixture B) is dependent on the history of the sample material. Actual experience with specific types of samples will dictate which acid system is most successful and if slight

modifications, e. g., a greater HF concentration, are needed.

8. The tube is placed in an aluminum block (Fig. 1) at $<70^\circ\text{C}$ and heated to 150°C for the HCl system and 200°C for the HNO_3 system, until the sample is dissolved. (Dissolution time is material dependent: small residues dissolve in a few hours, whereas 0.1-g samples of high-fired PuO_2 may take 24 h for complete dissolution.)

9. The tube is cooled to $<70^\circ\text{C}$ before the clamp and then the stopper are removed.

10. If the solution in the tube is part of a sample described in Step 2, the solution is quantitatively transferred by washing with 1 M HCl or HNO_3 into the container holding the previously dissolved portion of the sample. If the solution in the tube is the total sample from Step 7, it is quantitatively transferred by washing with 1 M HCl or HNO_3 into an appropriate container, such as a 50-ml volumetric flask.

11. The solution is thoroughly mixed, and aliquots are taken for analysis.

IV. EXPERIMENTAL

In determining optimum operating conditions for the sealed-reflux dissolution system, pressures developed by various acid mixtures at seven temperatures were measured (Table II). These pressures were determined by adding one of the following acid mixtures to the recommended size tube (300-mm-long by 8-mm-i. d.):

A (2 ml 12 M HCl , 1 drop 15 M HNO_3 , and 1 drop 0.4 M HF),

B (2 ml 15 M HNO_3 , 0.4 ml 12 M HCl , and 1 drop 0.4 M HF), or

C (2 ml 10 M HCl , 1 drop 15 M HNO_3 , and 1 drop 0.4 M HF).

A dial pressure gage was then sealed into the end of the tube, and the tube was placed in a heating block behind a safety shield. The top of the heating block was just below the level of the solution in the tube. This allowed the gas phase in the tube to be cooled by the surrounding air, resulting in a refluxing action. When the solution was heated to 150°C the measured temperature at the top of the tube was less than 50°C in a drybox having an air flow rate of approximately 0.5 m/s (100 ft/min). The solution was then heated to various temperatures ranging

TABLE I
PRESSURES DEVELOPED BY THE ACID MIX-
TURES AT VARIOUS TEMPERATURES USING
THE SEALED-REFLUX DISSOLUTION SYSTEM

Acid Mixture	Temperature (°C)	Pressure Developed [MPa (psi)]	
A	100	0.45	(65)
A	150	0.75	(115)
A	160	0.90	(130)
B	160	0.31	(45)
B	190	0.32	(46)
B	200	0.33	(48)
C	200	0.52	(75)

A: 2 ml 12 M HCl, 1 drop 15 M HNO₃, and 1 drop 0.4 M HF

B: 2 ml 15 M HNO₃, 0.4 ml 12 M HCl, and 1 drop 0.4 M HF

C: 2 ml 10 M HCl, 1 drop 15 M HNO₃, and 1 drop 0.4 M HF

from 100 to 200°C, and the indicated pressures were recorded. These pressures are approximate because of the increased system volume from the added pressure gage. However, the pressures are estimated to be accurate to within 10%, which is adequate for the approximate pressure readings desired.

The pressure generated by vaporizing HCl in either acid system allows the acid mixture to be heated to a higher temperature than would be possible at ambient pressure. The HCl system continues to increase in pressure when heated above 150°C; therefore, to prevent venting of the gas and resultant lower acid strength, the recommended temperature of 150°C should not be exceeded. The HNO₃ system reaches a maximum pressure (0.3 MPa) at 100°C. This pressure is adequate to prevent vigorous boiling at 200°C, the recommended temperature for this acid system, although a slight bubbling is desirable to help mix the solution. Also, solutions mix more quickly and the samples dissolve faster if the holes in the heating block are drilled at an angle, 20 to 45° from vertical.

Any impurities leached from a dissolution container that would cause interference in the subsequent analysis would be undesirable. Therefore, the amounts of impurities leached from fused-silica

tubes and borosilicate glass tubes by the HCl and the HNO₃ systems were determined by heating the tubes and acid mixtures to the recommended temperatures for 1 wk. The solutions were spectrographically analyzed for the amount of each of 34 impurity elements present. Most impurity levels were low in each solution (Table II), but, as expected, the fused-silica tubes contributed the least amount of impurities in either acid system. Therefore, the fused-silica tubes are recommended for all acid systems, although the less expensive borosilicate glass tubes can be used, providing the impurities dissolved from the glass do not interfere with subsequent analyses. Also, the impurity levels will be considerably less for a 24-h treatment than for the test's 1-wk exposure.

The sealed-reflux dissolution system was tested by dissolving irradiated fuel samples and high-fired ThO₂ and PuO₂ materials. Over 50 irradiated (U-Pu)O₂ samples ranging from 0.003 to 12.5% burnup were treated with mixtures of HCl and HNO₃ in open containers. Any remaining residue was then transferred to a fused-silica tube and successfully dissolved using the HCl system. Dissolution times varied with the amount of burnup of the samples and ranged from a few hours for samples with up to 8% burnup to 24 h for samples with up to 12.5% burnup.

As much as 0.1 g of high-fired (1000°C) ThO₂ and PuO₂ were dissolved in less than 24 h using the HCl system. Also, up to 0.25 g of low-fired (< 500°C) PuO₂ was dissolved in less than 24 h using either the HCl or the HNO₃ system.

This method has also been used for dissolving highly irradiated (Np-Zr-Pu-Ca) oxide samples using the HNO₃ system with increased HF concentration.

V. APPLICATION TO LARGER SAMPLES

The sealed-reflux dissolution system, with slight modification, has been successfully used to dissolve 500-mg samples of high-fired PuO₂ (1000°C in air) in less than 4 h. The necessary modifications, which differ from the RECOMMENDED PROCEDURE (Sec. III), include using a larger dissolution tube (Fig. 3), a different heating block (Fig. 4), and a different acid mixture, D (5 ml 12 M HCl, 3 drops 15 M HNO₃, and 5 drops 1.3 M HF). The

TABLE II
IMPURITIES LEACHED FROM BOROSILICATE GLASS AND FUSED-SILICA TUBES
DURING A 1-WK EXPOSURE

Impurity Element	Amount of Impurity (μg)			
	HCl System A ^a		HNO ₃ System B ^b	
	Borosilicate Glass	Fused Silica	Borosilicate Glass	Fused Silica
Li	4	< 0.2	2	< 0.1
Be	< 0.02	< 0.02	< 0.04	< 0.01
B	120	0.07	800	< 0.03
Na	300	1.5	200	< 0.3
Mg	10	1	8	0.5
Al	200	1	150	0.2
Si	120	70	40	20
P	< 6	< 5	--	--
K	10	< 3	12	< 1
Ca	20	2	16	0.5
Ti	4	< 0.2	0.8	< 0.1
V	< 0.4	< 0.3	< 0.8	< 0.2
Cr	0.4	< 0.2	0.4	< 0.1
Mn	0.4	< 0.2	0.8	< 0.1
Fe	10	0.3	16	0.4
Co	< 0.4	< 0.3	< 0.4	< 0.1
Ni	< 0.6	< 0.5	< 0.1	< 0.3
Zn	10	2	1	0.3
Ga	0.2	< 0.2	< 0.4	< 0.1
Ge	< 0.4	< 0.3	< 0.4	< 0.1
Sr	1	0.02	1	< 0.01
Zr	30	0.3	20	< 0.01
Nb	< 0.6	< 0.5	< 1	< 0.03
Mo	< 0.2	< 0.2	< 0.4	< 0.1
Ag	0.08	0.07	< 0.1	< 0.03
Cd	< 0.6	< 0.5	< 0.4	< 0.1
In	< 0.6	< 0.5	< 0.4	< 0.1
Sn	< 0.6	< 0.5	< 0.8	< 0.2
Sb	< 0.6	< 0.5	< 1	< 0.3
Ba	0.8	0.05	< 1	< 0.1
W	< 6	< 5	< 10	< 3
Pb	1	< 0.5	0.4	< 0.1
Bi	< 0.2	< 0.2	< 0.4	< 0.1
Cu	1.5	0.2	0.8	0.2

^a2 ml 12 M HCl, 1 drop 15 M HNO₃, and 1 drop 0.4 M HF, heated to 150°C for 1 wk.

^b2 ml 15 M HNO₃, 0.4 ml 12 M HCl, and 1 drop 0.4 M HF, heated to 200°C for 1 wk.

Fig. 3 Dissolution tubes for large samples.

pressures generated by this acid mixture in the larger dissolution tube (Table III) and the impurities leached from the borosilicate glass tubes during a 24-h exposure at 150°C with this acid mixture (Table IV) are similar to those found previously (Tables I and II).

Data are also included in Tables III and IV for another acid system, E (5 ml 15 M HNO_3 , 0.3 ml 12 M HCl , and 5 drops 1.3 M HF), which is applicable to the dissolution of uranium materials and nitride fuels. The recommended dissolution temperature is 150°C for the D acid mixture and 200°C for the E acid mixture.

Fig. 4. Heating block for large dissolution tubes.

TABLE III
PRESSURES DEVELOPED BY TWO ACID MIXTURES IN LARGE DISSOLUTION TUBES^a

Acid Mixture	Temperature (°C)	Pressure Developed [MPa (psi)]	
D	100	0.32	(47)
D	140	0.52	(75)
D	150	0.57	(82)
D	160	0.59	(86)
E	150	0.26	(38)
E	190	0.32	(47)
E	200	0.33	(48)
E	210	0.34	(49)

D: 5 ml 12 M HCl , 3 drops 15 M HNO_3 , and 5 drops 1.3 M HF .

E: 5 ml 15 M HNO_3 , 0.3 ml 12 M HCl , and 5 drops 1.3 M HF .

^aA large dissolution tube as shown in Fig. 3 was used.

TABLE IV

IMPURITIES LEACHED FROM LARGE BOROSIL-
ICATE GLASS TUBES DURING 24-H EXPOSURE

Impurity Element	Amount of Impurity (μg)	
	Acid Mixture D ^a	Acid Mixture E ^b
Li	< 1	< 1
Be	< 0.1	< 0.1
B	25	20
Na	60	40
Mg	3	3
Al	20	15
Si	200	150
P	< 30	< 30
K	< 10	< 10
Ca	3	5
Tl	1	< 1
V	< 1	< 1
Cr	< 1	< 1
Mn	< 1	< 1
Fe	5	1
Co	< 1	< 1
Ni	< 3	< 3
Cu	1	0.3
Zn	< 3	3
Ga	< 3	< 3
Ge	< 1	< 1
As	< 10	< 10
Rb	< 10	< 10
Sr	0.3	0.3
Zr	3	1
Nb	< 10	< 10
Mo	< 1	< 1
Ag	< 0.1	< 0.1
Cd	< 1	< 1
In	< 1	< 1
Sn	< 3	< 3
Sb	< 3	< 3
Te	< 10	< 10
Cs	< 10	< 10
Ba	< 1	< 1
Ce	< 10	< 10
Hf	< 10	< 10
Ta	< 30	< 30
W	< 10	< 10

TABLE IV (cont)

Impurity Element	Amount of Impurity (μg)	
	Acid Mixture D ^a	Acid Mixture E ^b
Tl	< 10	< 10
Pb	< 10	< 10
Bi	< 1	< 1

^a5 ml 12 M HCl, 3 drops 15 M HNO₃, and 5 drops 1.3 M HF, heated to 150°C for 24 h.

^b5 ml 15 M HNO₃, 0.3 ml 12 M HCl, and 5 drops 1.3 M HF, heated to 200°C for 24 h.

VI. DISCUSSION

The sealed-tube dissolution method has the advantage that a variety of acid systems, tailored for particular types of material, can be used. For example, the HF concentration can be increased if fluoride complexing is beneficial. The HF concentration in the acid solvent mixture can be increased as high as 0.5 M by adding 1 drop 27 M HF in place of the 1 drop 0.4 M HF. Also, an acid mixture consisting of HClO₄-HCl-HNO₃ has been successfully used, but extreme care must be taken with HClO₄.

If HCl is detrimental to subsequent analyses and is not wanted in the final solution, solid CO₂ can be used to generate the pressure in the HNO₃ dissolution system. A 100-mg pellet of CO₂ will generate approximately 0.3 MPa (40 psi) in the tube. Solid CO₂ can also be used with other acids, such as H₂SO₄, to enable them to be heated to temperatures higher than their normal boiling point at atmospheric pressure. Thus, a variety of other acids can be used, thereby greatly increasing the materials that can be dissolved using this method.

The rubber stopper used with the HCl system and the polyethylene stopper used with the HNO₃ system slowly deteriorated during a 5-day exposure to the acid fumes; therefore, a new stopper should be used with each sample. However, no pressure loss or particulate contamination of the sample from the stopper was observed after a continuous 7-day run with any of the acid systems.

With this dissolution technique several samples can easily be dissolved simultaneously, and a

considerable cost saving is accomplished by reusing the tubes. If dissolution tubes are reused, it is economical and convenient to have the top of the tube shaped to serve as a clamping surface (Fig. 5) for the semiball clamp. The rubber cushion and hose clamp are not needed with this tube design.

The sealed-reflux dissolution system is made of inexpensive and easily obtainable equipment and is safe, easy to use, and effective in giving a clean solution for subsequent analyses. The acid fumes are contained during dissolution to lessen the corrosion of surrounding equipment and enclosures.

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Fig. 5. Dissolution tube designed for repeated use.