

# AEC RESEARCH AND DEVELOPMENT REPORT

OAK RIDGE NATIONAL LABORATORY  
Operated By  
CARBIDE AND CARBON CHEMICALS COMPANY



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DATE: April 11, 1955  
SUBJECT: 25 PROCESS ASSISTANCE.  
For Period of March 21, 1955 to April 1, 1955  
TO: ~~W. A. Jenkins~~  
FROM: F. L. Culler

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OAK RIDGE NATIONAL LABORATORY  
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CARBIDE AND CARBON CHEMICALS COMPANY  
A DIVISION OF UNION CARBIDE AND CARBON CORPORATION

UCC

POST OFFICE BOX P  
OAK RIDGE, TENN.

April 11, 1955

Mr. W. A. Jenkins  
E. I. duPont de Nemours Company  
Explosives Department  
Wilmington 98, Delaware

Dear Bill:

25. Use of Thorex-type high temperature feed digestion at high  $\text{HNO}_3$  concentrations will prevent subsequent organic emulsion formation in the 25 extraction column, even when the dissolver solution is known to contain emulsion-producing impurities. Gross D.F.'s for three spiked-feed small pulse column runs were at least  $3 \times 10^4 \beta$  and  $5 \times 10^3 \gamma$  across both columns. Trickle dissolver tests using 2S Al sheet in the 5-in. D pipe unit yielded a 5 ft. packed height for a processing rate of 200 kg Al/day, equivalent to ~20 kg U/day when dissolving SR tubular elements. The packed height dropped to just under 3 ft. when the dissolving rate was cut in half.

Metallex. Thorium metal quality studies indicate that metal samples prepared by arc-melting sintered compacts are within target specifications (as set forth in DPST 54-582, Nov. 1954) except for the iron content. The Abbie "Dispersall" mixer has been tested briefly for the dry  $\text{ThCl}_4$  contacting with NaHg and probably will prove satisfactory for making 0.5 lb. batches of Th as quasi amalgam.

Very truly yours,

*F. L. Culler*

F. L. Culler, Director  
Chemical Technology Division

FLC:ACJ/pms

Attachment (1)

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## 1.0 25 PROCESS ASSISTANCE

### 1.1 LA Column Chemistry

Work is continuing on the organic emulsion problem under LA column feed-plate conditions. Application of variations of the Thorex head-end treatment, i.e., dehydration of feed impurities by high temperature digestion at high nitrate concentrations, has been studied using an emulsion-producing 2S Al bar-stock dissolver solution (1.8 M Al, 1 M H<sup>+</sup>, 0.008 M Hg<sup>+2</sup>) as the LAF. These experiments are summarized in Table 1. The results indicate that 3 hours digestion at the boiling point in the presence of 8 M HNO<sub>3</sub> at Al concentrations of 2 to 4 M, prior to readjustment to LAF Flowsheet conditions, will prevent organic emulsion formation. The treated LAF's (unfiltered) were batch-equilibrated for 1-1/2 minutes with 6% TBP-Amsco in the presence of neutral 0.75 M Al(NO<sub>3</sub>)<sub>3</sub> - 0.02 M Fe(NH<sub>2</sub>SO<sub>3</sub>)<sub>2</sub> scrub, using the volume ratio AF:AS:AX = 100:20:40, and the presence or absence of stable emulsions noted. Apparently the presence of H<sup>+</sup> ion during digestion is necessary for the dehydration, since digestion of ~5 M Al with essentially no acid present (see Experiment No. 3, Table 1) did not eliminate emulsion formation. In all other runs, a clear aqueous phase was obtained in 20 to 30 seconds and the organic cleared in 65-80 seconds, leaving a clean interface.

An attempt was made to produce emulsion by adding trace impurities to synthetic feed. This feed was batch equilibrated with 6% TBP-Amsco in the presence of 0.75 M Al(NO<sub>3</sub>)<sub>3</sub> - 0.02 M Fe (NH<sub>2</sub>SO<sub>3</sub>)<sub>2</sub> - 3.0 M HNO<sub>3</sub> scrub solution with the feed:scrub:solvent volume ratio of 100:20:40. Trace impurities (Fe, Mn, Cu, Ni, Ag, V, Ca, Mg, Si) in the same concentrations as determined by spectrographic analysis of 2S Al bar-stock were "spiked" into the system one at a time and the phase disengagement times noted after such addition. Although some variation of disengagement time was seen, no stable emulsions were produced by this method. Therefore, it was concluded that the impurities known to be present in the bar-stock must exist in different forms in actual dissolver solution.

### 1.2 0.75" Diameter Pulsed Column Facility

#### 1.21 Batch Dissolution of Dummy SR Fuel Elements

SR dummy fuel element #D-99 (2350 grams total weight) was dissolved in 50 liters of 7.4 M HNO<sub>3</sub> containing 0.005 M Hg(NO<sub>3</sub>)<sub>2</sub>. The reaction was initiated by heating to 90°C, and then controlled by applying cooling water for about 1 hour. Steam was then reapplied to maintain the dissolver at ~105°C. Table 2 shows the results of periodic sampling, and indicates that the element was essentially completely consumed within a period of about 2 hours or less.

*Handwritten notes:*  
SR  
D-99

Table 1

Feed-Al bar-stock dissolver solution:

1.8 M Al  
 1.0 M HNO<sub>3</sub>  
 0.008 M H<sup>+</sup>2

Standard equilibration test for emulsion:

50 ml of designated LAF  
 10 ml neutral 0.75 M Al(NO<sub>3</sub>)<sub>3</sub> - 0.02 M Fe(NH<sub>2</sub>SO<sub>3</sub>)<sub>2</sub>  
 as LAS  
 20 ml of 6% TBP-Amsco as LAX  
 Equilibrate 1-1/2 minutes

Experiments No.	Dissolver Solution Pretreatment	Observations
1	Evaporate to 1/4 vol.; add equal vol. 16 M HNO <sub>3</sub> ; digest 3 hr. Evaporate off acid (142°C) and readjust to 1.0 M H <sup>+</sup> and 1.8 M Al.	No stable emulsion
2	Evaporate to 1/2 vol. (130°C) add equal vol. 16 M HNO <sub>3</sub> ; digest 3 hr. Evaporate off acid (130°C); add equal vol. of 2 M HNO <sub>3</sub> : H <sup>+</sup> = 2.3 M, Al = 1.8 M.	No stable emulsion
3	Evaporate to 1/3 vol. (135°C), digest 3 hr. Add back condensate: H = 1.0 M, Al = 1.8 M.	Obtained stable emulsion
4	Evaporate to 1/2 vol. (130°C); add equal vol. 16 M HNO <sub>3</sub> ; digest 3 hr. Evaporate off acid (130°C); dilute back to original volume with H <sub>2</sub> O: H = 1.0 M, Al = 1.8 M.	No stable emulsion

(Note: In all cases a clear aqueous phase was obtained in 20 to 30 sec.; with the exception of Experiment No. 3, a clear organic phase was obtained in 65-80 seconds.)

Table 2

Dissolution of Dummy SR Tubular Fuel Element in 7.4 M HNO<sub>3</sub>-0.005 M Hg(NO<sub>3</sub>)<sub>2</sub>

Dissolving Time Hours	H <sup>+</sup> Conc., M	U Conc., mg/ml	Al Conc., mg/ml	Volume, liters	Weight Dissolved
0.5	1.76	2.89	36.7	50	84.5
1.0	--	3.80	40.9	--	--
2.0	0.74	4.12	42.7	--	--
2.5	--	3.97	43.7	--	--
3.0	0.79	4.01	44.1	--	--
3.5	--	4.05	47.2	--	--
4.0	0.83	4.01	44.3	48	99

1.22 Flowsheet Testing

To date, three column runs were made utilizing feed prepared by dissolving dummy SR tabular fuel elements, digesting, filtering, and spiking with fission products from irradiated U-Al alloy. Runs HCU-1 and HCU-2 were of 7 hours duration and Run HCU-3 lasted 11 hours. The following flowsheet conditions were used:

1AF/75 ml/min = 3.8 g U/l, 1.0 M HNO<sub>3</sub>, 1.8 M Al(NO<sub>3</sub>)<sub>3</sub>, 0.005 M Hg(NO<sub>3</sub>)<sub>2</sub>, 1.5 - 5.0 x 10<sup>7</sup> Gross β c/m/ml, 3.4 - 8.1 x 10<sup>7</sup> Gross γ c/m/ml.

1AX/30 ml/min = 6% TBP in Amsco Special Naptha No. 1

1AS/15 ml/min = 0.75 M Al(NO<sub>3</sub>)<sub>3</sub>, 3.0 M HNO<sub>3</sub>, 0.02 M Fe(NH<sub>2</sub>SO<sub>3</sub>)<sub>2</sub>

1BX/11 ml/min = 0.01 M HNO<sub>3</sub>

Results of run HCU-1 (AF = 1.5 x 10<sup>7</sup> Gr β c/m/ml) indicated that the A column had reached equilibrium with respect to the fission products at the end of about 5 hours (~6.5 volume changes), and that the B column had reached equilibrium at the end of about 6 hours. The Gross β decontamination factor (D.F.) across the A column was about 2 x 10<sup>4</sup>, and about 8 x 10<sup>4</sup> across both columns; the Gross γ DF across both columns was 1 x 10<sup>4</sup>.

Table 3 shows decontamination data from Run number HCU-2 (AF = 2.5 x 10<sup>7</sup> Gr β c/m/ml).

Table 3

First Cycle Decontamination - Run No. HCU-2

F.P. Activity	1AF, c/m/ml	1BP, c/m/ml	DF
Gross β	2.47 x 10 <sup>7</sup>	4.08 x 10 <sup>3</sup>	2.57 x 10 <sup>4</sup>
Gross γ	9.42 x 10 <sup>6</sup>	7.40 x 10 <sup>3</sup>	5.33 x 10 <sup>3</sup>
Ru β	1.38 x 10 <sup>6</sup>	148	3.91 x 10 <sup>4</sup>
Zr γ	1.81 x 10 <sup>6</sup>	2.3 x 10 <sup>3</sup>	3.29 x 10 <sup>3</sup>
Nb γ	3.62 x 10 <sup>6</sup>	2.4 x 10 <sup>3</sup>	6.32 x 10 <sup>3</sup>
TRE β	1.53 x 10 <sup>7</sup>	< 10 <sup>2</sup>	> 10 <sup>5</sup>

Results of Run HCU-3 confirmed these decontamination factors on a feed having about twice the gross activity of that in HCU-2. The decontamination factors for Gross β and Gross γ activities were 3 x 10<sup>4</sup> and 5 x 10<sup>3</sup>, respectively. Results of individual fission product decontamination are not presently available.

Column operation was very smooth throughout all runs, and essentially no interfacial material or emulsions built-up during the operation.

### 1.3 Mixer-Settler Facility

An excessive amount of difficulty with the Zenith metering pumps, caused by corrosion of internal parts (made of Type 400 stainless steel) in contact with TBP in Amsco, necessitated frequent shutdowns and repairs. All solutions in contact with the pumps have been changed to either water or straight Amsco in an effort to keep the pumps operating.

Pump failures ruined the tracer level run that had been started in the mixer-settler unit. Another run is scheduled for 3-28-55.

### 1.4 Trickle Dissolver Tests

Two trickle dissolvings of 2S Al sheet have been made in the 5-in. D pipe system. A packed height of 5 ft. was obtained in one run made at a processing rate of 200 kg Al/day (equivalent to ~20 kg U/day in SR tubular elements), while in a run at one half this rate the packed height was just under 3 ft. The results of these two runs parallel the results obtained earlier for Al slugs, but the rate vs. packed height curve is shifted to roughly a 65 kg/day higher rate for all packed heights.

About 10 g solids (mostly magnetic) was found in the bottom of the dissolver following the dissolution of about 500 lbs. of 2S Al. These solids dissolve in  $\text{HNO}_3$ . Analyses are currently being performed.

## 2:0 METALLEX

### 2.1 Reduction of $\text{ThCl}_4$ with NaHg

Experiments were continued in which  $\text{ThCl}_4$  powder was reacted with NaHg in glass apparatus at temperatures ranging from ~130-230°C using pitched blade agitators and no baffling in the system. Analytical results of these experiments show ~80-90% reduction of  $\text{ThCl}_4$  to Th quasi-amalgam based on analysis of acid and water wash solutions, in experiments carried out about 160°C. In one experiment a maximum temperature of 153°C was recorded and a low conversion of  $\text{ThCl}_4$  to thorium amalgam of ~25% was found.

Other experiments were carried out by W. Schaffer in which a small Abbie "Dispersall" mixing unit was used as a reactor. This unit may be described as containing a mixing device somewhat similar to a coffee mill. It provides a high shear to the reactants and may be operated at variable speeds. Analysis of reactants from the initial run using this equipment while operating at a temperature range of ~25-145°, and containing 195 gm Th as  $\text{ThCl}_4$  produced a good grade of quasi-amalgam with a yield of >50%  $\text{ThCl}_4$  reduction to Th amalgam. Incomplete analysis of later runs show this apparatus to be well suited to production of thorium quasi amalgam on a scale of the order of ~1/2 to 1 lb. Th per run.

Reduction of ThO<sub>2</sub> by NaHg

Experiments were carried out in an attempt to react ThO<sub>2</sub> (produced by thermal decomposition of Th<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub> at 650°C) with NaHg, without success. The reactants mixed extremely well, and visually appeared as the reactants did when ThCl<sub>4</sub> is used in place of ThO<sub>2</sub>. However, on washing the amalgam or dry filtering to separate the bulk of the Hg, no quasi or Hg containing Th was found. Likewise, the usual black thorium-mercury compound was not observed. Runs with ThO<sub>2</sub> prepared at lower temperatures, as well as dried Th<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>) and ThOCl<sub>2</sub>, are planned.

2.2 Metal Quality Studies

Samples of metal prepared by arc-melting sintered compacts showed the following properties:

Table 4

Component	Sample 1	Sample 2	Sample 3
ThO <sub>2</sub> , by HCl-insoluble	0.58%	0.76%	0.59%
HNO <sub>3</sub> -HF insoluble	0.45%	0.40%	0.35%
Oxygen by vacuum fusion	480 ppm	1220 ppm	420 ppm
Nitrogen by vacuum fusion	225 ppm	330 ppm	190 ppm
Nitrogen by Kjeldahl	150 ppm	330 ppm	190 ppm
Carbon	400 ppm	440 ppm	430 ppm
Hydrogen by vacuum fusion	8.2 ppm	13.0 ppm	7.8 ppm
Iron	1200 ppm	650 ppm	1100 ppm
Mercury	21 ppm	17 ppm	9 ppm
Sodium	12 ppm	<10 ppm	<10 ppm
Annealed density	11.67	11.65	11.63
Hardness as cast, R <sub>B</sub>	10, 10, 12	34, 34, 32	7, 11, 13
Hardness as annealed, R <sub>B</sub>	<0, <0, <0	24, 25, 26	3, 6, 2

All properties except iron content are within target specifications as set up by the Quality Working Committee on Thorium Specifications (DPST 54-582) Nov. 1954. It is of interest to note that chemically, the only significant differences which might account for the higher hardness of sample no. 2 are oxygen and hydrogen.

A study of possible reasons for spalling and cracking of sintered compacts showed that impurity contents of ThO<sub>2</sub> below 3.0%, sodium below 100 ppm, carbon, nitrogen, hydrogen and mercury in the quantities encountered prior to arc melting could not account for this type of behavior. Sodium ranged between 30 and 240 ppm; ThO<sub>2</sub> between 1.0 and 3.9%; Hg between 4 and 730 ppm; carbon between 210 and 790 ppm; nitrogen 72-310 ppm; hydrogen, 4 to 80 ppm. Sodium content above 100 ppm and ThO<sub>2</sub> above 3.0% appeared to increase cracking of sinters.

### 2.3 Phase Study of the Thorium-Mercury System

Studies of the thorium amalgams indicate that the  $\text{ThHg}_3$  hexagonal close packed phase is stable at elevated temperatures (about  $200^\circ\text{C}$ ) in the presence of free mercury. At room temperatures in the presence of free mercury a new phase appears which is identified by its X-ray diffraction pattern. This new phase (phase II) exhibits intense diffractions of the  $\text{Cu K}\alpha$  X-rays at Bragg angles of  $14.0^\circ$ ,  $17.5^\circ$  and  $29.0^\circ$ . This phase II forms slowly and becomes observable when the amalgam has been at room temperature for several days. Also phase II is the only solid phase found in amalgams which had been formed by low temperature reductions,  $50^\circ\text{C}$ .

Studies of the amalgam from the pressing step following filtration of the amalgam indicate that as the thorium concentration increases from 4 to 15% the amount of the  $\text{ThHg}_3$  hexagonal close packed phase increase and the amount of the phase II decreases.