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November 14-18, 1955

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Chemical Development Sub-Section
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TRIP REPORT
DuPONT SAVANNAH RIVER PLANT, O.R.N.L., AND K-25 PLANT

I. DuPONT SAVANNAH RIVER PLANT

The writers visited the du Pont Savannah River Plant on November 14 and 15, 1955, for discussions on operational and processing problems pertaining to the separations plants. Personnel contacted included J. W. Morris, R. I. Martens, D. S. Webster, G. S. Nichols, T. H. Siddal, D. G. Karraker, A. T. Davis, A. N. Parkes, L. C. Peery, D. Dahlstrom, M. Shroder, F. W. [illegible]ober, E. R. Fryer, and R. M. Girdler.

The following items were discussed in varying degrees of comprehensiveness. Only the highlights are given below and in some cases more information can be obtained by contacting the writers.

Paddle Pumps. The applicability of paddle pumps (4 blade flat paddle impeller, no submerged bearings) for low head applications has been demonstrated. Although the pump gives a head efficiency of 70% based on the centrifugal force at the impeller tip, pump application is limited by shaft length which is governed by critical speed. A five-foot long shaft for 1800 rev./min. service must be 4-inches in diameter at the top. Lower speeds, such as 900 rev./min., permit increasing shaft length by the square root of two, but correspondingly reduce head capacity characteristics. No significant advantage is seen by du Pont personnel in using other than a flat paddle impeller.

Continuous Solvent Washing. The testing of a continuous solvent washing technique in an agitated tank is being carried out on a "cold" plant scale (10-foot diameter by 10-foot high tank) and some of these units are already in use in the SRP Purex Plants. The ability of the unit to provide adequate agitation between organic (30% TBP in Ultrasene) and aqueous (5% sodium carbonate) phases while producing sparkling clear organic phase as effluent has been demonstrated.

Heat Balances as a Measure of Stage Efficiency. The thermal efficiency of a mixer-settler stage has been shown to correlate well with mass transfer efficiency. Temperature measurements of the influent and effluent streams are taken and

$$1 - E = \frac{\text{Output } \Delta t}{\text{Input } \Delta t}$$

where E is a measure of the stage efficiency. This method is being used in scouting the effect of changes in mixer speed, impeller design, interface position, etc., on mixer-settler stage efficiency.

Solvent Quality. It is the opinion of SRP personnel that the zirconium complexing agents which form in the solvent and contribute to poor decontamination are formed almost exclusively from olefins in the diluent. The complexing compounds are not now necessarily believed to be high molecular weight ketones and esters as previously reported. The use of an oxidant (Na_2CrO_4) for removing the zirconium complexing agents from solvent was studied, and it was found applicable if carried out at 70°C. However, the resulting solvent degraded 6 to 8 times as fast as unoxidized material. The known methods for removing the Zr complexing agents from the solvent include: a charcoal column, an alumina column, steam distillation, and vacuum distillation. Vacuum distillation is considered the most positive and is being considered for plant installation.

Technical personnel are continuing to develop the "F" test for solvent quality. This test measures the amount of zirconium which is irreversibly extracted by solvent and is said to be a measure of the change in solvent quality due to chemical degradation. Oak Ridge zirconium tracer is used to follow zirconium extraction. The tracer must be freed of oxalate and its specific activity determined. More reproducible results are obtained if the tracer is extracted into TBP and stripped into 3 M HNO_3 before use. Special counting techniques are used to determine zirconium beta activity in counted samples. Results are now expressed as moles of zirconium retained per billion liters of solvent. Results for virgin solvent range from five to ten on this scale. Details of the test including tracer preparation and counting methods may be obtained from R. E. Burns.

Silica Gel Columns. Savannah River silica gel columns are two feet in diameter by sixteen feet high. They are loaded with 14-40 mesh refrigerator grade Davison silica gel. The columns are operated at temperatures from 55 to 60°C. with a flow rate giving a residence time of about 30 minutes (less than 5-6 min. is considered critical). Feed solution to the columns is 1.6 M UNH-0.3 M HNO_3. Normal decontamination factors (gross gamma) range from eight to twenty. Down flow regeneration of the columns is done routinely after passing 600,000 pounds of solution through them. No prefilter is used. The gel is supported on a graded sand and gravel bed. There have been occasions when little or no decontamination was obtained on a particular batch of feed. These batches have been disposed of by blending with product which was better than specifications. Increased decontamination can be obtained by operating the columns at higher temperature. Increased standing time between solvent extraction and silica gel treatment decreases decontamination obtained in the latter.

Precipitation of Plutonium Trifluoride. A readily filterable plutonium trifluoride can be precipitated by the simultaneous addition of equal volumes of ion exchange eluate solution and 2.7 N HF solution to one half volume of 0.1 M HNO_3. Good agitation is required. About one-half hour is required for combination of the solutions on a 7 liter volume basis. The precipitate formed can be filtered in about one hour (plant scale). Washing the precipitate with ethanol produces a free flowing powder containing one to two per cent water although free flowing powders have been obtained without the ethanol wash. X-ray structure patterns of the ethanol washed powder show no lines except those for PuF_3, and it is believed the powder is at least 95 per cent PuF_3. No reduction experiments with the powder have been done. A plant scale reduction is planned for early in December.

Plutonium loss as a function of time between elution and precipitation increases 0.008 g./l. at very short times to 0.310 g./l. at six days. In the eluate, Pu (IV) increases six per cent per day for seven days and then remains constant at about 42 per cent. As much as 0.5 g./l. of iron in the eluate has no significant effect on the precipitation process or on the amount of iron in the precipitate. The presence of sulfate (ranging from 0.001 to 1 M) in the 0.1 M HNO_3 increases the filtering time but has no effect on plutonium loss. Teflon frits are used as filters.

Ferrous Sulfamate. Ferrous sulfamate is currently purchased (from du Pont or General Chemical) as a 50 per cent solution at 22 cents per pound in 150-pound carboys. After the carboys are opened, a slow oxidation of ferrous to ferric iron and precipitation of ferric hydroxide occurs. This has caused some plugging troubles but can be prevented readily by making the solution five per cent in HNO_3 when the carboys are opened.

Resin for Ruthenium Decontamination. If ICU solution is digested with 0.2 wt.% thiourea and passed through a tower of Permutit H or Amberlite IRC-50 (a carboxylic resin), a ruthenium D.F. of 8 to 16 is effected. The ruthenium is removed in a narrow band at the top of column. The operation is not a function of liquid flow rate, and the ruthenium can not be eluted from the resin. Urea, hydrazine, or oxalate in the digestion step do not permit similar decontamination.

Plutonium E_a^0 in IB Column. It has been demonstrated that the Pu E_a^0 increases from 5×10^{-3} to possibly as high as one as the Pu concentration decreases in the IB Column. SRP personnel believe this to be a chemical phenomenon. It is believed, however, that with sufficient stages in the IB Column (e.g., 12 agitated zones) all of the required U-Pu partitioning can be accomplished in one cycle.

Jets. The shops at TNX are now making all the transfer jets used at SRP. By utilizing a common body with screw-in nozzles and diffusers, jets can be fabricated quite cheaply. They indicate a willingness to help out on any particular jetting problem.

TNX Problems. The problems being investigated at TNX (the "cold" semi-works) include natural recirculation evaporation, vapor-liquid deentrainment, solvent washing, flat-plate dissolution, and jumbo (20 batches/day capacity) mixer-settler performance.

Calcination. Savannah River Plant produces UO_3 having a reactivity of about 1.15 (standard test: 590°C. reduction, 410°C. hydrofluorination). The process is carried out batchwise in 6-ft.-diameter pots having a capacity of 2400 pounds of UO_3. Agitators which rotate at 18 rev./min. are powered by 30 horsepower motors. The process is controlled by maintaining flue gas temperature at 500 to 550°C. This results in a pot wall temperature of 850°C. and a powder temperature between 200 and 225°C. Under these conditions, the sagging of pot bottoms up to one inch has been experienced. A program to minimize pot bottom sagging by heat control is underway. The denitration process is carried out on a 10 to 12 hour cycle consisting of:

Boil off	3 hr.
Conversion (to mastic stage)	4 hr.
Powder heating	2 hr.
Cooling with agitation	0.5 hr.
Gulping (powder unloading)	0.75 hr.

II. O.R.N.L.

O.R.N.L. was visited on November 16, 1955, for discussions of current developments on problems of interest to H.A.P.O. Personnel contacted included F. L. Culler, J. Moore, E. M. Shanks, A. C. Jealous, W. Lewis, Hancher, E. I. Higgins, R. Blanco, W. K. Eister, A. Irvine, and J. R. Engle.

Continuous Ion Exchange. Continuous ion exchange in the Higgins contactor as described in O.R.N.L. reports has been demonstrated in 2, 6, and 12-inch diameter columns and is considered ready for commercial use. The relative merits of the Jury contactor and the Weiss column for continuous ion exchange were discussed. The Weiss column which is essentially a hydraulic classifier can handle slurries containing 40% solids, which is about four times the solids content of slurries which can be handled by the Higgins unit. However, the Higgins unit has a considerably higher throughput than the Weiss unit (300 vice 90 gal./(hr.)(sq.ft.). It was found that the Higgins unit designed for U refining at Grand Junction, Colorado, demonstrated the need for redesign to reduce pressure drop and permit satisfactory resin movement without channeling. O.R.N.L. expects to have a Higgins unit for Pu purification and concentration installed in their Metal Recovery Plant in the near future.

Diban Process for the Decontamination of Aluminum-Containing Wastes. A process for removing cesium and strontium from aluminum-containing wastes is under development. The acidic wastes are evaporated to a temperature of about 163°C. At this point the material is nearly solid. Dilution of the material with water to about 1 M aluminum produces a colloidal suspension. The solid material present contains most of the aluminum. This suspension is then passed through a Higgins-type continuous cation exchange column. Most of the aluminum passes through the column while cesium and strontium are quantitatively adsorbed. For cesium and strontium recovery purposes, aluminum which does adsorb is eluted from the column first with oxalic acid. Cesium and strontium are eluted with HNO_3. Ref. ORNL-1084.

Jet Contactors. A few experiments have demonstrated the possibility of approaching 100 percent stage efficiency for liquid-liquid contacting by using a jet as the contactor.

Moving Bed Conversion of UO_3 to UF_4 and UF_6. The passage of UO_3 pellets mixed with starch (11 pounds UO_3 to 1 pound starch) countercurrent to HF in a tower produces UF_4 assaying 99+% UF_4. The current problem concerns the removal of 0.1 to 0.3% carbon in the UF_4.

Very limited experimental work has been done on the conversion of UF_4 to UF_6 by the following reaction:

$$2\ UF_4 + O_2 \xrightarrow{800^\circ C.} UO_2F_2 + UF_6$$

A tower for carrying out this process was attached to the bottom of the UO_3 to UF_4 tower and UF_6 production was demonstrated.

Purex Solvent Recovery. Solvents recovery in the Metal Recovery Plant is currently being done by a Na_2CO_3 wash in a pulse column followed by centrifugation. It is planned to install two spray columns in series, one for Na_2CO_3 wash and the second for dilute HNO_3 wash. It is also planned to test the use of Dorrclones for deentrainment removal in place of the centrifuge. The Dorrclones require a 25 lb./sq.in. pressure drop, and it is expected that a 5 to 30 percent solvent recycle to the spray columns will be required.

Continuous Uranium Dissolution. Continuous dissolution of aluminum-jacketed uranium Clinton slugs has been practiced in the Metal Recovery Plant for some time. The dissolver is a 42-in. I.D., 600-gallon tank (250 gal. working volume) equipped with a steam coil and jacket. Individual slugs are loaded at 10 to 15-minute intervals by a pneumatic ram device which requires some manual slug manipulation. Product is removed at a controlled rate and the 7 M HNO_3 (containing 0.005 M Hg) feed rate is controlled by liquid level in the dissolver. The dissolver contents are kept at 105°C. with 10 to 15 lb./sq.in. steam pressure on the coil. The capacity of the unit is estimated to be 1500 pounds U/day limited by the gas handling facilities. The unit had a maximum capacity for batch dissolution of 700 pounds U/day. No samples have been taken to define the amount of hydrogen in the off-gas, but it is expected that there is sufficient air in-leakage to keep the hydrogen concentration below 1 percent.

Slug Jacket Removal. Some progress has been made in the chemical removal of non-aluminum slug jackets. Mechanical dejacketing was attempted employing K.A.P.L.-type dies but failed due to jamming of the slugs in the dies. O.R.N.L. personnel are currently interested in rolling techniques, and report that heating the slugs to 400°C results in breaking the bond between the jacket and the slug.

III. K-25 PLANT

The K-25 Plant at Oak Ridge, Tennessee, was visited by the writers on November 17 and 18, 1955, to discuss the problems involved in converting continuously-produced UO_3 to UF_4 and to integrate the development efforts of K-25 and H.A.P.O. directed toward continuously-produced UO_3. Personnel contacted include: D. M. Lang, P. Van Strum, S. H. Smiley, D. C. Brater, J. Pashley, J. W. Michel, H. Bernhart, K. E. Rapp, E. J. Barker, and B. Thompson.

A meeting which included representatives of H.A.P.O., Hanford A.E.C., K-25, Oak Ridge A.E.C., Paducah, and Washington A.E.C. (about twenty-five people) was held to discuss the impact of continuously-produced UO_3 having similar quality to that produced to date on the conversion to UF_6. Production schedules for H.A.P.O. from July 1956 to March 1957 call for an average output of 475 tons U/month from the pots and 200 tons U/month from the continuous units. It was estimated by K-25 personnel that such quantities of continuously-produced UO_3 could be processed by consuming additional fluorine at a cost of $90,000/year. It was pointed out that if the ratio of pot-produced to continuously-produced decreased below 1.5/1, the material could not be processed because of capacity limitations which could not be compensated for by additional fluorine. It was decided that in view of the production schedules July 1956 would be satisfactory for a decision on the need for further conversion plant expansion. A review in July, 1956 would allow a year lead time to carry out the expansion.

The situation regarding the quality of continuously-produced UO_3 will be reviewed again at that time. In the interim both K-25 and H.A.P.O. will direct development efforts towards improving the UO_3 quality.

K-25 personnel believe that they can estimate a relative reactivity of UO_3 to UF_4 conversion from their pilot plant data. It was found further that a laboratory reactivity test using 925°C. and 2 hours for reduction and 550°C. and 3 hours for hydrofluorination conditions gives results in general agreement with pilot plant results. Under test conditions, the standard powder is almost completely converted to UF_4. While it is recognized that this test is not applicable for measurement of performance of powders better than the standard, it is believed that it more nearly represents plant conditions and that powders which exhibit less conversion than the standard in the test will also behave poorly in the plant.

The former standard reactivity test (2 hours at 590°C. for reduction and 1/2 hour at 410°C. for hydrofluorination) predicts appreciably higher conversions than obtained in the pilot plant. A comparison of the reactivity data, together with additional pilot plant and laboratory data on representative pot-produced and continuously-produced UO_3 samples, is given in Table I. A thermobalance reduction test is also proposed for characterizing new powders. To be considered satisfactory for plant use a UO_3 powder must be 98 percent reduced to UO_2 at 560°C. in no more than 10 minutes.

Material SHS - 11 was produced in the H.A.P.O. 16-in. calciner from 100 percent UNH containing a nominal 1000 ppm. SO_4 at a feed point temperature of 230°C. with steam injection to the reactor (same conditions as SHS - 10) and subsequently heated at 450° for two hours. This technique succeeded in producing a UO_3 of high surface area which was retained by the UO_2. Despite this, the conversion to UF_4 was not appreciably better than that shown by sample SHS-10 which was not heated subsequent to calcination.

Electron microscope pictures have been taken of a variety of oxides, but no definite correlation has as yet been established between structure and reactivity.

X-ray diffraction as an identification tool for reactive oxides shows some promise but a considerable amount of basic work remains to be done. The data below are excerpts from a recent K-25 Progress Report:

> A summary of crystal identities and reactivity ratios (vs. hydrate standard[1]) for all oxides examined during the past five months is as follows:
>
> 1. Seven crystals have been identified and designated as UO_3I, UO_3II, UO_3III, $UO_3 \alpha H_2O$, $UO_3 \beta H_2O$, $UO_3 2H_2O$, and the compound Y observed at Battelle. In addition, an amorphous UO_3 has been observed.
> 2. Compared to hydrate standard, which by X-ray diffraction is $UO_3 2H_2O$, all the oxides but three with reactivity ratios greater than 1.00 were UO_3 type II. Two were amorphous UO_3 and one was UO_3III[2].
> 3. Mallinckrodt, Savannah River, and SHS-4 (good sample) contained UO_3III and $UO_3 \alpha H_2O$ along with traces of compound Y.
> 4. Compound Y prepared in the laboratory had a reactivity ratio of 0.89 and $UO_3 \alpha H_2O$ had a reactivity ratio which ranged from 0.5 to 0.96.
> 5. All samples which were only UO_3III made by direct denitration (with the exception noted in 2) had reactivity ratios less than 0.6.
> 6. UO_3I oxides ranged in reactivity ratio from 0.82 to 0.91.
> 7. Three U_3O_8 oxides prepared from UO_3III showed reactivity ratios from 0.89 to 0.98.
> 8. The sample of SHS-4 with the higher reactivity was primarily $UO_3 \alpha H_2O$ while the sample with the lower reactivity was primarily compound Y.

Reduction and Hydrofluorination in a Fluidized Bed. Initial attempts at reduction and hydrofluorination in a fluidized bed were carried out batchwise in a 1.5-in. diameter by 24-in. high Monel reactor. Unground, continuously-produced UO_3, used as the feed for the reduction step, was found to fluidize well. About ten runs were made. Ninety-five to ninety-eight per cent reduction was obtained at temperatures above 950°F., and 95 per cent conversion to UF_4 was obtained with a 3-hour retention time at 770°F.

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(1) Hydrate has a reactivity of 2 to 2.5 compared to Mallinckrodt UO_3.
(2) The sample history is uncertain and is being checked.

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The reactor was scaled up to include two 6-in.-diameter-leg, 24-in.-high reactors in series. Ninety-seven to ninety-eight per cent reduction could be achieved at 1100°F., 20 to 25 pounds/hour, and 3 to 4 hours residence time. Results of the hydrofluorination tests are given in Table II. As can be seen conversions as high as 95 per cent have been obtained. It is visualized that the best conversion and HF utilization will result from a single reduction reactor followed by three hydrofluorinators in series.

UO_3 Additives. Until the magnitude of the sulfur corrosion problem in the reduction reactors is better defined, K-25 personnel would prefer to see the quantity of sulfur additive in UO_3 limited to no more than about 150 parts of S per 10^6 parts of uranium. Objectionable additives (because they form volatile fluorides) are Cr, W, Mo, Ta, Ti, Nb, and Ru. P, B, and C are also objectionable (0.1 wt.% C increases fluorine consumption approximately 5 per cent). Co, Ni, and Al are tolerable within metallic impurity specifications.

Fluorothene. The facilities at K-25 for fluorothene fabrication were inspected. K-25 personnel are willing to fill orders for either stock or specially fabricated items. Catalogs of stock items were obtained.

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TABLE I
UO_3 EVALUATION

Plant Hydrofluorination			Reactivity Tests					Surface Areas, Sq.M./G.						Percent Conversion In Thermobalance Tests			
idence me, urs	Percent Conversion	Reactivity(2) Ratio	590 and 410 °C.	590 and 550 °C.	760 and 550 °C.	925 and 410 °C.	925 and 550 °C.	UO_3	590 °C. UO_2	925 °C. UO_2	Plant UO_2	Plant UF_4	Lab. UF_4	410°C.		550°C.	
														30 Min.	90 Min.	30 Min.	90 Min.
.6	84.5	1.00	1.00	1.00 (95%)	1.00 (97%)	1.00 (80%)	1.00 (93%)	1.15	1.97	1.43	0.73		0.33			82.0	97.2
.0	75.0																
O_2 prepared at 925°C.																	
.7	93.0	0.90	1.25	1.02	1.01	1.15	0.99	1.54	3.23	2.48	1.71	0.35	0.26	73.0	85.7	71.2	90.8
.2	86.0															83.2	90.5
O_2 prepared at 925°C.																	
					0.97		0.97	1.68			1.04	0.19				80.2	93.9
O_2 prepared in plant screws																	
														70.2	83.7		
.7	89.0	0.99	1.27	1.00	1.03		1.03				1.48	0.35		84.4	94.0	90.1	98.0
.5	90.5	0.95	1.15	1.01	1.01		1.03										
.6	77.0	0.86	1.35														
.2	75.0																
.0	81.5	0.95	1.45														
			1.20				0.90										
.5	80.0	0.84	1.00														
.0	73.5	0.77	1.04	0.65			0.82										
O_2 prepared at 925°C.														84.8	92.5	82.2	90.6
			1.19		0.74		0.70									47.7	61.7
O_2 prepared at 925°C.																74.2	84.0
.0	60.0	0.63	1.01		0.88		0.76									49.9	62.0
d in pilot plant (700°C.)			0.58											76.4	86.3		
.1	65.8	0.68	1.38	0.92			0.78	4.69	4.92	3.66			0.19	90%/13 min.		39.0 83.5	47.6 87.0
d in pilot plant (670°C.)			0.78				0.73							58.3	66.3		
d at 925°C.																72.2	80.7

als designated SHS were produced in 321 Building continuous calciner.
ted from pilot plant tests. Standard conversion assumed to be 95% after 4 hours.

TABLE II

PRODUCTION OF UF_4 IN FLUIDIZED BED

UO_2 feed produced by fluid bed reduction of continuously produced UO_3

Run No.	Product Rate, Lb./Hr.	Retention Time, Hr.	Temp., °F.	Conversion, % UF_4 in Prod.	% HF in Inlet Gas	% HF in Outlet Gas
1	12		700	72	44	32
2	12		1000	75	100	75
3A	23	3.2	700	41.5	43	19
3B(1)	18	4.2	925	75.7	100	82
3B(1)		5.1	655	74.4	100	82
3C(2)	16.4	4.6	1000	91.8	100	76
4(3)			1000	9[illegible].8	100	-
5	5	14.8	700	84.6	100	82
6	6	12.2	700	95.4	100	84
7	12 to 15		800	78	100	78
8	12.5		700	84	100	-

Notes:
(1) Product from 3A used as feed.
(2) Product from combined 3B as feed.
(3) Batch run; 5 hr. duration.