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TRIP REPORT - CONTINUOUSLY PRODUCED UO_3
APRIL 25-29, 1955

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TRIP REPORT - CONTINUOUSLY PRODUCED UO_3
APRIL 25-29, 1955

I. K-25 PLANT, OAK RIDGE, TENNESSEE

INTRODUCTION

The writer visited the K-25 Plant at Oak Ridge, Tennessee on April 25-27, 1955 in order to observe the pilot-plant reduction and hydrofluorination of Hanford UO_3 produced continuously in the 16-inch-diameter by 8-ft.-long semi-plant-scale denitrator. Discussions were held principally with Messrs. S. H. Smiley, C. C. Littlefield, and J. H. Pashley. Other K-25 personnel contacted on the problem of UNH denitration included Messrs. B. H. Thompson, A. H. Marshall, H. E. Rapp, J. S. Fox, N. C. Orrick, E. J. Barnes, J. A. Bernhard, D. M. Lang, and P. Venstrum.

SUMMARY

The results of the vibrating tray pilot plant runs completed on the test lot of UO_3 produced during Run B-18A (described in Table I) showed that only about 80% of the as-produced material reduced to UO_2 at standard operating conditions. Increased retention time on the reduction tray increased the amount of material reduced but lowered the reactivity of the UO_2 to subsequent hydrofluorination. The conversion of UO_2 from the as-produced UO_3 was generally poor; i.e., 50 to 60% as compared to a normal conversion of 90-to-95%.

After grinding, about 95% of the UO_3 from Run B-18A reduced to UO_2 under standard conditions. Conversions of UO_2 to UF_4 up to 80% were achieved during the writer's stay. It was the opinion of the K-25 personnel that further adjustment of the hydrofluorination conditions would produce the desired 90-to-95% conversion.

DESCRIPTION OF PILOT PLANT

The pilot plant at K-25 consists of two vibrating trays, one for reduction of UO_3 to UO_2 and one for the hydrofluorination of UO_2 to UF_4.

Reduction Tray. Reduction is carried out on a tray 10-ft.-long by 6-in.-wide which vibrates between 500 and 850 cycles/min. at an amplitude of 0.25 in./cycle. The heating elements are divided into three sections of equal length and heat input. Pure hydrogen at a rate sufficient to produce a 1000 to 1500% excess flows countercurrent to the powder. Retention time which is controlled by the amount of tray vibration can be varied between 3/4 and 3 hr. Standard retention time is 1-1/2 hr. Maximum feed rate obtainable is 100 lb. UO_3/hr. A feed rate of 50 lb. UO_3/hr. is equivalent to a Feed Plant tray rate of 3 tons U/day.

Hydrofluorination Tray. Hydrofluorination is carried out on a tray 16-ft.-long by 6-in.-wide having the same vibrating characteristics as the reduction tray.

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The heating elements are divided into four sections of equal length and heat input. Tray temperatures for pot-produced UO_3 increase from 600°F. at the UO_2 inlet end in approximately equal intervals to 1000°F. at the discharge end. A retention time of 4 hr. is normally used during hydrofluorination. A feed rate of 15 lb. UO_3/hr. is approximately equivalent to a rate of 3 tons U/day in the feed plant trays. A feed rate of 15 lb./hr. and a retention time of 4 hr. was achieved for the UO_3 continuously produced during Run B-18A by vibrating the tray 6 sec. at 700 cycles/min. every 15 min.

DISCUSSION

Reactivity on Continuously Produced UO_3. The reactivity data determined at K-25 on the test lots of UO_3 are given in Table II. By requesting a U^{+4} analysis, the per cent of the UO_3 reduced can be calculated. The data show that the reduction of the UO_3 produced continuously during Run B-18A did not reduce well during the reactivity test. After grinding, however, reduction appeared satisfactory. The continuously produced UO_3 from Run B-19 appeared to reduce satisfactorily even unground. The results of the reactivity ratio determination carried out at 410°C. for 1/2 hr. (H.A.P.O. conditions) are in good agreement with those obtained at H.A.P.O. for both test lots.

Thermal Balance Data. The thermal balance test at K-25 uses 560°C. for reduction and 410°C. for hydrofluorination. Both reduction and hydrofluorination data on the two test lots as well as on six samples from other continuous denitration runs, are in the writer's possession. The results on reduction are in agreement with those obtained at H.A.P.O. in that the reduction time is slower than that of Mallinckrodt standard UO_3 but there are wide differences in reduction rate between the product produced in different runs. The hydrofluorination rates are essentially what would have been predicted from the reactivity values and a thermal balance run on standard UO_3.

A thermal balance incorporating improved temperature control has been constructed. It is expected that the new unit will give more reproducible results.

Pilot Plant Runs. H.A.P.O. analytical data on the two test lots of continuously produced UO_3 sent to K-25 for pilot plant evaluation are given in Table I. Initial pilot plant runs were made on the UO_3 produced during Run B-18A which contained a nominal 1200 ppm. SO_4. Following these runs a portion of the Run B-18A UO_3 was ground in a micropulverizer (screen analysis not determined) and pilot plant runs were made on the ground material. A summary of the pilot plant run data is given in Table III. Since pilot plant operation, under the conditions listed above as standard, with Hanford pot-produced UO_3 gives a 98-to-100% reduction to UO_2 and a 90-to-95% conversion to UF_4, it appears from Table III that neither the reduction nor the conversion characteristics of the unground, continuously produced UO_3 are equivalent to those of pot-produced oxide. An attempt to force reduction by doubling the retention time did increase the amount of material reduced but also decreased the amount subsequently converted.

After grinding, however, the reduction improved to above 95% and the conversion had improved to above 80%. The opinion of the K-25 personnel was that the reduction of the ground UO_3 was satisfactory and that temperature adjustment would improve the conversion sufficiently to make it also satisfactory.

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Despite the free-flowing and dust-free properties of continuously produced UO_3, the K-25 personnel could see no distinct advantages to its use. In fact, it was their opinion that the relatively large particle size might cause an excessive amount of ash in the UF_4-to-UF_6 step. Since grinding facilities for the continuously produced UO_3 have been included in the scope for the Hanford UO_3 expansion program, no changes in scope will be required to ship UO_3 of satisfactory reduction characteristics.

Further pilot plant runs were scheduled on the ground UO_3 from Run B-18A, and a similar series of runs will be undertaken on the UO_3 from Run B-19 to evaluate its reduction and conversion characteristics.

Cost to Feed Plant of a Poor Reducing UO_3. The problem of the cost to a feed plant of maintaining a fixed production rate with existing equipment in the face of a UO_3 difficult to reduce was discussed. If blending the material with UO_3 of satisfactory reduction characteristics is not possible, a mixture of UO_3 and UO_2 produced by standard reduction conditions can be fed to the hydrofluorination step. The product from the hydrofluorination step would consist of a mixture of UF_4 and UO_2F_2. As the feed to the UF_4-to-UF_6 step, a UF_4 + UO_2F_2 mixture would:

1. Use more fluorine,
2. Produce more ash (unreacted material requiring reprocessing),
3. Slow down the UF_6 conversion.

Items 1 and 2 are cost items, but Item 3 might result in the plant's inability to maintain the desired production rate.

A second approach which would not be feasible in the K-25 or Paducah tray lines without revision since they are limited to 1200°F. in the reduction step, but would be feasible in the screw lines being installed at Paducah, would be to force the reduction by increasing the temperature. Past experience has indicated that this method of forcing reduction is deleterious to conversion to UF_4 so that product from the hydrofluorination step would be a mixture of UO_2 and UF_4. The use of such a mixture as feed to the UF_6 step would:

1. Require more fluorine,
2. Produce more than the normal amount of ash,
3. Probably decrease capacity because of the high heat release.

As in the first alternative, Items 1 and 2 are cost items and Item 3 is a capacity item.

In connection with the effect of reactivity on conversion, the writer obtained a plot of UF_4 and UO_2F_2 analysis of the Paducah product during the time that seven drums of continuously produced UO_3 (reactivity ratio = ca. 0.6) which had been inadvertently shipped from Hanford were introduced into the process. In general, abrupt decreases in UF_4 content and increases in UO_2F_2 content of the product resulted following each introduction.

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Surface Area. Surface area measurements on the test lots of as-produced UO_3 sent to K-25 indicated that the UO_3 had a surface area of 0.5 sq. meters/gm., which is about 20% of the surface area of a ground, pot-produced powder. The UO_2 produced from the UO_3 had a surface area of 3 to 4 sq. meters/gm., which is about equal to the surface area of UO_2 produced from pot-produced UO_3. Since only gross correlations exist between surface area and reduction or hydrofluorination characteristics and since surface area determinations are laborious (liquid-nitrogen absorption), it does not seem necessary that H.A.P.O. become involved with such determinations at the present time.

Surface area measurements can be used to calculate particle size, but this had not been done on the test lots of UO_3. It was the opinion of K-25 personnel that the particle size estimations obtained from surface area measurement would not check very well with particle size estimations obtained from electron microscope determinations.

Reactivity Improvement. Discussions involving means of increasing the reactivity of UO_3 by means other than additives elicited the information that laboratory results indicated that either the high temperature (450 to 500°C.) calcination of 100% UNH or the calcination of uranium nitrate concentrated to about the point where the trihydrate changes to the dihydrate produces highly reactive UO_3 (reactivity$>$1.2). The concentration of feed to the continuous calciner would probably involve operational difficulties since if the dihydrate crystallizes it can not be reliquified without the introduction of water. The high temperature calcination results check similar data obtained at H.A.P.O., and it was tentatively agreed that a continuous calcination run would be made at at feedpoint temperature of 450°C., and samples of the UO_3 sent to K-25 for evaluation.

Hydrated UO_3. The pilot plant personnel at K-25 still think highly of the possibilities of hydrated UO_3. Their tests show that a 93% conversion from UO_2 to UF_4 can be achieved at 500°F., 1 hr. retention time, and UO_2 feed rates of 30 lb./hr., all of which are much less stringent conditions than used for pot-produced UO_3. Discussions with Operations personnel indicated that the low bulk density of hydrate caused problems in the UF_4-to-UF_6 reactor.

II. X-10 PLANT, OAK RIDGE, TENNESSEE

The writer visited the X-10 Plant at Oak Ridge, Tennessee on April 28, 1955, to discuss problems of mutual interest to H.A.P.O. Separations Technology Section and O.R.N.L. Chemical Technology Division personnel. X-10 personnel contacted included Messrs. F. L. Culler, J. E. Moore, D. Foster, W. K. Eister, R. Wischow, and D. Ferguson. Subjects discussed included:

Moving Bed Denitration. No work has been done on moving bed denitration beyond that reported in CF-54-6-60, CF-54-10-137, and CF-54-12-97. X-10 personnel feel that the work to date has demonstrated the feasibility of denitrating pellets of UNH and UO_3 by a stream of hot air. In view of the success of trough-type continuous calcination at H.A.P.O., further moving bed denitration studies have been cancelled.

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Moving Bed Hydrofluorination. The writer witnessed a demonstration of a moving bed hydrofluorination process being demonstrated for Fernald and Mallinckrodt personnel. The process consists of mixing 1 part by weight of starch with 12 parts of UO_3, slurrying in water, and pelletizing. The pellets are fed into a 4-in.-diameter by 6-ft.-long tower, HF is introduced near the top and the bottom of the tower, and off-gases leave at about the middle of the tower. The pellets leaving the bottom of the tower assay 99+% UF_4. Both sugar and activated carbon were used to supply the carbon for reduction in place of starch; sugar gave pelletizing problems and the carbon did not produce as pure UF_4. More than moderate interest in the process was exhibited by the Mallinckrodt and Fernald representatives.

Continuous Uranium Dissolution. X-10 personnel are convinced that a pot-type unit is superior to a tower-type unit for continuous metal dissolution, particularly for those cases in which jacketed slugs are used. Their feelings are based on experience with thorium slugs in a tower-type unit in which product composition was extremely inconsistent. A 60 l. pot-type unit has been built and tested. It was found that a consistent product suitable for Purex HW No. 3 Flowsheet (320 g./l. U and 2.0 M HNO_3) could be obtained during continuous aluminum jacketed uranium slug dissolution by using a feed containing 8.3 M HNO_3 and 0.005 M $Hg(NO_3)_2$. Hydrogen accounted for from 7 to 15% of the gases leaving the dissolver pot. No solution other than dilution by air inleakage has been suggested for the hydrogen problem.

Mechanical Slug Dejacketing. A unit embodying the latest X-10 thinking on the mechanical dejacketing of slugs is being constructed. It is expected that it will be ready for operation early in July. Details of the unit can be found in O.R.N.L. Drawings D-18997, D-18998, and D-18999.

Slug Loading. A model of an automatic slug loader was observed. The unit consists of a double ram mechanism, located below a slug reservoir, which picks up a slug and pushes it into a split pipe. The slugs are held in the split pipe by the tension of external springs. Repeated slug injection to the split pipe results in slug discharge from the top. It is planned to construct a unit of this type for use in the X-10 Pilot Plant.

Thorex. The flowsheet supplied by O.R.N.L. for thorium extraction at Mound Laboratory has been carefully scrutinized and remains essentially unchanged.

Pilot plant thorium processing has progressed smoothly and no problems due to high radiation levels have arisen. It has been shown that if a feed batch after FAT treatment is aged for two weeks before processing the A Column ruthenium dF decreases from 1000 to less than 100. A second FAT step before processing restores the dF to its original value.

Homogeneous Reactor Fuel Processing. Experiments have shown that simulated rare earth fission products will plate out on a zirconium heater immersed in a stainless steel vessel containing UO_2SO_4 at temperatures approximating those expected in the homogeneous reactor. The effect of fission-product plating can not be exactly determined but is expected to be detrimental. Therefore, it is planned to operate the Dorrclone system for fission-product separation about 20°C. above the temperature of the reactor core. It is hoped that the core solution can be kept below saturation with respect to fission products in this manner.

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If concentration factor is defined as concentration of particles in the Dorrclone concentrate divided by the concentration of particles in the Dorrclone effluent, the following results have been obtained during operation at 2000 lb./sq.in. and 350°C. with a 35 lb./sq.in. pressure drop across the Dorrclone:

Material	Particle Size, Microns	Concentration Factor
ThO_2	1	35
ThO_2	4-8	2000
Fe	Sub	1000

The particle size of ThO_2 calculated from surface area measurements checked well with particle size calculated from X-ray diffraction. Electron microscope data are not believed to be too reliable to determine particle size.

Homogeneous reactor construction is about six months behind schedule.

Discussion with Fernald Personnel. Brief discussions were held with Messrs. Mulhauser, Sisson, and Loudin on UO_3 and its conversion. Fernald is convinced that sulfur activation of UO_3 (increased reactivity) has a very beneficial affect on conversion plant capacity. They have been using 700 ppm. SO_4 on a UO_3 basis. Corrosion difficulties which affect reduction screw agitators at a point 6 ft. from the UO_3 inlet are believed to be due to high temperatures rather than to the presence of sulfur in the UO_3.

III. MALLINCKRODT CHEMICAL WORKS, ST. LOUIS, MISSOURI - APRIL 29, 1955

The writer visited Mallinckrodt Chemical Works, St. Louis, Missouri on April 29, 1955, to present to them the H.A.P.O. experience on continuous denitration of UNH. Discussions were held with Messrs. W. M. Leaders, J. H. Yager, R. M. Edwards, E. K. Teeter, A. E. Ruehle, C. W. Kuhlman, R. H. Ferris, and J. C. Graham.

Mallinckrodt has embarked on a program using X-ray diffraction to study UO_3 in an attempt to better correlate crystal structure to reactivity. Discussions between their personnel and H.A.P.O. personnel who have been connected with this problem might prove fruitful.

During a trial period of sulfur activation (700 ppm. SO_4) of UO_3, the reduction screw agitator was rendered unusuable by corrosion after 30 days of operation. Pictures of the agitator are in the writer's possession.

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TABLE I

TEST LOTS OF CONTINUOUSLY PRODUCED UO_3 SENT TO K-25 FOR PILOT PLANT EVALUATION

Calcination Conditions: Feed point temp. = 290°C.
Discharge temp. = 300°C.
Agitator speed = 80 rev./min.

	Run B - 18A: Nominal 1200 ppm SO_4				Run B - 19: Nominal 3000 ppm SO_4			
Drum No.	62	63	64	65	79	80	81	82
Pounds UO_3	903.5	886.5	823.5	931.5	861.5	873.5	885.5	839.5
S ppm	544	480	408	386	1088	1164	1080	1331
Bulk Density	4.00	4.07	4.03	3.99	4.00	3.09	3.34	3.83
Packed Density	4.26	4.43	4.38	4.33	4.16	4.44	4.00	4.04
Reactivity (1)	1.14	1.11	1.14	1.12	1.29	1.31	1.29	1.29
Particle Size								
Thru 8 mesh	100	100	100	100	100	100	100	100
16	99.8	99.8	99.5	99.8	99.9	99.9	99.7	99.8
40	99.3	99.3	99.8	99.2	99.4	99.1	99.4	99.0
60	85.7	93.2	93.0	93.7	83.7	64.4	57.9	32.4
80	29.8	43.4	47.9	27.6	25.9	8.6	4.4	4.2
100	16.7	37.1	43.2	13.2	17.3	4.1	1.6	2.2
200	6.1	13.1	8.0	3.0	4.1	2.1	0.5	0.6
325	0.5	0.2	1.1	0	0	0	0	0
NO_3		0.23% (2)				0.35% (2)		
H_2O		0.47%				0.46%		
U		82.75%				82.62%		
Al		5 ppm				5 ppm		
Ca		5				5		
Cr		2				5		
Fe		<50				<50		
Na		20				20		
Ni		10				10		
Si		10				50		
Mo		ND				ND		
P		<100				<100		

(1) Reactivity determined on milled sample.

(2) Chemical and spectrographic data on composite samples.

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TABLE II

REACTIVITY OF TEST LOTS OF CONTINUOUSLY PRODUCED UO_3

Reduction Conditions: 590°C. for 2 hr.

Run B - 18A: Nominal 1200 ppm SO_4

	Hydroflourination			Reactivity
Wt. Sample, Gm.	Temp., °C.	Time, Hr.	% Reduction	Ratio(1)
3	410	0.5	62.7	0.98
3	410	0.5	65.9	0.93
3	410	0.5	93.7	1.21
5	410	0.5	59.2	0.89
5	410	0.5	82.9	1.06
3(2)	410	0.5	99.4	1.18
3(2)	410	0.5	98.8	1.19
3	490	0.5	47.5	1.29
3	490	0.5	97.4	1.22
3(2)	490	0.5	99.4	0.89
3	260	0.5	68.1	0.32(3)
5	260	0.5	54.4	0.14(3)
3(2)	260	0.5	99.5	0.58(3)

Run B - 19: Nominal 3000 ppm SO_4

	Hydroflourination			Reactivity
Wt. Sample, Gm.	Temp., °C.	Time, Hr.	% Reduction	Ratio(1)
3	410	0.5	100	1.34
3	410	0.5	99.2	1.29
3	410	0.5	97.4	1.32
5	410	0.5	99.4	1.29
5	410	0.5	99.2	1.24
3(2)	410	0.5	100	1.29
3(2)	410	0.5	99.1	1.28
3(2)	410	0.5	99.6	1.38
3	490	0.5	86.0	1.16
3	490	0.5	78.5	1.13
3(2)	490	0.5	100	1.25
[illegible]	260	0.5	96.4	0.65(3)
5	260	0.5	98.9	0.61(3)
3(2)	260	0.5	99.9	0.66(3)

(1) Compared to Mallinckrodt Standard.
(2) Ground
(3) Compared to Hydrate Standard.

TABLE III

K-25 PILOT PLANT TESTS ON CONTINUOUSLY PRODUCED UO_3

Unground UO_3 from Semi-Plant Scale Calciner Run B-18A

Run No.	REDUCTION(3) Temp., °F.	Retention Time, Hr.	Feed Rate, Lb. UO_3/Hr.	% UO_3 Reduced	HYDROFLUORINATION Temp., °F. (1)	Feed Rate, Lb. UO_2/Hr.	Retention Time, Hr.	% HF Excess	% Conversion To UF_4 & UO_2F_2	Remarks
1	1200	1.5	50	72.1	5,6,7,8	14	1.6	196	57.8	
2				78.2	6,7,8,9	18	1.5	289	61.5	
3				67.0	9,9,10,10	11	1.5	350	60.2	
4	1200	3	50	93.2	7,8,9,10	18	4	60	52.8	Slight cake
5				98.1	7,8,9,9.5	17	6	41	52.6	Slight cake
6				88.1	6.5,7.5,8.5,9	17	3	53	51.8	
7	1200	[illegible]	75	77.5	6.5,7.5,8.5,9	18	2.5	12	50.3	
8				86.9	8,9,10,10	(2)	(2)	(2)	45.9	Caked badly
9				71.4	8,9,9.5,9.5	17	1.7	74	38.8	

Ground UO_3 from Semi-Plant Scale Calciner Run B-18A

Run No.	REDUCTION(3) Temp., °F.	Retention Time, Hr.	Feed Rate, Lb. UO_3/Hr.	% UO_3 Reduced	HYDROFLUORINATION Temp., °F. (1)	Feed Rate, Lb. UO_2/Hr.	Retention Time, Hr.	% HF Excess	% Conversion To UF_4 & UO_2F_2	Remarks
1	1200	1.5	50	97.4	7,8,9,10	16	4	(2)	75.0	Slight cake
2	1100	1.5	75	94.0	7.5,8.5,9.5,10	18	3	(2)	65.5	
				86.8	7,8,9,9	15	4	(2)	81.0	Lumpy product
				(2)	7,7.5,8.5,9	(2)	(2)	(2)	(2)	

(1) Hydrofluorination tray has four heated sections. Temperatures indicated are in hundreds of degrees Fahrenheit and from the feed point to the discharge end.

(2) Data not available.

(3) Reduction tray had sufficient capacity so that one reduction run produced sufficient UO_2 for two or three hydrofluorination runs.