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SPECIAL

SUMMARY TECHNICAL REPORT

FOR THE PERIOD

JULY 1, 1956 TO SEPTEMBER 30, 1956

AEC RESEARCH AND DEVELOPMENT REPORT

FEED MATERIALS PRODUCTION CENTER
NATIONAL LEAD COMPANY
OF OHIO

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SUMMARY TECHNICAL REPORT
FOR THE PERIOD
JULY 1, 1956 TO SEPTEMBER 1, 1956

EDITED BY
JOHN W. SIMMONS

F. L. CUTHBERT, DIRECTOR
TECHNICAL DIVISION

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NATIONAL LEAD COMPANY OF OHIO
Box 158, Mt. Healthy Station
Cincinnati 31, Ohio

Date: OCTOBER 15, 1956
Contract No. AT(30-1)-1156

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1. ABSTRACT

The activities of the Technical Division of the National Lead Company of Ohio are reported for the period of July 1, 1956, to September 30, 1956.

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2. SUMMARY

- 3.1 A procedure has been developed whereby Q-11 feed for the Refinery can be digested to a 2400-gallon batch containing 140 to 145 g/l uranium and 3.0N nitric acid. The seven-hour time cycle required is an improvement over the time required when the standard digestion cycle is used for Q-11. In addition, safety hazards caused by foaming-over and excessive fume evolution are minimized by the new procedure.
- 3.2 A program is in progress to develop processing techniques for thorium-containing feed materials whereby the thorium specification of 50 ppm can be met. A slurry was made that contained 199 g/l uranium, 3.8 g/l thorium, and 7 per cent phosphate. After a three-equilibration batch-shakeout test, the organic solution contained only 0.02 g/l thorium.
- 3.3 In work evaluating urea solution as a stripping agent in the Refinery strip columns, urea nitrate was successfully reconverted to urea by the use of anion exchange resins.
- 3.4 Tests evaluating urea as a stripping agent were carried out in the Pilot Plant two-inch-column system. The best results obtained were a 388 g/l uranium content of the aqueous product stream and a 0.024 g/l uranium content of the organic raffinate. The above-described test did not reach steady-state operation, however.
- 4.1 Operation of a pilot-scale drum dryer and rotary calciner continued to indicate changes which can be incorporated into the design of plant-scale units. The splash feeder sprocket drive mechanism was relocated outside the drum dryer. It was determined that the knives had been made from badly warped blanks and that this resulted in nonuniform contact of the knife blade with the drum surface. True blanks for the preparation of better knife blades are on order. On the basis of experimental runs the calciner screw feeder was redesigned so that the calciner was sealed elsewhere than at the feed hopper.
- 5.1 Hydrogen reduction rates of various screen fractions of orange oxide have been determined with a thermobalance. The smaller the particle size, the faster National Lead Company of Ohio orange oxide was found to reduce. Mallinckrodt orange oxide showed the same effect, but to a much smaller degree. Porosity variations have been suggested as a possible explanation for the differences between these pot-denitrated products.
- 5.2 The kinetics of the hydrofluorination of a series of screen fractions of a single sample of orange oxide were evaluated. It was found that with a programmed hydrofluorination temperature, there is no significant difference in reaction rates for different screen fractions from a single orange oxide lot. With an isothermal hydrofluorination temperature, however, there is a trend toward faster conversion to UF_4 with increasing particle size. This may be caused by increased caking in the static bed with decreased particle size.
- 5.3 Orange oxide samples were reduced in the reactivity train and hydrofluorinated in the thermobalance. Their hydrofluorination rates were not affected by variations in their HCl-insoluble content between 0.42 per cent and 4.54 per cent.

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5.4 In laboratory - scale tests, wide differences were found in the hydrofluorination reactivity and the impurity content of the three typical products from a denitration pot - bulk UO_3 powder, UO_3 scale, and UO_3 lumps. Differences also were found between corresponding materials from different pots.

6.1 This section is concerned with: (1) Reduction and hydrofluorination of orange oxide which had been produced at Port Hope (from uranyl nitrate produced at National Lead Company of Ohio) and (2) development of plant processing conditions for processing of Port Hope UO_3 .

The orange oxide described in (1) above was sensitive to reduction temperature.

With a modification of operating conditions, Port Hope orange oxide can be processed to in-specification green salt at a feed rate of 300 lb/hr.

6.2 A thermobalance study was made of the reactions involved in the reduction and hydrofluorination of hydrated pellets prepared from a mixture of pot-denitrated orange oxide and corn starch. It was determined that the reduction and hydrofluorination could be performed as a two-step operation or as a simultaneous operation. The residual carbon content of the UO_2 pellet could not be reduced to specification, however.

6.3 The oxidation of UO_3 to form U_3O_8 , the reduction of U_3O_8 to form UO_2 , and the repeated recycling of U_3O_8 to UO_2 were studied.

7.1 On the bases of Reduction Run 31 of the moving bed reactor and cold flow studies in the hydrofluorination reactor, it was recommended that

1. Light continuous vibration of the reactor and feed hopper be employed during reactor operation in order to obtain uniform feed pellet flow to the reactor, and
2. A solids flow study be initiated in the reduction reactor in order to determine the existence of preferential solids flow as related to the phenomenon of reaction level variation.

7.2 Preliminary evaluation tests with muller mixing showed it to be an excellent continuous technique for producing uniform water- NH_3 - UO_3 mixtures for pelleting. The procedure used was:

1. The orange oxide was fed continuously to the muller from the Omega feeder at 425 lb/hr.
2. The orange oxide was mixed with 10.5 to 11.0 per cent liquor containing water and 10 per cent NH_3 .
3. The mixture was discharged intermittently to the Bonnot pug mill in 1 to 1-1/2-minute cycles.
4. The mixture was extruded through a high-free-area die.

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- 8.1 Metal quality from four-derby charges, as measured by slug yields, is better than that from charges consisting of three derbies and scrap or two derbies and scrap. Of the cleaning methods investigated, leaching followed by pickling caused the greatest weight loss.
- 8.2 Uranium derbies were cleaned by water leaching, acid pickling, and both water leaching and acid pickling. When the derbies were (1) leached and pickled or (2) pickled, there was no significant difference in the weight losses for dolomite-liner derbies and slag-liner derbies. For slag-liner derbies, a 12-hour water leach gave twice as much weight loss as did a 6-hour water leach.
- 8.3 A reactor is described that is being used for development of a continuous reduction process for the production of uranium metal. The modifications incorporated in the improved design have resulted in decreased preheat time, decreased down time, and fewer instances of pour hole plugging. Charging of UF_4 -Mg briquettes to this reactor at the rate of 37.5 pounds per minute gave improved metal-slag separation and casting yields.
- 9.1 Uranium - 10 wt% niobium ingots were cast from low-carbon virgin melts, from high-carbon virgin melts, and from uranium-niobium metal that had been previously melted and cast. These ingots were extruded to bars. The best yield obtained was from the four ingots made from low-carbon virgin melt stock; 100 per cent of the bars extruded from these ingots met specifications.
- 10.1 The high-temperature calcination of the diuranate product of the Scrap Plant was evaluated in a plant test.
- 10.2 Uranium is leached from carbon cake with 3N nitric acid and is then water-washed on the filter. The resulting residue contains 0.3 per cent uranium or less.
- 10.3 When uranium from uranium-niobium alloys is dissolved in nitric acid, explosions can occur. Burning the alloy to 1200°F prior to dissolution is being studied as a method of avoiding this hazard.
- 11.1 The Sylvania process for producing thorium metal powder from thorium oxide was successfully demonstrated, with 50-pound and 100-pound yields obtained in 10-inch and 14-inch stainless steel pots. Recovery yields after reduction, water leaching, acid neutralization, and water washing varied from 76 to 100+ per cent.
- A thorium fire and explosion, during a filter operation which followed acid pickling, pinpointed a process hazard and gave valuable information for improving preparation and handling techniques.
- The feasibility of pressing thorium powder into electrodes by the use of a hydraulic pressing technique was demonstrated. Electrodes of 3/4-inch diameter and 3-inch length and other electrodes of 7/8-inch diameter and 5-3/4-inch length were pressed at a pressure of 40,000 psi, giving an electrode that had a density of 9 to 10 grams per cubic centimeter.

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A small cylinder of solid thorium metal having a Brinell hardness of 135 was successfully made by melting seven pounds of thorium electrodes in an induction furnace. The critical impurity levels for ThO_2 , Fe, and C were determined to be approximately equal to the impurity levels in metal produced in the existing Thorium Plant.

- 11.2 A process has been developed which is more efficient than the old method of fabricating 7-inch-diameter thorium ingots from dezincd thorium derbies. The steps of the new process include (1) crushing the dezincd derby, (2) compacting the small particles to form an electrode, (3) butt-welding the compacts, (4) arc-melting the metal to form a primary ingot, (5) scalping the primary ingot, (6) butt-welding the primary ingots to form a secondary electrode, and (7) arc-melting the metal to form a secondary ingot.

The over-all efficiency of the new process is 85.4 per cent, as compared to 56.2 per cent for the old process.

- 12.1 ADU precipitate which settled rapidly and filtered easily was produced by batch precipitation in a pilot-scale unit. (ADU is a precipitate formed by the reaction of uranyl nitrate solution with ammonium hydroxide.)
- 12.2 The conditions are described for producing a filterable uranium cake (on a laboratory scale) when ammonium hydroxide is added to a solution of uranyl nitrate. Such a precipitation process is being considered for replacing the thermal denitration step in the production of green salt plant feed.
- 12.3 Pellets of improved strength were prepared from the precipitate formed (ADU) when ammonium hydroxide is added to an aqueous solution of uranyl nitrate. To obtain pellets which possess good strength and do not develop cracks, concentrated uranyl nitrate should be added to the ADU paste. Such pellets, after reduction, have been hydrofluorinated at rates much greater than those observed for UO_2 pellets prepared from pot-denitrated UO_3 .
- 12.4 UF_6 was converted to UO_2 by reaction of UF_6 gas with steam to produce UO_2F_2 , followed by hydrogen reduction of UO_2F_2 to UO_2 . The former reaction was found to proceed well at 400°F in a vertical tube reactor. The reduction reaction had a yield of 98.6 per cent UO_2 at a reactor temperature of 1400°F .
- 12.5 UO_3 and UO_2 can be heated to temperatures in excess of 800°F by the use of a dielectric heater (high-frequency heater). With a properly designed container, the heat generated is evenly distributed through the bed of powder, and any temperature gradient through the bed is dependent upon the radiant heat lost from the bed.
- 12.6 The results of tests in reactivity trains in which orange oxide was converted to green salt showed that only meager information is supplied by a reactivity train test under the test conditions used.

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- 12.7 An instrument for the comparative measurement of the velocity of propagation of an ultrasonic pulse through uranium slugs is described. The purpose of the instrument is the differentiation of material of dissimilar preferred orientation. In preliminary tests, the results obtained with this instrument have been in close agreement with "Sonotest" results.
- 12.8 A weight recorder has been assembled that continuously records the weight changes of thermobalance samples. The system is linear within ± 0.5 milligram at any point in the 100-milligram range and has held its calibration point over a two-month period.
- 12.9 Further progress in the centrifugal casting of precision hollow fuel elements is described.
- 12.10 Some of the uranium shot produced at National Lead Company of Ohio have small center cavities, but these are too few to affect significantly the true density of the shot. The bulk density of shot averages approximately 11.6 grams per cubic centimeter. Spectrographic analyses of the shot showed that there was no pickup of impurities in the shotting process.
- 12.11 An instrument constructed by the Ohmart Corporation is evaluated for the measurement of the density of uranium slugs. The density of the slugs tested varied from less than 18.800 to 18.999 grams per cubic centimeter. The 95 per cent confidence interval for the reproducibility of an individual determination is ± 0.037 gram per cubic centimeter. Possible sources of error are considered. Instrument drift is thought to result from changes in leakage resistance in connectors, these changes being related to humidity variations. Changes in connector design to reduce such leakage effects should result in increased precision and greater instrument stability.
- 13.1 The moisture loss values for Blockson Uranous Phosphate samples were found to vary with relative humidity in tests conducted at National Lead Company of Ohio and at the New Brunswick Laboratory. Blockson Uranous Phosphate was found to be hygroscopic after ignition at 1000°C , but not after ignition at 1200°C .
- 13.2 A fluorometric method was successfully adapted to the determination of 10 to 200 ppm of oil in aqueous solutions.
- 13.3 The method of Gertner and Ivekovic was found to give satisfactory results in the determination of urea in uranyl nitrate solutions that were 1 to 8 molar in urea.
- 13.4 Calibration curves have been prepared for the spectrophotometric determination of fluoride ion by the thoron method. Fluoride in nitric acid (in the concentration range of 1 to 20 ppm) can now be determined accurately despite varying nitric acid concentrations in the original samples.
- 13.5 Results of laboratory tests indicated that a sulfate concentration corresponding to 50 micrograms of sulfate per final volume of 50 milliliters can be determined accurately in orange oxide. The precision of the determination can be increased by backwashing the aqueous extracts of UO_3 with carbon tetrachloride.

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- 13.6 Hydrolysis of orange oxide does not occur during the wet screen test, and orange oxide particle size apparently does not change as a result of the washing.
- 13.7 UO_3 was shown to be very soluble in hot saturated ammonium oxalate solution. Therefore, its presence in UF_4 should have little effect on the results of the ammonium oxalate insoluble (AOI) determination.
- 13.8 Two methods of determining UO_2F_2 in UF_4 were compared. The method based on alcohol solubility of UO_2F_2 appears to be less suitable than the method based on water solubility.
- 14.1 The tributyl phosphate - HCl method was used for separating rare earths from uranium (in preparation for the quantitative analysis of the rare earths), and 99.6 per cent of a radioactive $\text{Eu}^{152-154}$ "spike" was recovered at the end of the separation.
- 14.2 Assays of K-65 samples for radium by National Lead Company of Ohio agreed, within the limits of error obtained, with values obtained by New Brunswick Laboratory and Massachusetts Institute of Technology.
- 14.4 In the spectrographic impurity analysis of uranium-molybdenum alloy materials, substitution of a graphite-gallium oxide carrier for AgCl carrier improves the analysis of 18 impurity elements.

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3. REFINERY PROCESS

In the Refinery process, the uranium concentrate feed materials are digested in a nitric acid solution, producing a slurry. The uranium in the feed slurry is separated and purified by a process wherein the uranium is extracted, scrubbed, and re-extracted in pulse-type perforated plate columns. The uranium first is extracted in two parallel columns by a tributyl phosphate-kerosene solvent, then the uranium-containing solvent (extract) is scrubbed in one column to remove impurities, and finally the uranium is re-extracted by water in two parallel strip columns. The final product of the Refinery process is thus an aqueous solution of uranyl nitrate hexahydrate.

3.1 DIGESTION OF Q-11 ORE - C. W. Huntington, R. H. Ellerhorst, J. R. Nelli, and T. J. Collopy

Considerable difficulty has been encountered during past months with the digestion of Q-11 ore in the Refinery. The violence of the reaction between the ore and nitric acid has in many cases resulted in foaming-over and fume liberation in excess of that which could be handled by the off-gas system. In order to control the reaction effectively when the normal (ore to acid) digestion procedure is used, it is necessary to reduce drastically the rate of ore addition, as compared to the rate of addition of other ores. These difficulties not only interrupt the production cycle but present safety hazards for operating personnel.

Laboratory tests have shown that there is a direct relationship between the sulfur content of Q-11 ore and its digestion reactivity and that roasting of the ore decreases this reactivity.¹ A survey of existing units on the site revealed, however, that suitable roasting facilities for Q-11 are not available. An investigation was therefore made during the last quarter to determine whether the digestion reactivity can be reduced by other means.

Initial experiments were designed to determine whether the digestion reactivity can be reduced by chemical means - i.e., whether it is possible to effect part of the oxidation involved with an oxidizing agent other than HNO_3 so that the subsequent reaction with HNO_3 is less vigorous. The ore was pretreated with varying amounts of sulfuric acid, potassium permanganate, potassium dichromate, and hydrogen peroxide. Of these reagents, hydrogen peroxide was the only one which showed possibilities of being effective; however, the small advantage offered and the high cost of the reagent precluded consideration of pretreatment with hydrogen peroxide.

Since chemical treatment did not prove to be effective, alternative digestion cycles with nitric acid were investigated. The normal digestion cycle used in the Refinery involves addition of ore to nitric acid of sufficient concentration to yield a slurry containing 3.0N excess nitric acid. The acid consumption requirements for Q-11 are high. Hence, during the initial part of the normal digestion cycle, the ore is added to rather concentrated (8 to 10N) nitric acid. The resulting reaction

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¹ Collopy, T. J. and Blum, J. F., *Summary Tech. Rpt.*, Vol I, pp. 17-18, NLCO-600, January 16, 1956.

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can be controlled to some degree by varying the rate of ore addition; however, this method of control involves "on-off" ore addition, which is time-consuming and requires constant attention by the operators. Control of liquid streams is considered easier than control of solid addition, and laboratory tests were made in order to determine whether inverted addition of reagents (concentrated acid to a slurry of ore and weak acid) would prove advantageous.

Qualitatively, the digestion reactivity seemed reduced by the use of the alternative digestion cycle. The most promising procedure, from the standpoint of reducing the vigorous evolution of gases, proved to be:

1. Rapid addition of the ore to 3N HNO_3 ,
2. Allowing the reaction to subside and cooling, and
3. Controlled addition of concentrated (15N) HNO_3 .

By the use of this procedure, the acid consumption of a test lot of Q-11 was 0.0171 equivalent HNO_3 /gram ore, compared to 0.0318 equivalent HNO_3 /gram ore by the normal digestion procedure. This reduction in acid consumption was a quantitative indication that the digestion reactivity was reduced.

Accordingly, a plant test was made in order to determine the applicability of the alternative digestion procedure to Refinery operations. A stainless steel rotameter and valve were installed in the acid line to one of the digesters so that the flow of nitric acid could be closely controlled. The plant test showed that:

1. A one-half-volume batch (approximately 1250 gal), involving a minimum of 1000 pounds of uranium, can be digested without difficulty in six hours (the approximate cycle required for a full-size batch of normal feed),
2. Complete uranium dissolution is effected, with little post-digestion reactivity,
3. The acid consumption of the ore is reduced when the alternative method is used, and
4. The rate of gas evolution (NO_2 , etc) is relatively low and should permit more than one digestion to be made at a time (although digestions will be staggered).

A disadvantage of the alternative procedure is that it yields slurries of lower uranium concentration than does the standard procedure. The limiting factor is the ore-dilute acid ratio. Laboratory work indicated that no stirring difficulties would be encountered at a ratio of 4.17 lb ore/gal 3N HNO_3 , and this ratio was used in the plant test. The use of 4N HNO_3 in the laboratory resulted in excessive foaming. By blending high-assay and low-assay lots, the Q-11 currently being received can be digested to yield a slurry containing at least 150 g/l uranium and 3.0N HNO_3 .

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On the basis of the test results, it was recommended that the alternative method for digesting Q-11 be adopted for production until roasting facilities are available. The nitric acid lines to all of the digesters on the side of the Refinery where Q-11 is processed were therefore equipped with stainless steel rotameters, and a Q-11 campaign was begun in the Refinery, initially under the supervision of Technical Division personnel. During the period of supervision, a total of 22 digestions were made with the threefold purpose of:

1. Increasing batch size,
2. Reducing the digestion time cycle, and
3. Demonstrating that digestions can be made simultaneously with proper scheduling.

The objectives were accomplished. The tests demonstrated that 2400-gallon digestion batches containing 140 to 145 g/l uranium and 3.0N HNO₃ can be processed in seven hours and that more than one batch can be made at a time if the digestion steps are alternated.

Refinery digestions of Q-11 are now performed by the alternative digestion technique. Although this procedure does not surmount all of the problems associated with Q-11 digestion, it is considered to be more desirable than the standard digestion cycle, in that safety hazards are minimized and the time cycle per digest batch is reduced from that required when the standard digestion procedure is used. Q-11 must still be processed on a campaign basis, however, and production during the campaign must be supplemented by other feed materials, whereas roasting of the ore would permit processing of Q-11 at a rate commensurate with the rates of other concentrates.

3.2 PROCESSING OF THORIUM-CONTAINING URANIUM CONCENTRATES - C. W.

Huntington, R. H. Ellerhorst, J. R. Nelli, J. H. Krekeler, and H. T. Doty

Future feed materials for the Refinery will include thorium-bearing uranium concentrates, which are expected to contain up to 2 per cent thorium (U basis). An active program is in progress to develop processing techniques for these concentrates whereby the thorium specification of 50 ppm (U basis) in the aqueous product of the Refinery can be met. Initial work has been performed upon Pronto concentrate from the Blind River area in Canada.

It had been determined that roasting the Pronto concentrate does not preferentially reduce the acid solubility of the contained thorium.¹ Initial extraction tests in two-inch-diameter and six-inch-

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¹ Ellerhorst, R. H. and Huntington, C. W., Summary Tech. Rpt. pp. 20-21, NLCO-625, April 16, 1956.

diameter pulsed perforated-plate columns^{1,2} showed that: (1) With the normal refinery flowsheet, decontamination factors of 4 to 6.8 were achieved from feed slurries containing 1.7 to 2.0 per cent thorium, (2) At 97 per cent of the theoretical uranium saturation of the organic extract, a decontamination factor of 62 was obtained, and (3) A decontamination factor of 60 was obtained with a feed slurry containing 0.15 per cent thorium.

During the current quarter, development work on the program to increase the thorium tolerance of the Refinery system has been largely concerned with a study of possible techniques for preferentially complexing the thorium in the extraction feed slurry and thus withdraw it in the extraction raffinate stream.

Laboratory and pilot plant tests were made in order to investigate the effect of phosphate and fluoride addition. It had been shown³ that the presence of phosphate has a marked depressing effect on thorium extraction at low initial thorium concentrations. The use of fluoride to precipitate thorium tetrafluoride (an extremely stable compound) is widely used in analytical procedures.⁴ If little excess fluoride is added, most of the fluoride in the feed slurry will be complexed and should not be a source of corrosion difficulties.

Three-equilibration tests at an organic to aqueous ratio of 1 to 1 (with a slurry containing 199 g/l U and 3.8 g/l Th) indicated that both fluoride and phosphate hinder thorium extraction from Pronto feed slurries without seriously affecting uranium extraction. A phosphate concentration of seven per cent (U basis) was used, since this concentration is the present feed materials tolerance limit. The fluoride concentration was limited to 10 per cent in excess of the stoichiometric requirements of the thorium in the slurry. The results of the batch shakeout tests are summarized in Table 3.2-1. The effect of the two agents upon the thorium distribution in the aqueous and organic phases is depicted in Figure 3.2-1, which shows that the phosphate decreased the thorium extraction more than the fluoride did. These findings were the justification for the pilot-scale investigation described below.

A series of tests with 6-inch-diameter columns has been begun in order to determine the effect of phosphate and fluoride upon the thorium distribution in a pulse column extraction system. The results of these tests (now in progress) will be outlined in the next quarterly progress report.

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1 Huntington, C. W., Manser, W. C., Nelli, J. R., Krekeler, J. H., Fasnacht, E. J., Ellerhorst, R. H., and Stock, D. A., *Summary Tech. Rpt.*, pp. 19-20, NLCO-625, April 16, 1956.

2 Huntington, C. W., Nelli, J. R., Ellerhorst, R. H., and Krekeler, J. H., *Summary Tech. Rpt.*, p. 17, NLCO-640, July 18, 1956.

3 Ewing, R. A., Fishel, J. B., Kiehl, S. J., Sharpe, R. E., and Bearse, A. E., *Purification of Thorium Nitrate by Solvent Extraction with Tributyl Phosphate; Laboratory Investigations*, BMI-262, July 31, 1952.

4 Rodden, C. J. and Warf, J. C., "Analytical Chemistry of the Manhattan Project", NNES VIII-1, p. 160, McGraw-Hill, New York, 1950.

FIGURE 3.2-1 Effect of Phosphate and Fluoride upon Thorium Distribution Coefficient in Batch-Shakeout Extraction of Pronto Feed Slurries

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TABLE 3.2-1

EFFECT OF PHOSPHATE AND FLUORIDE UPON THORIUM AND URANIUM EXTRACTION FROM PRONTO FEED SLURRIES*

(Batch - Shakeout Tests)

Equilibration	U Conc. (g/l)		U Distribution Coefficient E_A^O	Th Conc. (g/l)		Th Distribution Coefficient E_A^O
	Org	Aq		Org	Aq	
Pronto Feed Slurry						
1st	108	93	1.16	0.18	3.57	0.050
2nd	79	10	7.9	0.48	3.20	0.150
3rd	12	1.2	10.0	1.04	2.31	0.450
Pronto Feed Slurry + $H_3PO_4^{**}$						
1st	110	85	1.29	0.069	3.74	0.018
2nd	74	11	6.73	0.090	3.95	0.023
3rd	14	2.2	6.36	0.020	3.35	0.060
Pronto Feed Slurry + $HF^\dagger$						
1st	112	83	1.35	0.11	4.27	0.026
2nd	72	1.5	11.1	0.28	3.89	0.072
3rd	10	1.0	10.0	0.74	3.27	0.226

* Original slurry concentrations: 199 g/l U, 3.1N HNO_3 , 3.8 g/l Th. The slurry was divided into three portions for these tests.

** 7% PO_4^{3-} (U basis) added as H_3PO_4 .

† 10% excess F^- (above ThF_4 requirements) added as HF.

3.3 UREA SOLUTION AS A STRIPPING AGENT (See also Section 3.4) – P. S. Gentile

Increased scrubbing capacity in the National Lead Company of Ohio Refinery can be gained by releasing one strip column on each side of the Refinery for scrub column utilization. For these columns to be released, the same volume of scrubbed organic extract solution (BP) must be re-extracted (stripped) in two columns as is now stripped in four columns. This can be accomplished if the deionized water now used is replaced with a stripping agent capable of completely re-extracting the uranium at an organic to aqueous ratio of 5 to 1 with a total throughput of 750 gsfh in the 26-inch-diameter re-extraction columns. Earlier laboratory work¹ showed pilot plant testing of urea solutions as re-extraction agents to be feasible.

¹ Gentile, P. S. and Collopy, T. J., Summary Tech. Rpt., pp. 17-22, NLCO-640, July 18, 1956.

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Additional laboratory work has been done. Urea has been successfully recovered as urea nitrate and reconverted to urea, using anion exchange resins. If the urea can also be recycled on a production scale, this process will be economic. A mechanism for the various stripping agents has been postulated.

These results will be reported in detail in a topical report.

3.4 PILOT PLANT EVALUATION OF UREA AS A STRIPPING AGENT – J. R. Nelli and J. H. Krekeler

The objective for this project is given in Section 3.3 of this report.

Preliminary pilot plant tests¹ in which an 8.5M urea solution was used as the stripping agent have shown that a maximum throughput of 600 gsfh can be obtained at an organic to aqueous ratio of 5 to 1 with the aqueous phase continuous. When this ratio is used in the plant, a throughput of 740 gsfh is required in order to strip all of the organic scrub product (BP) in two columns.

Three re-extraction tests, reported below, further demonstrated the possibility of using urea as a stripping agent in the Refinery. The objectives for this quarter were to adjust the process variables so that both complete stripping of uranium and the required throughput rate were achieved.

In the first test, BP containing 100 g/l uranium was stripped in the two-inch column system with the organic phase continuous. The organic to aqueous flow ratio was 5 to 1, the frequency was 70 cpm, and the amplitude was 0.75 inch. (These pulse conditions are the final ones developed during the test and are the optimum ones as determined by visual observation.) Although the throughput was 600 gsfh (the same as that obtained in the two previous tests with the aqueous phase continuous), the uranium loss in the organic raffinate (CR) was much higher, 9 g/l, compared to 1 g/l.

The organic to aqueous ratio was then changed to 4 to 1 in an attempt to demonstrate higher throughput levels, and the second test consisted of stripping BP containing 103 g/l uranium with 8.5M urea solution, the aqueous phase being continuous. Flow rates were begun at a low level and were raised gradually during the test period. The initial pulse conditions were 35-cpm frequency and 0.75-inch amplitude. The desired throughput of 770 gsfh was finally attained by lowering the frequency to 30 cpm. The aqueous product stream contained 388 g/l uranium, while the organic raffinate contained 0.024 g/l uranium. A material balance could not be obtained, however, because the column had not attained steady-state operation. Column action had been upset many times by physical manipulations made in striving for optimum operating conditions.

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¹ Nelli, J. R., Krekeler, J. H., and Huntington, C. W., Summary Tech. Rpt., p. 22, NLCO-640, July 18, 1956.

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The purpose of the third test was to operate the columns at constant operating conditions for a sufficient period of time to allow steady-state operation to be attained. The test period was ten hours; the operating conditions were the same as for the second test, except that the BP contained 92 g/l uranium. Although the end-stream concentrations were fairly constant (336 g/l uranium in the aqueous product stream and 0.29 g/l uranium in the stripped organic stream), a material balance again was not obtained, which indicated that the column had not reached steady-state operation despite the fact that five volume changes had occurred in the column.

Tests are in progress to determine the time required to reach equilibrium.

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4. NITRIC ACID RECOVERY PROCESS

When uranium is extracted from the feed slurry in the Refinery (Section 3), an aqueous raffinate results which contains free nitric acid. This free nitric acid is recovered for recycle to the digestion area by evaporation followed by concentration in a plate type fractional distillation tower.

4.1 PILOT-SCALE RAFFINATE DRUM DRYER AND ROTARY CALCINER – E. J. Beer and J. H. Cavendish

Expansion of raffinate-processing facilities led to the installation of a pilot size drum dryer and calciner at National Lead Company of Ohio. The purposes of this project are to determine process operating difficulties and to obtain information on necessary modifications for plant-scale drum dryers and rotary calciners now on order. Early operational difficulties (scale formation and condensation in the drum dryer; bridging in the rotary calciner) pertaining to these pilot units have been discussed in detail in a previous report.¹

Drum Dryer Operation

A schematic diagram of the pilot raffinate drum dryer unit is given in Figure 4.1-1. In the drum dryer (24-inch diameter by 36-inch length), the material from the raffinate evaporator must have enough nitric acid vapor driven off so that the product is easily conveyable in a screw conveyor.

During the past quarter, the drum dryer case was completely insulated. This, and the steam-tracing completed during the previous quarter, has solved the problem of nitric acid condensation inside the dryer case and has aided in the production of a drier product. The problem of scale formation on the drum rolls has not yet been solved.

Principal objectives during the past quarter's work on the drum dryer were: (1) to evaluate various knife materials, (2) to investigate scale formation, (3) to determine corrosion resistance of drums, and (4) to compare drying characteristics of various raffinate feeds. Data are summarized in Table 4.1-1.

A. Evaluation of Knife Materials

Stellite knives were evaluated, two feeds being used. One feed raffinate resulted from the extraction of an ore containing 50 per cent Canadian orange oxide, 20 per cent Colorado black oxide, and 10 per cent Portuguese ore, the balance being black oxide and South African ore. The second feed raffinate used resulted from the extraction of Q-11 ore. It was found that when either of the two feeds were used, stellite knives were usable for an average of 20 hours before regrinding was necessary. Type 440 stainless steel knives were found to be unsuitable, due to their extreme brittleness. These knives broke easily under the stress caused by scale formation on the drum rolls.

¹ Beer, E. J., Cavendish, J. H., Dumas, B. C., and Whitman, A., Summary Tech. Rpt., p. 41, NLCO-640, July 18, 1956.

FIGURE 4.1-1 Schematic Diagram of Pilot Raffinate Drum Dryer Unit

TABLE 4.1-1

**OPERATING CONDITIONS, DATA, AND RESULTS FOR OPERATION
OF THE PILOT RAFFINATE DRUM DRYER**

Run No.	Type of Feed	Type of Knife	Drum Spacing (in)	Steam Pressure (lb)	Drum Speed (rpm)	Feeder Speed (rpm)	Tot. Vol. Slurry Used (gal)	Wt. of Prod. (lb)	Time Operated (hr)	Weight Loss* of Product (%)	Scale Thick-ness (in)	On – Stream Factor (%)
1	**	Stellite	0.005	91	1	350 - 550	63.9	—	3.00	—	0.008	—
2	†		0.0059	92	1.5	650	306.8	1837	15.00	24	0.009	62.5
3				91	1		225.4	710	16.42	18	0.007	69
4							199.6	1289	17.25	17.8	0.007	72
5							408.5	1769	20.00	—	—	83.5
6							389.5	2266	18.83	—	—	77
7							331.3	1645	21.50	—	—	89.5
8				90	1.25 - 1.50		423.6	1201	22.17	—	—	93
9					1.50 - 1.25		193.0	1149	17.30	—	0.010	72
10	††		0.010	91	2 - 1.75	750 - 650	351.5	3374	21.75	—	0.0072	90.5
11					92	1.25	750	282.7	2178	17.67	—	—
12				254.0				2026	14.33	—	—	60
13				393.5				2420	24.00	—	—	100
14				146.8				1553	17.50	—	—	73
15				301.8				1881	16.00	—	—	67
16		1 Stellite 1 S. Steel		—	43.6	104	33.08	—	—	—		

* Weight loss determined with Cenco moisture balance after 15 minutes of exposure at 234° F.

** Unknown.

† Raffinate obtained when the slurry to the columns in the Refinery consisted of ~50% Canadian orange oxide, ~20% Colorado black oxide, ~10% Portuguese ore, and ~20% South African and black oxide.

†† Raffinate obtained when the slurry to the columns in the Refinery consisted of 100% Q-11 ore.

B. Investigation of Scale Formation

A run was made in which Stellite knives and a cold feed of unknown composition were used in an effort to determine the rate of scale buildup on production. (In this section, "hot" and "cold" refer to radioactivity.) During an 8-hour period, scale built up to a thickness of 0.009 inch and remained at that thickness for the remaining hours of the run. The results (presented in Table 4.1-2) indicate that feed usage and product rate did not vary appreciably.

TABLE 4.1-2

Time from Start (hr)	Feed Usage (gal)	Production (lb)	Scale Thickness (in.)	Weight Loss of Product (%)
1	32.8	55	0.0020	27
2	25.5	38	0.0025	20
3	19.5	27	0.0060	20
4	25.0	24	0.0070	22
5	20.8	24	0.0075	20
6	23.9	40	0.0075	20
7	26.3	36	0.0075	25
8	21.0	36	0.0080	21
9	21.7	34	0.0090	21
10	21.3	51	0.0080	20
11	22.0	39	0.0090	22
12	22.0	36	0.0090	22
13	22.0	57	0.0090	23
14	—	46	0.0090	—
15	—	38	0.0090	—

C. Corrosion Resistance of Drums

The chromium plating has begun to flake from the drums in areas having diameters as large as one inch. The flaking occurs where the cracks had formed during earlier operations. The cast iron heads of the drums remain in good condition and show no signs of corrosion.

The carbon steel knife-holders have shown signs of severe corrosion. A spare knife-holder was metallized with stainless steel and installed in the dryer to determine the effectiveness of this method of protection. No corrosion has been observed after about 50 hours of operation.

D. Drying Characteristics of Different Feeds

Dry, flaky drum dryer product was obtained when cold raffinate feed was used, and a weight loss of 14 to 18 per cent was indicated. The product from Q-11 raffinate was more finely divided in appearance and showed a weight loss of 10 to 15 per cent. All of the raffinate that was dried appeared to be dry enough to be handled by plant conveying equipment.

Drum Dryer Maintenance

- A. The carbon steel drive sprockets for the splash feeder, which were located inside the dryer case, had been failing after approximately 200 hours of operation. This corrosion problem was solved by moving the splash feeder sprocket drive mechanism to the outside of the dryer case.

During the past quarter, severe corrosion made necessary the replacement of (1) four bearings which hold the splash feeder in the feed pan and (2) the spur gears which drive the splash feeder.

- B. The OVC scrubber system, which had been set up as a separate off-gas system for the drum dryer, was diverted to other uses. Therefore, the dryer and rotary calciner off-gas systems were connected to the Peabody scrubber system.
- C. Difficulty has been encountered in using Stellite knives due to irregularities in the edges making it difficult to obtain a flush fit of the knife edge against the drum. It was determined that the knives had been made from blanks which were badly warped and that this was the cause of the trouble. True blanks for the preparation of better knife blades are on order.

Rotary Calciner Operation

The function of the rotary calciner (6-1/2-inch diameter by 7-foot length) is to denitrate the drum dryer product completely.

Principal objectives during the past quarter's work on the indirect-fired rotary calciner were: (1) to determine the optimum temperature and retention time for denitration of various feeds, (2) to determine the cause of solids buildup in the feed end of the calciner, and (3) to investigate feeding problems likely to be encountered in operation of the plant-scale units. Data and results are summarized in Table 4.1-3. A schematic diagram of the pilot rotary calciner unit is given in Figure 4.1-2.

A. Optimum Denitration Temperature and Retention Time

Erratic results obtained for Runs 1 through 4 are attributed to the variation in moisture content of the feed used in these runs. When wet material was used in the calciner, large lumps were formed which were more difficult to denitrate than was the finely divided dry material. Results of Runs 5 through 11 indicate that dried Q-11 raffinate can be denitrated satisfactorily at 800° to 900°F with a retention time in the heated zone of 5 to 8 minutes.

FIGURE 4.1-2 Schematic Diagram of Indirect-Fired Pilot Rotary-Calcliner Unit

TABLE 4.1-3

**OPERATING CONDITIONS, DATA, AND RESULTS FOR OPERATION
OF PILOT ROTARY CALCINER**

Run No.	Conditions					Results			
	Temp (°F)	Feeder Speed (rpm)	Tube Speed (rpm)	Total Retention Time (min)	Retention Time, Heated Zone (min)	NO ₃ in Feed (%)	NO ₃ in Product (%)	Denitration Efficiency* (%)	Feed**
1	600	5	4	28	10.8	35.4	10.71	81.5	1
2	1000			28	10.8	35.4	3.51	94.5	
3	600			20.7	8.1	35.4	7.48	88.7	
4	500			29.6	11.4	35.4	0.04	99.9	
5	700			19.0	7.4	11.89	1.19	92.35	
6	800	2		15.8	6.2	11.89	0.30	97.68	2
7	900			14.0	5.5	11.89	0.04	99.75	
8	700			13.6	5.31	11.89	0.74	96.94	
9	1000			43.5	17.0	20.7	0.06	99.82	
10	800			20.3	7.9	20.7	0.72	97.50	
11	700			29.7	11.6	20.7	0.99	97.0	

* These values were calculated on the basis of the NO₃ balance and the silica balance.

** Feed 1: South African Ore. Feed 2: Q -11.

B. Solids Buildup in the Feed End of Calciner

During several runs, solids built up excessively at the feed end of the calciner and plugged the off-gas outlet. It was thought that this buildup may have been caused by material being carried back by the purging air flow and that it might give trouble in the plant-scale calciners. Some tests were performed in which the bed thickness in the calciner was reduced in order to study the effect of this variation on solids buildup. Results of these tests led to the conclusion that the buildup was caused by operating with too thick a bed of material and that solids buildup would not present a problem in the plant calciners. The plant-scale calciners will have flights at the feed end which are designed to move incoming material forward into the calciner.

C. Feeding Problems

Considerable difficulty was encountered in feeding the drum dryer product down through the hopper and into the feed screw on the pilot-scale calciner. Since the plant-scale hopper and feed screw are to be much larger than the pilot ones, it was not known whether the problem will be serious in the plant-scale equipment.

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Therefore, a hopper and feed screw assembly (which had been received for installation on the plant calciners) was set up for a series of feeding tests on drum dryer product. The tests were run, and it was found that if the level of material in the hopper was maintained high enough for sealing purposes (as had been planned), the material bridged between the screw feeder and the bridge breaker. However, if no material was held up in the hopper and if the screw was turning fast enough to take the feed away as fast as it was fed in, no trouble was encountered in feeding even excessively wet material. It was decided, therefore, by design engineers of Singmaster and Breyer (architect-engineers for the new plant) to alter the feed screws so as to give the necessary calciner seal elsewhere than at the hopper and to run the hopper empty.

Future Work - Drum Dryer

A. Knife Testing

A series of runs are planned whose objective will be to determine the best knife material and knife construction for use on the pilot drum dryer. Knife materials which are available for testing are (1) Stellite, (2) Armco 17 PH stainless steel, and (3) carbon tool steel. Two types of knife construction will be tested: First, the standard 3/32-inch-thick by 5-inch-wide knife which is rather flexible, and second, a 1/2-inch-thick Stellite-tipped stainless steel knife which is very rigid. It is hoped that the more rigid knife will be more efficient in removing scale than is the standard knife.

B. Scale Problems

Attempts to solve the scale problems will include the testing of the rigid knife described above, as well as a series of tests in which the rate of scale buildup and the effect of scale buildup on production will be measured.

C. Drum Corrosion and Chromium Plate Deterioration

The drum dryer will be operated as much as possible and the condition of the drum ends will be checked for any corrosion. **The drums will be observed to determine whether flaking of the chromium plating continues.** The effect of loss of chromium plating on dryer efficiency also will be noted.

Future Work - Rotary Calclner

A program of testing the various drum dryer products for optimum conditions for denitration will be continued.

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4.2 ELECTROLYTIC REMOVAL OF CHLORIDES FROM NITRIC ACID - W. S. Miller

Currently, at the National Lead Company of Ohio, the free nitric acid in the Refinery raffinate is recovered by evaporation followed by concentration in a bubble cap plate type distillation tower. During the course of these recovery operations, it has been determined that there is a definite buildup of chloride ion concentration on the concentrator tray containing 10 to 20 weight per cent nitric acid. Since chloride buildup is undesirable from a corrosion standpoint and since the present method of sparging with ozone has several disadvantages,¹ attention was given to the possibility of removing chlorides from the acid by electrolysis.

Laboratory experiments designed to study the electrolytic removal of chlorides from nitric acid solutions have been continued during the past quarter.

The objective was to reduce the chloride concentration from 500 mg/l to 50 mg/l.

The anodic process ($2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$; $E^\circ = -1.358$ volts) is greatly affected by electrode material, temperature, concentration of electrolyte, current density, and cell construction. Each of these factors will be discussed in a following paragraph.

Experiments performed with various acid-resistant alloy steels and graphite electrodes indicate that all of these materials are readily attacked by dilute nitric acid or by chlorine during electrolysis. Graphite has the best electrical properties for a chlorine-cell anode, but nitric acid rapidly eroded all graphite electrodes tested in this work. Smooth platinum plates were used as they are resistant to dilute acid and because the chlorine concentration is too low to affect platinum appreciably at 65°C.

A cell temperature of 65°C has been found to be attained by dilute nitric acid during electrolysis. A constant temperature bath has been used to keep the cell at this temperature and to reduce heat loss during electrolysis. The electrolytic cell used consisted of an 800-ml beaker (500 ml of electrolyte) which was kept in the constant-temperature bath during electrolysis.

Dilute nitric acid (10% by volume) was employed as the electrolyte and the initial chloride concentration was 500 mg/l. Variations in initial chloride content of the electrolyte between 130 mg/l and 520 mg/l had little effect on the rate of chloride removal by electrolysis.

The effect of increased current density on the rate of chloride removal is being studied. Low current densities (~ 30 amp/sq ft) are desirable to attain good current efficiency. However, the present investigation is primarily concerned with rapid, effective chloride removal.

Results obtained with a small laboratory continuous-flow cell have been inconclusive. A more systematic study is being conducted with an individual cell without moving electrolyte so that a more accurate design of a flow cell may be made.

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¹ Doyle, R. L., Summary Tech. Rpt., pp. 43-44, NLCO-640, July 18, 1956.

5. STUDY OF ORANGE OXIDE FACTORS AS RELATED TO THE PRODUCTION OF METAL-GRADE GREEN SALT

The chemical composition or physical properties of orange oxide and brown oxide may have important effects on the speed and degree of conversion to green salt. In this section are reported attempts to establish relationships between convertability to green salt and (1) particle size of orange oxide, (2) particle size of brown oxide, (3) HCl-insoluble content of orange oxide, and (4) physical and chemical properties of the various orange oxide products found in the denitration pot. Throughout this report, the name of a product is used interchangeably with the name of the uranium compound that is its major constituent. Thus, UF_4 , UO_3 , UO_2 , and U_3O_8 are used as general terms for green salt, orange oxide, brown oxide and black oxide, and do not indicate the stoichiometry of these materials.

5.1 THE EFFECT OF PARTICLE SIZE ON THE HYDROGEN REDUCTION RATE OF ORANGE OXIDE -- K. J. Notz and M. G. Mendel

As part of a general program investigating the reactivity (convertability to UF_4) of orange oxide, it was desired to determine what effect, if any, particle size of orange oxide has upon its rate of reduction to UO_2 with hydrogen. This information is essential in prescribing sample preparation, either for purposes of comparing various samples of orange oxide or for evaluating the kinetics of the reduction reaction. The results will also be useful in evaluating the guiding operation in the plant.

Data and Discussion

The thermobalance equipment and procedure used to determine reduction rates have been described previously.¹

Reproducibility of the method is shown in Table 5.1-1.

TABLE 5.1-1

EXAMPLE OF THERMOBALANCE REDUCTION DATA REPRODUCIBILITY

Sample Used: National Lead Company of Ohio sulfated orange oxide, Lot 3E-16-706.

Elapsed Time (sec)	Unconverted UO_3 (%)			Std Dev	Elapsed Time (sec)	Unconverted UO_3 (%)			Std Dev
	Run 1	Run 2	Run 3			Run 1	Run 2	Run 3	
0	100.0	100.0	100.0		500	27.4	28.1	27.8	0.29
50	99.9	99.8	100.0	0.08	550	19.0	19.9	20.3	0.55
100	98.4	98.2	98.7	0.21	600	12.0	13.2	13.9	0.79
150	94.2	94.5	94.8	0.24	650	6.6	8.1	8.5	0.82
200	84.9	86.3	86.4	0.69	700	3.4	4.3	4.2	0.22
250	71.7	72.7	73.1	0.29	750	1.5	1.9	1.5	0.19
300	61.2	62.0	61.2	0.38	800	0.5	0.9	0.4	0.22
350	53.0	53.3	52.5	0.33	850	0.1	0.3	0.0	0.13
400	44.3	45.0	44.3	0.33	900	0.0	0.0	0.0	—
450	35.9	36.7	36.2	0.33					

¹ Notz, K. J., Summary Tech. Rpt., p. 34, NLCO-640, July 18, 1956.

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The first set of rate determinations was made on National Lead Company of Ohio sulfated orange oxide, Lot 3F-16-928. This lot was selected because it was the most recently produced orange oxide available at the time this work was started. Chemical and spectrochemical analyses showed nothing unusual. The bulk sample was separated into various screen fractions (Table 5.1-2) and the reduction rate of each fraction was determined at 890° F, 990° F, and 1020° F.

TABLE 5.1-2

**DRY SCREEN FRACTIONS OF
NATIONAL LEAD COMPANY OF OHIO
ORANGE OXIDE**

(Lot 3F-16-928)

Screen Range	Per Cent
+20	0.3
-20, +40	3.0
-40, +80	13.9
-80, +325	44.7
-325	38.1

Figures 5.1-1, 5.1-2, and 5.1-3 present all results except those for the +20 fraction. A family of curves was formed at each temperature, the finer fractions being reduced fastest. Variations in rate for the various screen fractions manifested themselves in three ways:

1. A gradual change in the time required for the reaction to get under way,
2. Small differences in the rate over the large central portion of the reduction, and
3. A pronounced difference in the rate for the final 10 per cent converted.

The +20 fraction behaved in an anomalous manner, possibly because the individual particles were large enough to permit an increase in temperature within the particle during the early portion of the exothermic reaction. This temperature rise resulted in a shortened acceleration period and an increased rate while the first 60 per cent or so reacted. However, during the conversion of the final 10 per cent of the orange oxide, when heat was again being dissipated as rapidly as it was produced, the rate slowed down sufficiently so that the +20 fraction took its appropriate position in the family of curves. This type of behavior was also shown by the -20, +40 fraction at 1120° F (Fig. 5.1-3). The extreme of this condition was demonstrated by a single particle of orange oxide weighing 1.5 grams.

Since the characteristics of orange oxide may vary from lot to lot, as well as from plant to plant, it was thought necessary to repeat the above work on other samples. Since all three temperatures used gave the same results, only 990° F was used for the repeat work. Two National Lead Company

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FIGURE 5.1-1 H_2 Reduction Rate (At 890°F) of Various Screen Fractions of National Lead Company of Ohio Sulfated UO_3

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FIGURE 5.1-2 H_2 Reduction Rate (At 990°F) of Various Screen Fractions of National Lead Company of Ohio Sulfated UO_3

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FIGURE 5.1-3 H_2 Reduction Rate (At 1020°F) of Various Screen Fractions of National Lead Company of Ohio Sulfated UO_3

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of Ohio orange oxides were used, a fresh sample (Lot 3F-16-1023) and an old, stored sample (Lot 3F-16-249). Both gave results identical to those obtained in the original series with Lot 3F-16-928.

When the same work was done at 990°F with Mallinckrodt orange oxide (identified as C-61SNO-406, 81102) with the fractions, -40, +80; -80, +325; and -325, different results were obtained (Fig. 5.1-4). All three fractions followed essentially the same path to 90 per cent conversion, after which they diverged.

On the basis of previous experience with this equipment and procedure, it is thought that the differences shown are real, even though they are small. While the magnitude of the reduction rate variation with particle size is much less for Mallinckrodt orange oxide than for National Lead Company of Ohio orange oxide, the direction of change is the same.

Two pertinent questions present themselves at this point:

1. Why does the reduction rate of orange oxide vary with particle size?
2. Why is this variation much more pronounced for National Lead Company of Ohio orange oxide than for Mallinckrodt orange oxide when both are pot-denitrated?

The first question was answered, in part, by Maness and Moore,¹ who worked with spherical, relatively nonporous particles of orange oxide produced by continuous calcination of uranyl nitrate hexahydrate. They proposed that the reaction proceeded across the face of the phase boundary between UO_2 and the unreacted orange oxide, and they obtained a good fit between experimental data and the rate equation derived from that hypothesis. Rate data obtained in this laboratory² for National Lead Company of Ohio nonsulfated orange oxide and Mallinckrodt orange oxide agreed quite well with the phase-boundary theory. National Lead Company of Ohio sulfated orange oxide, however, fitted the phase-boundary theory only for the final 30 per cent of the reduction. Figures 5.1-1, 5.1-2, and 5.1-3 are typical reduction patterns for National Lead Company of Ohio sulfated orange oxide.

As shown in Table 5.1-3, there is no correlation between apparent rate-law conformity and the effect of particle size on reduction rate.

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¹ Moore, R. H. and Maness, R. F., *Reduction of UO_3 to UO_2 with Hydrogen*, HW-38321, July 22, 1955.

² Notz, K. J., *op. cit.*, pp. 33-39.

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FIGURE 5.1-4 H_2 Reduction Rate (At 990°F) of Various Screen Fractions of Mallinckrodt "60" UO_3

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TABLE 5.1-3

**RATE LAW CONFORMITY VERSUS VARIATION OF
REDUCTION RATE WITH PARTICLE SIZE**

Type of Orange Oxide	Conforms to Phase - Boundary Rate Law	Reduction Rate Varies with Particle Size
Mallinckrodt, pot-denitrated	Yes	Very little
Hanford, continuous -calcined	Yes ¹	Yes ¹
National Lead Company of Ohio pot-denitrated, sulfated	No	Yes

Failure of Mallinckrodt orange oxide to show the expected variation in reduction rate with particle size may be explained on a porosity basis. If the macro particles (as separated by the screening process) are assumed to consist of relatively "solid" micro particles (crystallites) bound together in a loose enough fashion to permit ready passage of both hydrogen and steam through the macro particle, there should be no great difference in the reduction rates of the various fractions. On the other hand, if the screen fractions of National Lead Company of Ohio orange oxide are sufficiently dense to prohibit free passage of either hydrogen or steam within the gross particle, a decrease in reduction rate with increasing particle size would be expected. Equipment has been purchased in order to further pursue this approach.

Conclusions

1. The hydrogen reduction rates of three samples of National Lead Company of Ohio orange oxide were shown to decrease with increasing particle size up to the point where heat buildup within the particle obscured this effect.
2. The hydrogen reduction rate of a Mallinckrodt orange oxide sample was slightly affected by particle size, mostly in the final 10 per cent converted.
3. Therefore, in preparing orange oxide samples (particularly National Lead Company of Ohio product) for hydrogen reduction, these two precautions should be observed:
  - a. For purposes of obtaining kinetics data, a narrow particle size range should be used.
  - b. For purposes of comparing two samples, identical particle size ranges should be used.
4. The particle size distribution of the orange oxide feed to the green salt plant may have an effect on reactivity, due to resultant variations during the reduction step.

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¹ Moore, R. H. and Maness, R. F., *op. cit.*

Future Work

In the hope of reconciling these particle-size-effect differences between National Lead Company of Ohio and Mallinckrodt orange oxides and perhaps also aiding the evaluation of reaction kinetics, porosity studies have been initiated.

5.2 THE EFFECT OF PARTICLE SIZE ON THE HYDROFLUORINATION OF BROWN OXIDE AFTER HYDROGEN REDUCTION OF THE UO_3 AT 1700°F - J. W. Votaw, R. C. Abbott, and D. C. Bonfer

The objective is to determine what effect, if any, particle size has upon the hydrofluorination of UO_2 with anhydrous HF. The method of sample selection for this study is given in Section 5.1 of this report. However, this hydrofluorination investigation was concerned with only a sample from Lot 3F-16-928 (sulfated orange oxide). For convenience, the particle size of the fractions into which the sample was separated and the per cent represented by each fraction are repeated in Table 5.2-1. The fraction remaining on the 20-mesh screen was discarded because of wide variance in particle size. Otherwise, the fraction samples were the same as those employed in the work reported in Section 5.1. A sample of Lot 3F-16-928 which had not been screened was included in this study.

Methods and Discussion

All samples were reduced in the reactivity train (See Section 12.6 of this report) for 30 minutes at an indicated temperature of 1700°F , and a hydrogen flow rate of 1.5 liters per minute was used. The reaction chamber was cooled as rapidly as possible to 100°F , and the samples were removed and stored in closed containers.

Two and one-half grams of each sample was hydrofluorinated in the thermobalance at an HF flow rate of approximately 1.0 liter per minute. Two determinations were made on each sample under the following conditions of temperature:

In the determination in which a programmed temperature was used, the sample was placed in the thermobalance at room temperature. With the sample under a nitrogen purge, the temperature was raised to 400°F , at which point the nitrogen flow was replaced with HF. The temperature was raised at the maximum heating rate to 1200°F , which required approximately 50 minutes. The sample was held at 1200°F for the balance of the two-hour hydrofluorination period.

In the determination in which an isothermal temperature was used, the sample was placed in the thermobalance at a temperature of 1200°F . With the sample under a nitrogen purge, the head was bolted to the reaction chamber and the nitrogen flow was replaced with HF. The temperature was maintained at 1200°F for the entire two-hour hydrofluorination period.

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The results (conversion to UF_4 versus time) of the programmed temperature hydrofluorination are reported in Table 5.2-1. The isothermal hydrofluorination results are given in Table 5.2-2.

It is apparent from Table 5.2-1 that there is no significant difference in the hydrofluorination rates of the five samples tested when a programmed temperature is used. However, an increase in completeness of conversion to UF_4 (at the end of 120 minutes) with decreases in particle size is noted.

TABLE 5.2-1

THERMOBALANCE HYDROFLUORINATION - PROGRAMMED TEMPERATURE

Screen Fraction	Per Cent* Represented by Each Fraction	% Conversion to UF_4 at Indicated Times											
		10 min	20 min	30 min	40 min	50 min	60 min	70 min	80 min	90 min	100 min	110 min	120 min
+40, -20	3.04	39.7	59.5	75.3	85.5	91.0	93.4	95.1	95.3	96.0	96.1	96.1	96.1
+80, -40	13.88	35.5	58.1	75.5	86.0	90.2	93.8	95.6	96.3	96.8	97.1	97.3	97.3
+325, -80	44.68	37.7	58.1	73.3	84.2	89.8	92.4	94.1	95.1	96.2	96.6	97.1	97.3
-325	38.14	36.7	58.0	72.9	83.4	89.7	92.9	94.9	96.3	97.6	98.2	98.2	98.2
Lot 3F-16-928 (Unscreened)	100	41.0	62.0	76.6	85.5	91.0	93.4	95.1	95.8	96.3	96.8	97.3	97.3

Test Conditions:

1. Reduction - Temperature - 1700°F
- Time - 30 Minutes
2. Hydrofluorination - Sample weight - 2.5 g
- Temperature - Programmed from 400 - 1200°F
- Time - 120 Minutes

* The +20 fraction, which was discarded, was 0.26 per cent of the sample.

For isothermal conditions, there is a definite trend toward faster conversion to UF_4 as particle size increases, as is shown in Table 5.2-2. This discrepancy in results between the two methods of hydrofluorination can be explained, however, by the fact that 2.5 grams of the two larger size fractions provide essentially no bed depth in the thermobalance reaction pan except the thickness of the particle. On the other hand, the bed depth of the two smaller size fractions is measurable (1 to 2 mm). Because of the much faster reaction during the initial part of the hydrofluorination, caking in the static bed develops to a much higher extent when a temperature of 1200°F is used than when the temperature is programmed from 400° to 1200°F . Further evidence of the inhibiting effect of high initial temperature on hydrofluorination of UO_3 powder in the thermobalance is shown by the higher over-all final conversion to green salt in the case of the programmed temperature runs.

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Microscopic examination of the starting orange oxide and the brown oxide and green salt products from each fraction indicated that particle size remained essentially unchanged through the reduction and hydrofluorination steps.

TABLE 5.2-2

THERMOBALANCE HYDROFLUORINATION - ISOTHERMAL TEMPERATURE

Screen Fraction	Per Cent* Represented by Each Fraction	% Conversion to UF ₄ at Indicated Times											
		10 min	20 min	30 min	40 min	50 min	60 min	70 min	80 min	90 min	100 min	110 min	120 min
+40, -20	3.04	69.3	79.5	84.4	87.5	89.7	91.6	92.9	93.9	94.6	95.4	95.6	95.7
+80, -40	13.88	67.2	77.2	82.2	85.0	87.7	89.4	90.9	92.2	93.1	94.1	94.9	95.3
+325, -80	44.68	66.0	75.7	80.5	83.7	86.1	87.8	89.3	90.9	92.2	92.9	93.4	93.7
-325	38.14	65.9	74.3	78.8	82.2	84.8	86.3	87.7	89.0	90.0	91.2	91.9	92.4
Lot 3F-16-928 (Unscreened)	100	69.4	78.0	82.9	85.6	88.0	89.7	91.2	92.2	92.9	93.6	94.1	94.6

Test Conditions:

1. Reduction - Temperature - 1700° F
- Time - 30 Minutes
2. Hydrofluorination - Sample weight - 2.5 g
- Temperature - 1200° F
- Time - 120 minutes

* The +20 fraction, which was discarded, was 0.26 per cent of the sample.

Conclusions

1. Under stated conditions of reduction and when programmed hydrofluorination temperature is used, there is no significant difference in reaction rates of four different fractions screened from a single lot of UO₃.
2. Under stated conditions of reduction and with an isothermal hydrofluorination, there is a trend toward faster conversion to UF₄ with increasing particle size. However, this trend is wholly or partially explained by the increased caking in the static bed with decreasing particle size.

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5.3 EFFECT OF HCl-INSOLUBLE CONTENT ON THE HYDROFLUORINATION CONVERSION OF BROWN OXIDE AFTER HYDROGEN REDUCTION OF THE UO_3 AT $1700^\circ F$

— J. W. Votaw, D. C. Bonfer, and R. C. Abbott

The objective of this study was to investigate the effect of HCl-insoluble content of sulfated orange oxide on the hydrofluorination conversion after hydrogen reduction of the UO_3 at $1700^\circ F$. HCl-insoluble content is considered to be indicative of the amount of U_3O_8 present in the material.

Samples of four orange oxide lots from among those produced early in July, 1956, were selected for study on the basis of their differing HCl-insoluble contents. The lot numbers and the HCl-insoluble contents of the samples are shown in Table 5.3-1.

TABLE 5.3-1

THERMOBALANCE HYDROFLUORINATION OF ORANGE OXIDE SAMPLES HAVING DIFFERING HCl-INSOLUBLE CONTENTS

Lot	HCl- Insol. (%)	% Conversion to UF_4 at Specified Times											
		10 min	20 min	30 min	40 min	50 min	60 min	70 min	80 min	90 min	100 min	110 min	120 min
3F-16-898	0.42	39.1	54.3	67.2	77.1	83.0	86.8	89.0	90.7	92.0	93.4	94.2	96.0
3F-16-894	1.45	35.5	53.3	66.0	75.6	82.7	86.6	89.5	91.7	93.4	94.6	95.8	96.6
3F-16-887	2.63	35.0	51.6	65.2	75.4	83.3	87.2	90.2	92.1	93.7	94.8	95.6	96.2
3F-16-902	4.54	38.7	55.2	68.9	78.8	85.4	89.2	92.1	93.6	94.6	95.9	96.8	97.3

Methods and Discussion

Conditions of reduction and hydrofluorination were:

1. Reduction in the Reactivity Train
  - a. Indicated Temperature: $1700^\circ F$
  - b. Time: 30 minutes
2. Hydrofluorination in the Thermobalance
  - a. Sample weight: 2.5 grams
  - b. Temperature: Programmed from 400° to $1200^\circ F$
  - c. Time: 120 minutes

Hydrofluorination data are reported in Table 5.3-1. Analytical results (spectrochemical, wet chemical, bulk density, and screen analysis) are given in Table 5.3-2. It is apparent from Table 5.3-1 that no significant differences exist in the hydrofluorination rates of the four samples tested. Lot 3F-16-902, with the highest HCl-insoluble content, showed the highest rate of conversion to

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green salt, while Lot 3F-16-898, with the lowest HCl-insoluble content, showed the lowest per cent conversion after two hours' hydrofluorination. Analyses for the four samples, reported in Table 5.3-2, show very little variation, with the exception of the HCl-insoluble analysis.

TABLE 5.3-2
ANALYSIS* OF ORANGE OXIDE SAMPLES

	Lot 3F-16-898	Lot 3F-16-894	Lot 3F-16-887	Lot 3F-16-902
Al	<4	<4	<4	<4
B	<0.2	<0.2	<0.2	<0.2
Ba	<6	<6	<6	<6
Bi	<1	<1	<1	<1
Ca	<5	<5	<5	<5
Cd	<0.2	<0.2	<0.2	<0.2
Co	<2	<2	<2	<2
Cr	<4	<4	6	<4
Cu	<1	<1	1	<1
Fe	16	21	19	17
Li	<5	<5	<5	<5
Mg	1	1	6	3
Mn	<4	<4	<4	<4
Mo	<4	<4	<4	<4
Na	4	2	<1	3
Ni	1.8	2.6	1.8	2.1
P	<20	<20	<20	<20
Pb	<1	<1	<1	<1
SiO ₂	<20	<20	<20	<20
Sn	<1	<1	<1	<1
Sr	<12	<12	<12	<12
V	<20	<20	<20	<20
Zn	<20	<20	<20	<20
Total U (%)	82.01	82.11	82.49	82.36
UO ₃ (%)	98.54	98.66	99.12	98.96
NO ₃ (%)	0.57	0.55	0.32	0.32
SO ₄	470	500	480	490
HCl-Insoluble (%)	0.42	1.45	2.63	4.54
H ₂ O (%)	0.89	0.79	0.56	0.72
Bulk Density (g/ml)	2.33	2.63	2.38	2.70
Screen Analysis (%)				
on 40	5.4	6.6	3.0	6.4
on 80	10.6	10.8	7.2	12.2
on 325	22.0	21.8	23.0	22.4
through 325	62.0	60.8	66.8	59.0

* All results in parts per million unless otherwise noted.

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Conclusions

Under the stated test conditions, hydrofluorination rates of samples from four production lots of National Lead Company of Ohio orange oxide were not affected by variations between 0.42 and 4.54 per cent in the HCl-insoluble content of the samples.

5.4 LABORATORY INVESTIGATION OF BULK UO_3 POWDER, UO_3 SCALE, AND UO_3 HARD LUMPS FROM VARIOUS DENITRATION POTS - J. W. Votaw, D. C. Bonfer, and R. C. Abbott

When orange oxide produced at National Lead Company of Ohio comes from the denitration pot, it is normally a composite of three different types of product:

1. Bulk powder,
2. Scale scraped from the sides of the pot and from the agitator, and
3. Hard lumps formed in the bulk powder during denitration.

It has been estimated that the two latter types each average five to ten per cent by weight of the ground orange oxide product.

The objective of this study was to examine the three types of orange oxide from three different denitration pots and to determine what differences in analysis and/or reactivity existed (1) between the three products from any one pot and (2) between the same types of orange oxide product from all three pots. (Reactivity refers to convertability to UF_4 .)

Samples of sulfated orange oxide described below were taken and were submitted to the laboratory for spectrochemical and wet chemical analyses and for the determination of hydrofluorination reactivity in the thermobalance:

Pot 203

pot powder
scale from sides of pot
lumps

Pot 206

pot powder
scale from agitator
lumps

Pot 214

pot powder
scale from agitator
lumps

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Methods, Data, and Discussion

All samples were ground to pass a 100-mesh sieve.

Conditions of reduction and hydrofluorination were:

1. Reduction in the Reactivity Train (See Section 12.7 of this report)
  - a. Temperature: 1700° F (indicated)
  - b. Time: 30 minutes
2. Hydrofluorination in the Thermobalance¹
  - a. Sample weight: 2.5 grams
  - b. Temperature: Programmed from 400° to 1200° F
  - c. Time: 120 minutes

The hydrofluorination curves (per cent conversion versus time) are shown in Figures 5.4-1, 5.4-2, and 5.4-3. Analytical results are given in Table 5.4-1.

As can be seen in Figures 5.4-1, 5.4-2, and 5.4-3, wide variations in hydrofluorination reactivity did exist, not only between the three types of product from the same pot, but also between the same type of material from different pots. The pot scale and lump samples from Pot 203 showed very poor conversion to green salt after two hours' residence time in the thermobalance. On the other hand, the bulk powder sample from the same pot hydrofluorinated satisfactorily. The bulk powder sample from Pot 214 exhibited a low reaction rate throughout hydrofluorination, while the lump and agitator scale samples from Pot 214 showed good reactivity. All three samples from Pot 206 showed high reactivity throughout hydrofluorination in the thermobalance.

Examination of the analytical data compiled in Table 5.4-1 also reveals wide differences in some instances between corresponding materials from the three pots. Nevertheless, none of the analyses can be correlated with hydrofluorination reactivity of any of the samples. Neither high sodium content (Pot 206 agitator scale) nor high NO₃ content (Pot 206 scale and lumps and Pot 214 scale and lumps) seemed to inhibit the hydrofluorination reactivity under the conditions used.

It is evident from nitrate and H₂O analyses that the scale sample from the side of the pot is entirely different from the agitator scale samples. Since the pot scale sample showed very low reactivity under stated test conditions, further investigation of this type of UO₃ product appears to be justified.

¹ Williamson, J. A., *Summary Tech. Rpt.*, Vol II, pp. 68-70, NLCO-601, January 16, 1956.

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FIGURE 5.4-1 Hydrofluorination Versus Time – Pot Powder

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FIGURE 5.4-2 Hydrofluorination Versus Time -- Scale

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FIGURE 5.4-3 Hydrofluorination Versus Time – Lumps

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TABLE 5.4-1

ANALYSES OF ORANGE OXIDE

	Pot 203			Pot 206			Pot 214		
	Powder	Scale	Lumps	Powder	Scale	Lumps	Powder	Scale	Lumps
Al	<4	<4	<4	<4	<4	<4	<4	25	<4
B	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Ba	<6	<6	<6	<6	<6	<6	<6	<6	<6
Bi	<1	<1	<1	<1	<1	<1	<1	<1	<1
Ca	<5	5	8	8	<5	<5	5	10	10
Cd	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Co	<2	<2	<2	<2	<2	<2	<2	<2	<2
Cr	<4	<4	<4	<4	6	<4	<4	4	<4
Cu	12	8	2	2	12	5	2	6	6
Fe	4	20	12	55	40	18	6	25	7
Li	<5	<5	<5	<5	<5	<5	<5	<5	<5
Mg	3	3	3	4	5	3	1	2	2
Mn	<4	<4	<4	<4	<4	<4	<4	<4	<4
Mo	<4	<4	<4	<4	<4	<4	<4	<4	<4
Na	20	15	15	10	200	12	10	40	8
Ni	<2	3	<2	2	15	<2	2	4	<2
P	<20	<20	<20	<20	<20	<20	<20	<20	<20
Pb	<1	5	<1	4	3	<1	4	<1	<1
SiO ₂	<20	<20	<20	<20	30	<20	<20	30	20
Sn	<1	<1	<1	<1	<1	<1	<1	<1	<1
Sr	<12	<12	<12	<12	<12	<12	<12	<12	<12
V	<20	<20	<20	<20	<20	<20	<20	<20	<20
Zn	<20	<20	<20	<20	<20	<20	<20	<20	<20
NO ₃ (%)	0.32	0.76	0.74	0.54	8.53	4.89	1.36	7.57	5.78
H ₂ O (%)	1.02	2.29	2.30	1.43	7.05	3.69	1.69	4.30	3.36
HCl - Insoluble (%)	0.29	0.05	0.01	0.15	<0.01	<0.01	0.04	0.01	0.01
SO ₄	530	950	590	510	810	480	510	520	480

* All results expressed in parts per million unless otherwise noted.

Conclusions

1. Hydrofluorination reactivity measurements and analytical data reveal wide differences in the three typical denitration pot products — bulk powder, scale (side scale or agitator scale), and lumps.
2. No correlation between reactivity and analytical results can be made.

100

100

6. GREEN SALT PROCESS

The feed material to the Green Salt Plant is orange oxide. The orange oxide is fed through a heated horizontal screw reactor, where it is reduced to UO_2 by hydrogen (dissociated ammonia). The brown oxide (UO_2) is then fed through three successive screw reactors, where it is converted to green salt by anhydrous hydrogen fluoride.

(NOTE: ADU, described in Sections 12.1, 12.2, and 12.3 of this report, is being considered not only as an MBR feed but as a substitute for the pot-denitrated UO_3 now used as feed for the green salt process.)

6.1 INVESTIGATION OF THE PROCESSING CHARACTERISTICS OF PORT HOPE UO_3 - R. C. Abbott, D. C. Bonfer, R. L. Maddox, J. A. Massei, H. F. Muhlhauser, L. P. Trimmerger, and J. W. Votaw

During this period, emphasis was placed on problems related to the conversion of Port Hope UO_3 to UF_4 . Two approaches were taken:

1. UO_3 which had been produced at Port Hope from uranyl nitrate which had been produced at National Lead Company of Ohio was evaluated in the plant and laboratory, and
2. Plant conditions for achieving greater throughput for Port Hope UO_3 were to be developed.

Summary

The results of work with orange oxide produced at Port Hope from National Lead Company of Ohio uranyl nitrate (UNH) indicate:

1. On the basis of laboratory data, this orange oxide has a slightly greater hydrofluorination conversion under the test conditions than has the Port Hope UO_3 used for comparison, but a lower hydrofluorination conversion than has National Lead Company of Ohio UO_3 .
2. This UO_3 appears to be sensitive to reduction temperature, as is Port Hope UO_3 .
3. Although a gross difference was not seen, plant processing results appeared to show a lower conversion for this material than for contemporary sulfated UO_3 produced by National Lead Company of Ohio.

Operating conditions have been selected which make possible the conversion of Port Hope UO_3 to metal grade UF_4 at a UO_3 feed rate of 300 lb/hr/bank.

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Evaluation of UO_3 Produced at Port Hope from National Lead Company of Ohio Uranyl Nitrate

Initial processing of Port Hope UO_3 to UF_4 was conducted during December, 1955, and January, 1956. The results of this work indicated that this UO_3 would be difficultly processed at feed rates greater than 200 lb/hr.¹ It was decided that information of value could be obtained by denitrating a quantity of National Lead Company of Ohio uranyl nitrate at the Port Hope refinery and returning the UO_3 to National Lead Company of Ohio for processing to UF_4 .

As a result, approximately 14 tons of a uranyl nitrate solution from National Lead Company of Ohio production (containing 1322 g/l uranium) were converted to UO_3 at Port Hope. Operating conditions for denitration were those normally used at Port Hope, with the exception that sulfuric acid was added to achieve a 750 ppm sulfate ion concentration on a uranium basis, as is the practice at National Lead Company of Ohio. No major difficulties were noted in the denitration operation. The product UO_3 was ground and packaged at Port Hope and was returned to National Lead Company of Ohio for processing. The UO_3 was characterized in the laboratory by chemical and spectrochemical analyses and by thermogravimetry and was evaluated in the plant by using existing processing conditions.

A. Sampling (Laboratory Characterization)

All drums were sampled at this site and the samples were composited to form Parts I, II and III, each part representing one-third of the total UO_3 received. The three samples were submitted to the laboratory and were composited again to form one sample for the examination of hydrofluorination reactivity in the thermobalance.

For comparison, samples of Port Hope normal production UO_3 were taken immediately preceding and immediately following the test run with National Lead Company of Ohio uranyl nitrate.

B. Hydrofluorination of UO_2 Produced by High-Temperature Reduction

Reduction of all samples was effected in the reactivity train. The boat containing the samples was placed in the train and the temperature was raised to 1700°F (indicated), with nitrogen used as a purge. A hydrogen flow rate of 1.5 liters per minute was admitted to the reaction chamber, and the reduction was continued for 30 minutes.

The brown oxide samples were cooled to 100°F as rapidly as possible, under a hydrogen purge, and then were removed from the train and stored in closed sample bottles. After passing a 60-mesh screen, 2-1/2 grams of each sample was hydrofluorinated in the thermobalance. The HF flow rate was approximately 1.0 liter per minute and the temperature was programmed from 400°F to 1200°F. Hydrofluorination was allowed to continue for two hours.

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¹ Burkhardt, W., Maddox, R. L., Mautz, E. W., Massei, J. A., and Schonberger, J. F., Summary Tech. Rpt., pp. 59-62, NLCO-625, April 16, 1956.

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The hydrofluorination data, including those for National Lead Company of Ohio sulfated standard (Lot 3E-16-706) determined under the same conditions, are reported in Table 6.1-1. Analytical results for the three samples are given in Table 6.1-2.

TABLE 6.1-1

**THERMOBALANCE HYDROFLUORINATION OF UO_2
PRODUCED BY 30-MINUTE REDUCTION AT 1700° F**

Source of UO_2	Per Cent Conversion to UF_4 at Indicated Times											
	10 min	20 min	30 min	40 min	50 min	60 min	70 min	80 min	90 min	100 min	110 min	120 min
1. Composite of Parts I, II, and III of National Lead Company of Ohio UNH Denitrated to UO_3 at Port Hope	31.2	45.6	58.2	68.5	75.4	79.5	82.2	84.6	86.6	88.3	89.7	90.6
2. Port Hope Normal Production UO_3 Sampled Immediately Preceding the Denitration Experiment	29.6	44.2	57.2	66.7	72.5	76.2	79.4	82.2	83.5	85.3	86.5	87.5
3. Port Hope Normal Production UO_3 Sampled Immediately Following the Denitration Experiment	28.9	43.5	56.9	66.4	73.0	76.6	80.4	82.4	84.1	85.4	86.8	87.7
4. National Lead Company of Ohio Sulfated Standard UO_3 (Lot 3E-16-706)	27.7	45.6	62.7	78.2	87.7	91.7	94.1	95.8	96.8	97.5	97.8	97.8

From Table 6.1-1, it can be seen that the National Lead Company of Ohio uranyl nitrate, denitrated at Port Hope and reduced at National Lead Company of Ohio at 1700° F, had a slightly higher rate of hydrofluorination than either sample of normal Port Hope production. The National Lead Company of Ohio sulfated standard, however, shows a significantly higher conversion to UF_4 after two hours' hydrofluorination time than does the sulfated National Lead Company of Ohio material denitrated at Port Hope.

The two samples of Port Hope normal production UO_2 hydrofluorinated at almost exactly the same rate. Their per cent conversion to UF_4 at the end of 120 minutes is also in the range (85 to 90%) of conversion found for every sample of Port Hope product UO_3 examined in the thermobalance before July 1, 1956, under the stated conditions of reduction and hydrofluorination.

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TABLE 6.1-2

ANALYSES* OF PORT HOPE UO_3

	Composite** of Parts I, II, and III	Port Hope UO_3 Before Trial Run	Port Hope UO_3 After Trial Run
Al	<4	<4	<4
B	<0.2	<0.2	<0.2
Ba	<6	<6	<6
Bi	<1	<1	<1
Ca	<5	5	5
Cd	<0.2	<0.2	<0.2
Co	<2	<2	<2
Cr	<4	4	4
Cu	2	4	4
Fe	25	35	40
Li	<5	<5	<5
Mg	3	5	4
Mn	<4	<4	<4
Mo	<4	<4	<4
Na	<6	6	5
Ni	8	5	7
P	<20	<20	<20
Pb	<1	<1	3
SiO_2	<20	<20	<20
Sn	<1	<1	<1
Sr	<12	<12	<12
V	<20	<20	<20
Zn	<20	<20	<20
NO_3 (%)	0.98	0.69	0.59
H_2O (%)	1.41	1.12	1.56
HCl-Insoluble (%)	<0.01	<0.01	0.02
SO_4	430	430	430
Bulk Density (g/ml)	2.74	2.50	2.33
Wet Screen Analysis (%)			
on 40 mesh	3.5	1.6	4.4
on 80 mesh	10.3	5.4	3.2
on 325 mesh	23.2	32.0	14.8
through 325 mesh	63.0	61.0	77.6

* All results in parts per million (ppm) unless otherwise noted.

** This represents the UO_3 that was produced at Port Hope from National Lead Company of Ohio uranyl nitrate.~~CONFIDENTIAL~~

The analytical data (Table 6.1-2) show no wide discrepancies between either of the samples of Port Hope production and the experimental product from denitration of National Lead Company of Ohio uranyl nitrate. Since the form in which the sulfur occurs in the Port Hope normal production has never been established, it is possible that the sulfation (H_2SO_4) of the National Lead Company of Ohio UNH, during denitration at Port Hope, produced the slightly higher hydrofluorination reactivity shown in Table 6.1-1.

C. Hydrofluorination of UO_2 Produced by Low-Temperature Reduction

Reduction of all samples was performed in the thermobalance at a set temperature of 1200°F . The sample weight in each case was 2.5 grams and the hydrogen flow rate was 2.0 liters per minute.

At completion of the reduction, the temperature was reduced to 1100°F and the hydrogen was replaced by anhydrous HF at a flow rate of approximately 1.0 liter per minute. Hydrofluorination was allowed to continue for 60 minutes. Reaction rates of the various samples were compared with that of National Lead Company of Ohio sulfated standard (Lot 3E-16-706) determined under the same conditions. Results are given in Table 6.1-3.

TABLE 6.1-3

THERMOBALANCE HYDROFLUORINATION OF UO_2 PRODUCED BY REDUCTION AT 1200°F

Source of UO_2	Per Cent Conversion to UF_4 at Indicated Times												
	0.5 min	1 min	2 min	3 min	4 min	5 min	10 min	15 min	20 min	30 min	40 min	50 min	60 min
1. Composite of Parts I, II, and III of National Lead Company of Ohio UNH Denitrated to UO_3 at Port Hope	18.6	36.4	58.8	66.8	71.5	75.5	84.3	88.3	91.7	94.2	95.8	96.3	96.5
2. Port Hope Normal Production UO_3 Immediately Preceding the Denitration Experiment	11.5	28.5	57.2	64.5	72.3	75.2	83.3	86.9	89.6	91.6	92.7	94.0	95.0
3. Port Hope Normal Production UO_3 Immediately Following the Denitration Experiment	18.1	38.8	64.0	70.3	74.8	77.2	83.5	86.6	88.7	90.6	92.1	92.9	93.7
4. National Lead Company of Ohio Sulfated Standard UO_3 (Lot 3E-16-706)	16.2	34.6	53.0	61.1	65.9	70.3	81.6	86.5	89.2	92.4	93.8	94.1	94.9

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As can be seen in Table 6.1-3, there is no significant difference in per cent conversion to UF_4 after 60 minutes between any of the samples tested and the sulfated standard. The sulfated standard had the slowest initial rate of hydrofluorination, while the sample of National Lead Company of Ohio material denitrated at Port Hope reached the highest per cent conversion after 60 minutes.

From the above observations, it appears that some inherent characteristic of the denitration equipment, denitration cycle, or grinding equipment at Port Hope produces an orange oxide product which is highly sensitive to temperature of reduction.

D. Plant Operating Data

TABLE 6.1-4

REACTOR OPERATING CONDITIONS*

Gas Flow Rates:

Dissociated Ammonia: $1.5 \times$ theoretical

Anhydrous Hydrogen Fluoride: $2.5 \times$ theoretical

Reactor	Temperature ($^{\circ}$ F)				Main Screw Speed (rpm)
	Zone 1	Zone 2	Zone 3	Zone 4	
Reduction	1100	1100	1180	1100	8
First Hydrofluorinator	—	—	925	950	12
Second Hydrofluorinator	950	975	1000	1075	12
Third Hydrofluorinator	1050	1100	1125	1175	12

* Operating conditions were not changed from those which were in existence just prior to the test, when National Lead Company of Ohio sulfated UO_3 was being processed.

TABLE 6.1-5

COMPARISON OF AVERAGE GREEN SALT ANALYSES — NATIONAL LEAD COMPANY OF OHIO SULFATED UO_3 AND PORT HOPE UO_3 MADE FROM NATIONAL LEAD COMPANY OF OHIO URANYL NITRATE

Source of Product	Feed Type	Avg Feed Rate (lb/hr)	UF_4 (%)	UO_2F_2 (%)	AOI (%)
Experimental Reactor Bank	NLO Sulfated	360	94.27	3.08	2.65
Experimental Reactor Bank	NLO UNH, denitrated at Port Hope	360	92.70	2.79	4.51
Plant (Avg Analysis)	NLO Sulfated	370	95.05	2.89	2.06

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Plant Processing of Port Hope UO_3 to UF_4

Development work on a plant basis has been directed toward obtaining process conditions which will give maximum throughput for Port Hope UO_3 .

Previous tests¹ had shown that this material is sensitive to high temperatures in the reduction and first hydrofluorination reactors, and that in-specification green salt is only produced at low feed rates. Based on the above information, the initial conditions for this test specified lower-than-normal temperatures in the reduction and hydrofluorination reactors and a 200 lb/hr/bank feed rate. A production bank of reactors (Bank 3) was used for this study. The initial processing conditions are given in Table 6.1-6:

TABLE 6.1-6

**INITIAL PROCESSING CONDITIONS FOR
REDUCTION AND HYDROFLUORINATION**

Feed rate: 200 lb/hr/bank

Anhydrous hydrogen fluoride rate: $2.5 \times$ theoretical

Dissociated ammonia rate: $1.5 \times$ theoretical

Cooling: large exhaustor on first zone of first hydrofluorination reactor

Reactor	Temperature ($^{\circ}\text{F}$)				Screw Speeds (rpm)
	Zone 1	Zone 2	Zone 3	Zone 4	
Reduction	1075	1075	1075	1075	8
First Hydrofluorination	500	600	725	825	10
Second Hydrofluorination	850	900	975	1050	10
Third Hydrofluorination	1075	1100	1125	1150	12

It is required that the maximum AOI content be 1.9 per cent, the maximum UO_2F_2 content be 2.9 per cent and the minimum UF_4 content be 96 per cent. The UO_2F_2 content of the product from the third hydrofluorination reactor was slightly high, as shown in Line 1 of Table 6.1-7. The temperatures in the reduction reactor were increased 50°F in each zone. In-specification green salt was produced with these conditions (Table 6.1-7, Line 2).

¹ Burkhardt, W., Maddox, R. L., Mautz, E. W., Mazzei, J. A., and Schonberger, J. F., Summary Tech. Rpt., pp. 59-62, NLCO-625, April 16, 1956.

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TABLE 6.1-7

COMPARISON OF AVERAGE ANALYSES WITH PROCESSING CONDITIONS

Feed Rate (lb/hr)	Processing Conditions	Avg Analysis of Third Hydrofluorination Reactor Samples			Avg Analysis of Lots		
		AOI (%)	UO ₂ F ₂ (%)	UF ₄ (%)	AOI (%)	UO ₂ F ₂ (%)	UF ₄ (%)
1. 200	Original conditions.	0.77	3.54	95.69	0.56	1.89	97.55
2. 200	Reduction reactor temperature increased to 1125° F.	0.82	2.22	96.96	1.23	1.46	97.31
3. 250	Same conditions as 2. above.	1.93	2.27	95.80	2.22	0.82	96.96
4. 250	Most of the hydrofluorination reactor temperatures were elevated and the first and second zone reduction reactor temperatures were reduced.	1.76	2.90	95.34	1.70	0.99	97.31
5. 250	Reduced hydrofluorination reactor temperatures to minimize plugging conditions.	1.40	2.74	95.86	1.52	0.67	97.81
6. 324	Anhydrous hydrogen fluoride rate: 2.1 × theoretical; dissociated ammonia rate: 1.1 × theoretical.	1.08	5.02	93.90	0.86	4.06	95.08
7. 250	No forced-air cooling on the first zone of first hydrofluorination reactor.	2.38	1.87	95.75	2.18	1.22	96.60
8. 300	Final conditions – The temperatures of the first and second zones of the reduction reactor were reduced and the temperatures of the third and fourth zones of the first hydrofluorination reactor were increased.	2.56	1.46	95.98	2.34	1.58	96.08

After five days of satisfactory operation, the feed rate was increased to 250 pounds per hour. This resulted in a large increase in the AOI content (Table 6.1-7, Line 3). Therefore, over a one-week period, the temperatures of the reactors were changed to:

Reactor	Temperature (°F)			
	Zone 1	Zone 2	Zone 3	Zone 4
Reduction	1075	1075	1125	1125
First Hydrofluorination	500	600	775	875
Second Hydrofluorination	925	975	1050	1100
Third Hydrofluorination	1100	1125	1150	1175

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In -specification green salt was produced at these temperatures (Table 6.1 -7, Line 4), but the torques of second and third hydrofluorination reactors showed a definite increase, which is one indication of excessive temperatures. Therefore, the temperatures of these reactors were reduced as follows:

Reactor	Temperature (°F)			
	Zone 1	Zone 2	Zone 3	Zone 4
Second Hydrofluorination	900	950	1025	1100
Third Hydrofluorination	1080	1110	1140	1160

In addition, the speed of the main screw in the second hydrofluorination reactor was increased from 10 rpm to 12 rpm.

These process changes had little effect on the AOI content of the green salt, and in -specification material was still produced (Table 6.1 -7, Line 5). However, the torques of the second and third hydrofluorination reactors remained slightly high. It was believed that these reactor tubes were internally "slagged up" and that further temperature reductions in these reactors would not reduce the torques.

Besides increasing the torque and thereby endangering the main reactor screws, slagging of a tube has a second adverse effect on processing. The slag acts as an insulator, reducing the heat transfer from the external heaters to the reactants in the reactor tube. Since this reaction is dependent upon temperature, the AOI content of the green salt is increased.

For the next 48 hours of operation, although the target feed rate remained at 250 lb/hr, the actual feed rate averaged 324 lb/hr. The actual anhydrous hydrogen fluoride and dissociated ammonia feed rates averaged less than $2.1 \times$ theoretical and less than $1.1 \times$ theoretical, respectively. Line 6 of Table 6.1 -7 shows that the AOI content was satisfactory during this time, but that the UO_2F_2 content was well above the specification limits. This period was also characterized by high reactor temperatures, especially in the second and third zones of the reduction reactor and in the second and third zones of the first hydrofluorination reactor.

Because of maintenance scheduling problems, Bank 3 operated for the next four days without forced -air cooling, but with all other conditions identical to those last used to produce in -specification green salt. In -specification green salt was not produced during this time. However, throughout this period it was observed that the analyses of material taken from the second and third hydrofluorination reactors were very much the same, indicating that little conversion took place in the third hydrofluorination reactor - probably because of slagging.

For the final two days of processing, the target feed rate was increased to 300 lb/hr. In order to remove, more effectively, the additional heat resulting from the higher feed rate, a blower having approximately twice the capacity of the exhaustor formerly used was installed in the first zone of

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the first hydrofluorination reactor. The operation of the blower was controlled by the same control circuit which controlled the heating elements of this zone. In addition, temperatures in the first two zones of the reduction reactor were decreased 35°F, and temperatures in all zones of the first hydrofluorination reactor were increased by 25° to 125°F. As is seen in Line 8 of Table 6.1-7, in-specification green salt was not produced under these conditions. Again the analyses of the second and third hydrofluorination reactors indicated that little conversion had been carried out in the last hydrofluorination reactor. Slagging was considered to be the reason for the poor conversion.

Considerable overheating was observed in the second zone of the reduction reactor when the feed rate was increased. To compensate for this, the set temperatures of the first two zones of this reactor were decreased.

The final reactor temperatures and screw speeds used in the processing of Port Hope orange oxide were:

Reactor	Temperature (°F)				Screw Speed (rpm)
	Zone 1	Zone 2	Zone 3	Zone 4	
Reduction	1040	1040	1125	1125	8
First Hydrofluorination	600	700	825	900	10
Second Hydrofluorination	900	950	1025	1100	12
Third Hydrofluorination	1080	1110	1140	1160	12

The over-all on-stream factor for Bank 3 (a 27-day period) was 93.1 per cent. Plant difficulties which caused downtime were hydrofluoric acid vaporizer failure, refrigeration failure, and hydrofluoric acid leaks. The major difficulty of Bank 3 was high torques in the second and third hydrofluorination reactors.

6.2 A THERMOBALANCE INVESTIGATION OF STARCH AS A REDUCING AGENT FOR ORANGE OXIDE - G. G. Briggs

Starch has been employed successfully as a reducing agent for orange oxide. Pellets have been formed by hydrating mixtures of UO_3 and starch to form feed for pilot plant-scale reduction and hydrofluorination in a moving bed reactor. This work, which was done at Oak Ridge, met with considerable success in that green salt assaying 99 per cent UF_4 was produced.¹

Interest at National Lead Company of Ohio has centered upon the possibility of employing starch as the reducing agent in the moving bed reactor. Possible advantages of using starch in place of hydrogen from cracked ammonia appear to be: better temperature control and the production of material possessing greater reactivity towards hydrofluorination.

¹ Chemical Technology Division Semiannual Progress Report for Period Ending September 30, 1955, pp. 42-44, ORNL-2000.

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In the laboratory, a brief thermobalance study was made in order to gain information of a preliminary nature concerning the reactions involved in the reduction of pot denitrated UO_3 with starch and its subsequent hydrofluorination to UF_4 . The starch performed the function of reducing the hexavalent uranium to the tetravalent state. In addition to work in which the reduction and hydrofluorination were carried out in two separate steps, some work was done in which both processes were performed simultaneously.

Results

The following paragraphs summarize the work:

1. UO_3 pellets containing starch can be readily reduced to UO_2 at temperatures above 1100°F in an inert atmosphere. Under optimum conditions, the UO_2 can be prepared in a form which is much more reactive towards hydrofluorination (a greater reaction rate) than that produced by reduction with hydrogen.
2. The thermobalance work indicated that the reactivity of the UO_2 was affected adversely when the temperature was maintained above approximately 1300°F during the reduction.
3. Although most of the reduction is accomplished by reaction of the UO_3 (or U_3O_8) with carbon at temperatures above 1100°F , some of the reduction might be accomplished when the starch is thermally decomposed at temperatures as low as 600°F .
4. The thermobalance data indicated that the reduction and hydrofluorination can be performed simultaneously. When this is done, the primary rate-controlling reaction is probably the reduction of uranyl fluoride by the carbon of the starch.
5. The removal of residual carbon from UO_2 pellet samples was attempted: The pellets were contacted with carbon dioxide and steam at elevated temperatures. The experiments were unsuccessful, as the residual carbon content (0.42 per cent) remained far above the specification for carbon in uranium metal (0.062 per cent).
6. In another study, it was established that the ability of orange oxide to form hard structures by hydration is lost within a day or two, when mixtures of the UO_3 and starch are stored at temperatures no greater than 100°F . The effect is accelerated at higher temperatures. It is recommended that blending of starch and UO_3 be carried out just before pelleting.

Conclusions

1. Corn starch can be used for the reduction of orange oxide.
2. Green salt may be prepared either (a) by subsequent hydrofluorination of the reduced material or (b) by simultaneous reduction and hydrofluorination.

6.3 TWO-STEP REDUCTION OF ORANGE OXIDE TO UO_2 - K. J. Notz and W. C. Manser

A fuller knowledge of the kinetics of the hydrogen reduction of orange oxide to UO_2 (see note on limitations of terminology in Section 5.) has long been desired in order to better evaluate the reactivity (convertability to UF_4) of various orange oxide samples. The over-all objective is to increase the production capacity of existing Green Salt Plant facilities.

Reduction data obtained in this laboratory¹ showed the apparent existence of two rate-law conformity types. Work at Mallinckrodt Chemical Works^{2,3} indicated a third type.

A number of factors could be responsible for this variation in over-all reduction kinetics. One of the most plausible is that the reduction proceeds by way of consecutive reactions through an intermediate phase or phases of composition between UO_3 and UO_2 , and that differences between the relative reaction rates approaching and leaving this intermediate product cause the observed rate variations. Since orange oxide can be thermally decomposed to U_3O_8 several experiments were carried out in which various orange oxides were converted to U_3O_8 and then reduced to UO_2 , with the hope of determining the kinetics for the hydrogen reduction of U_3O_8 . Since it has been reported that oxidation of low-reactivity UO_2 to U_3O_8 , followed by reduction to UO_2 , results in a reactive UO_2 ,⁴ it was decided to study, concurrently, the effect of oxidation-reduction recycling on the reduction rate of the resultant U_3O_8 .

Experimental Method

The thermobalance used for making a one-step reduction of orange oxide to UO_2 , as well as the procedure, has been described previously.⁵

The procedure used in these experiments is as follows:

1. A 1.5 to 2.0-gram sample of orange oxide is placed in the hot (approximately 1000°F) reaction chamber, through which helium is flowing.
2. The temperature is increased to 1150°F , which causes thermal conversion to U_3O_8 .
3. After a constant weight is reached, the temperature is reduced to 990°F and hydrogen is introduced to complete the reduction.

This completes the two-step reduction of orange oxide, and the UO_2 product is ready for recycling. This is done without removing the sample by flushing the hydrogen out with helium and then passing air or oxygen through the chamber to re-oxidize to U_3O_8 , which is then ready for another reduction. Recycling is then repeated a second time. A complete weight recording is shown in Figure 6.3-1.

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1 Notz, K. J., *Summary Tech. Rpt.*, pp. 33-39, NLCO-640, July 18, 1956.

2 Ludwig, F. J., *Process Devel. Quart. Rpt.*, Part I, pp. 46-63, MCW-1385, April 1, 1956.

3 Kuhlman, C. W. Jr., *Reduction of Uranium Trioxide to Uranium Dioxide With Hydrogen - Reaction Rates at Various Temperatures*, October 12, 1948.

4 Willson, K. S., *The Reactivity of Uranium Oxides*, NYO-1466, February 15, 1952.

5 Notz, K. J., *loc. cit.*

FIGURE 6.3-1 Two-Step Reduction of Orange Oxide, Followed by Recycles

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By the use of the above procedure, reduction rates were obtained for four orange oxides:

National Lead Company of Ohio sulfated, Lot 3E-16-706

National Lead Company of Ohio nonsulfated, Lot 3E-16-1027

Mallinckrodt, C-61SNO 406, 81102

Port Hope, Composite of Lots 84 through 93

Preliminary observations can be summarized as follows:

1. Thermal decomposition of orange oxide is first order (Fig. 6.3-2). This was noted by Kuhlman.¹
2. The times required for (1) orange oxide and (2) the corresponding U_3O_8 to be reduced to UO_2 at 990° F are very nearly the same. This only applies the first time the U_3O_8 is reduced. Figures 6.3-3 and 6.3-4, which present the data for two National Lead Company of Ohio samples show that the paths followed were different however. Kuhlman² used samples for which the kinetics of the two reactions were indistinguishable.
3. The rate at which UO_2 oxidizes in air and pure oxygen is apparently limited, during the initial 90 per cent conversion, by the rate at which oxygen is supplied, since re-oxidation proceeds at a constant rate except for the final 5 to 10 per cent (Fig. 6.3-1).
4. The U_3O_8 formed by thermal decomposition of orange oxide has a higher oxygen content (by about 1 to 2 mg per 1.5-gram sample) than has the U_3O_8 formed by oxidation of the corresponding UO_2 , in the temperature range, 990° to 1150° F.
5. The reduction rate of U_3O_8 is considerably faster on the second reduction than on the first, but increases only slightly on the third reduction (Fig. 6.3-5). Bard³ et al. report a continuing rate increase up to 12 recycles.
6. In the reduction of U_3O_8 , a rate offset, indicating some sort of transition, occurs in the area representing 12 to 15 per cent conversion (Fig. 6.3-5). This offset is slight during the first reduction, becomes very pronounced on the second, and increases somewhat on the third reduction. This phenomenon was also observed with U_3O_8 produced from $UO_4 \cdot XH_2O$ and ADU (ammonium diuranate). This may correspond to the crystal phase transition occurring at $UO_{2.56}$ reported by Hoekstra et al.⁴ and may have significance with respect to sintering.

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1 Kuhlman, C. W., *Rate of Decomposition of Uranium Trioxide on Heating*, MCW-225, October 7, 1949.

2 Kuhlman, C. W., *Reduction of U_3O_8 with Hydrogen Reaction Rate*, MCW-210, August 19, 1949.

3 Bard, R. J., Bunker, D. L., Greenough, R. C., and Kalmus, E. H., *Activation of Low-Reactivity Uranium Dioxide, Particles*, LA-1952, October, 1955.

4 Hoekstra, H. R., Siegel, S., Fuchs, L. H., and Katz, J. J., *J. Phys. Chem.*, 59, 136 (1955).

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FIGURE 6.3-2 Thermal Decomposition of Orange Oxide to U_3O_8 at 1150°F (Source Material: National Lead Company of Ohio Lot 3 E-16-1027)

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FIGURE 6.3-3 Comparison of H_2 Reduction Rates at 990°F of UO_3 and of U_3O_8 Prepared by Thermal Decomposition of UO_3 at 1150°F . (Source Material: National Lead Company of Ohio Lot 3 E-16-1027 Nonsulfated UO_3)

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FIGURE 6.3-4 Comparison of H_2 Reduction Rates at 990°F of UO_3 and of U_3O_8 Prepared by Thermal Decomposition of UO_3 at 1150°F . (Source Material: National Lead Company of Ohio Lot 3 E-16-706 Sulfated UO_3 .)

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FIGURE 6.3-5 Effect of Recycling on the H_2 Reduction Rate of U_3O_8 , at 990°F. (Source Material: Mallinckrodt UO_3)

7. Three of the samples (National Lead Company of Ohio sulfated, National Lead Company of Ohio nonsulfated, and Mallinckrodt samples) seemed to be approaching a common "stable solid state" by the third reduction. Their rate differences in the first reduction were rather large (the time for 97 per cent completion being 840, 980, and 1220 seconds, respectively) but had narrowed down considerably in the third reduction (the time for 97 per cent completion being 490, 530, and 600 seconds, respectively).
8. Reduction recycle characteristics of U_3O_8 from Port Hope orange oxide differed in two ways from the other three samples. The reduction rate was faster throughout (97 per cent completion in 500 seconds during the first reduction cycle and in 340 seconds during the third reduction cycle) although qualitatively, the same effects of rate increase with recycling and the same rate offset were noted. Also, the acceleration period at the beginning of the reaction is much shorter for Port Hope U_3O_8 on the second and third reductions.
9. All four samples of U_3O_8 gave similarly shaped percentage converted versus time curves, although this was not true for the one-step reductions of the corresponding orange oxides.
10. The first reduction of U_3O_8 (for all samples) proceeds at an accelerating rate for the first 10 per cent converted, at nearly zero-order from 10 to 70 per cent, and at approximately phase-boundary conforming during the final 30 per cent.
11. The third reduction of U_3O_8 (for all samples) is nearly zero-order from 20 to 90 per cent converted, with a very pronounced "tailing-off" which does not fit phase-boundary during the final 10 per cent.

Future Work

During the succeeding quarter, work on the kinetics of the hydrogen reduction of U_3O_8 and orange oxide is to follow these two approaches:

1. Evaluation of whether or not the apparent zero-order region represents a surface-area-limited reaction.
2. Investigation of the abrupt rate changes or offsets in order to determine whether a structural rearrangement is taking place, possibly without the formation of a discrete intermediate compound.

10/10/12

10/10/12

7. MOVING BED REACTOR

(See also Sections 12.1, 12.2, and 12.3, which are concerned with the development of a process for the production of ADU, a possible moving bed reactor feed.)

A pilot-scale moving bed reactor (MBR) has been constructed at National Lead Company of Ohio to determine whether it can be adapted economically to the reduction of UO_3 to UO_2 and the subsequent hydrofluorination of UO_2 to UF_4 . The pellets used are formed by mixing orange oxide, water, and ammonia, and then extruding, curing, and screening. The MBR consists of two vertical reactors and accessory equipment. Hydrated UO_3 pellets, which are fed into the top of the upper reactor (the reduction reactor) are dehydrated and then reduced by hydrogen as they move downward by gravity. In a similar manner, the UO_2 pellets are converted to UF_4 by countercurrent contact with HF as they pass downward through the lower reactor. Modifications of the MBR have been reported in interim reports^{1,2} and in quarterly reports.^{3,4}

7.1 MOVING BED REACTOR DEVELOPMENT – W. Burkhardt, R. H. Sisson, P. W. Henline, A. J. Klee, D. J. Loudin, C. L. Schrader, and E. J. Walter

A pilot-scale moving bed reactor for the production of uranium tetrafluoride is expected to have the following advantages over screw reactors (Section 6): Reduced complexity of equipment, a smaller initial capital investment, and reduced operating expenses.⁵ The major problems remaining are (1) effective control of temperature both in reduction and hydrofluorination and (2) obtaining a uniform flow of solids through the reactor system.

Evaluation of data from the recent reduction test (Run 31) and the cold solids flow studies in the hydrofluorination reactor has been completed and is reported below. (The moving bed reactor system was not operated during the quarter whose work is reported here.)

Reduction Test (Run 31)

The objectives, primary conclusions, and recommendations for the recent reduction test have been presented previously.⁶ Data from the test has since been more fully evaluated and on the basis of this evaluation it was concluded that:

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1 Muhlhauser, H. F., Loudin, D. J., Briggs, G. G., and Mautz, E. W., *The Evaluation of the Moving Bed Reactor for the Production of Uranium Tetrafluoride*, FMPC-524, January 1, 1955.

2 Loudin, D. J. and Muhlhauser, H. F., *The Evaluation of the Moving Bed Reactor for the Production of Uranium Tetrafluoride*, NLCO-620, March 15, 1956.

3 Burkhardt, W., et al., *Summary Tech. Rpt.*, pp. 65-79, NLCO-625, April 16, 1956.

4 Sisson, R. H., et al., *Summary Tech. Rpt.*, pp. 65-72, NLCO-640, July 18, 1956.

5 Muhlhauser, H. F. and Loudin, D. J., *Interim Economic Evaluation of the Moving Bed Reactor Process for Production of Uranium Tetrafluoride*, NLCO-646, August 2, 1956.

6 Burkhardt, W., Sisson, R. H., Henline, P. W., Klee, A. J., Loudin, D. J., Muhlhauser, H. F., Schrader, C. L., and Walter, E. J., *Summary Tech. Rpt.*, pp. 66-68, NLCO-640, July 18, 1956.

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1. During the greater part of the reduction test, the flow of feed pellets to the reactor from the hopper was erratic and nonuniform.
2. Variation of reaction level between different areas of the reactor cross section occurred, despite centering of the pellet feed pipe.
3. At conditions approximating steady state, the calculated average heat losses from the surfaces of the reduction reactor were 235 and 300 to 350 Btu/hr/ft², respectively, for dehydration and reduction operations.

The following recommendations have been made for eliminating operational problems and improving reactor performance and data evaluation:

1. Employment of light continuous vibration of the reactor and feed hopper during subsequent reactor operation. Purpose: to obtain uniform feed pellet flow to the reactor.
2. Initiation of a solids flow study in the reduction reactor. Purpose: to determine the existence of preferential solids flow as related to the phenomenon of reaction level variation.
3. Installation of additional thermocouples in the reactor system. Purpose: to further refine the reactor heat-loss calculations.
4. Conducting another reduction test at the same operating conditions. Purpose: to determine process reproducibility and to verify heat-loss calculations.
5. Consideration of the use of a 50 to 60 per cent hydrogen concentration in the feed gas. Purpose: to eliminate the need for the manifold steam injection used at present.

Hydrofluorination Reactor Cold Flow Studies

Work has been completed on the study of the flow of cold solids through the hydrofluorination reactor. The objective of these studies and a description of them were given in a previous report.¹

From the work performed, it was concluded that:

1. The main causes of preferential flow of solids in the hydrofluorination reactor are bridging and buildup due to internal reactor appurtenances.
2. The rotary motion of the star valve has little effect on solids flow in the reactor.
3. Differential densities, heating, gas flow, and flow rates have little effect on solids flow characteristics.

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¹ *ibid.*

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4. The current design of the gas distributor plate within the reactor is responsible for solids bridging and buildup.
5. Continuous, mild vibration of the reactor effectively prevents bridging and buildup with no change in flow rate.

On the basis of these conclusions, it has been recommended that structures within the reactor be removed or modified, and that continuous mild vibration be used to facilitate uniform cross-sectional flow of solids through the reactor. In accordance with these recommendations, the safety off-gas line (which protruded into the cone of the hydrofluorination reactor and obstructed pellet flow) has been removed.

Future Work

Plans are being made for another series of reactor tests with muller-mixed and extruded pellets. These tests will embody those recommendations which are based on the analysis of the recent reduction and hydrofluorination runs.

With regard to the evaluation of reactor test data, improved techniques of analysis (incorporating the application of statistics and matrix algebra) are being investigated.

7.2 MBR PELLET DEVELOPMENT - R. H. Sisson, P. W. Henline, and E. J. Walter

When the work reported here was started, the continuous pug mill tests¹ (in which the feed liquor contained 2-1/2 per cent NH_3) had been completed. During these continuous pug mill tests, curing technique was revised so that pellets could be retained in the system in relatively large masses for two to three hours. Then the pellets were crushed by the Fitzmill so that they would pass through a 1/2-inch mesh screen. Manpower requirements were reduced by use of the continuous pug mill and pelleting runs of six to seven hours were achieved. Yields varied between 56 and 67 per cent, however, and were considered too low to be of commercial interest.

The objective of the work reported here was to obtain higher yields in sustained runs by achieving more uniform mixtures and thereby reducing the necessity for Fitzmill crushing through a 1/2-inch screen. The pellet desired will be of - 1/2-inch, +6 mesh size and will be strong enough to withstand movement through the moving bed reactor.

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¹ Sisson, R. H., Henline, P. W., Walter, E. J., and Klee, A. J., *Summary Tech. Rpt.*, pp. 65-66, NLCO-640, July 18, 1956.

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Muller mixing

A Cincinnati muller mixer has been installed in the MBR pelleting process. In preliminary evaluation tests of the unit, orange oxide was (1) fed continuously to the muller from the Omega feeder at 425 lb/hr, (2) mixed with 10.5 to 11.0 per cent liquor containing water and 10 per cent NH_3 , (3) discharged intermittently to the Bonnot pug mill in 1 to 1-1/2-minute cycles, and (4) extruded through a high-free-area (H.F.A.) die. Discharge time per cycle was 5 to 10 seconds.

Results of tests in which this revised continuous mixing technique was used are as follows:

1. Operating difficulties have been fewer than with continuous pug mill mixing (previously used). Die plugging and heavy buildup of hydrated cake on mixer flights at points of liquid contact have been minimized, and sustained runs of 4 to 6 hours have been realized. No serious mechanical difficulties have been encountered.
2. Significantly higher pellet yields (high enough to be of commercial interest) have been obtained. Data in Table 7.2-1 indicate that:
  - a. Muller mixing, for all practical purposes, approaches the ideal batch technique in producing uniform mixtures for pelleting. Manpower requirements are no greater than for continuous pug mill mixing.
  - b. Improved pellet yield can not all be credited to the attainment of uniform mixtures. The importance of proper pellet handling after extrusion can not be overemphasized.
  - c. Oversize (+1/2 inch) pellets produced by muller mixing are too long rather than having excessive diameter and should have relatively little effect on reactor operation. On the other hand, oversize pellets produced by starch-batch mixing and continuous pug-mill mixing of NH_3 -containing mixtures include agglomerates of excessive diameter. It is believed that all material may be handled by the method described in footnote (3), Table 7.2-1.
  - d. It is not expected that bypassing the Fitzmill will result in the yield shown in Table 7.2-1 for Method (4). The pellets for which the 85 to 89 per cent yields were obtained were not subjected to the drop through the Fitzmill system. It is estimated that an additional 5 to 7 per cent loss would be incurred by the drop. Modification of the process will minimize this effect.

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TABLE 7.2-1

COMPARISON OF PELLET YIELDS

Pellet Handling Method	Type of Mixer	Type of Mixing	Extrusion Die Type	Additive*	Yield of Pellets (%)	
					+ 1/2 - inch	+ 6M
(1)	Hobart	Batch	Normal**	3 to 5% NH ₃	0.0	60.1
(1)	Hobart	Batch	Normal**	3 to 5% NH ₃	0.0	63.1
(2)	Hobart	Batch	Normal**	Starch	0.0	72.4
(2)	Pug	Continuous	Normal**	10% NH ₃	0.0	58.3
(2)	Pug	Continuous	H.F.A.	2-1/2% NH ₃	0.0	55-67 [†]
(2)	Muller	Continuous	H.F.A.	10% NH ₃	0.0	70.5
(3)	Muller	Continuous	H.F.A.	5% NH ₃	7.3	78.5
(3)	Muller	Continuous	H.F.A.	10% NH ₃	2.0	80.7
(4)	Muller	Continuous	H.F.A.	10% NH ₃	2.4	89.0
(4)	Hobart	Batch	Normal**	Starch	—	87.2
(4)	Pug	Continuous	Normal**	10% NH ₃	13.9	85.0

* The per cent ammonia is on the basis of per cent of the liquor.

** Normal Bonnot die

† Yield dependent upon spray type

- (1) Not retained at the end of dryer — crushed through the 1/2 - inch Fitzmill screen
- (2) Cured, then crushed through the 1/2 - inch Fitzmill screen
- (3) Cured, then passed through the Fitzmill with the 1/2 - inch screen removed
- (4) Cured and screened through the Sweco without Fitzmill crushing or passage through the transition piece to the Fitzmill

3. In continuous pug mill mixing, sustained extrusion of a mixture containing 2 - 1/2 per cent NH₃ was possible through a high-free-area (H.F.A.) die. Muller mixing, however, requires a mixture containing 10 per cent NH₃ in the liquor. With 2 - 1/2 per cent NH₃, the mix tends to hydrate in the muller; with 5 per cent NH₃, operation (as judged by die plugging) is relatively difficult.

One lot of orange oxide containing 3.5 per cent NO₃ could not be muller mixed although it contained 10 per cent NH₃ in the liquor. This mixture, also, hydrated in the muller.

4. Discharge of the mixture from the muller occurs through a manually operated bottom gate, requiring constant attention. It is believed, however, that this operation may be made automatic.

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Other Studies

In conjunction with the muller mixing tests, other studies concerned primarily with solids flow problems have been made. These are as follows:

1. Determination of solids patterns through the Omega transition chute.

Previously, a Densitron Level-Indicator was installed in the Omega transition chute. Its purpose was to detect voids below the bridges which sometimes form in the feed hoppers. When these bridges break, the Omega feeder is overloaded and subsequent floods shut down the pelleting process. Frequent "floods" of powder during operation had proved that the Densitron Level-Indicator is unreliable for this purpose.

The Densitron was replaced by a Fielden-Tektor probe type level-indicator, which was installed in a section of the chute where voids most frequently occur. The Fielden-Tektor has proved more reliable than the Densitron in indicating voids in the feed hopper.

2. Comparative rate studies between a screw feeder and the Omega to determine whether the Omega delivers at a more uniform rate as a result of overcoming differences in orange oxide density. This study is still in progress.

Present Status

We have achieved the target yield of greater than 80 per cent in our pelleting. On the basis of laboratory studies, the 20 per cent fines can be directly recycled in the pelleting process. More complete data on all phases of these pelleting studies will be available when feed pellets are prepared for Reactor Run 34.

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8. REDUCTION TO METAL PROCESS

In the Metals Production Plant, green salt (UF_4) is reduced to uranium metal by a thermite type reaction. The UF_4 is blended with crushed magnesium metal and is charged into a refractory-lined metal pot (a "bomb"). The bomb is heated in a Rockwell furnace until the reaction occurs, forming a metallic uranium "derby" at the bottom of the pot and an overlying crust of slag that largely consists of MgF_2 . After cooling and after the derby is cleaned of adhering slag, the derby is used as part of the charge to a remelt furnace, where the uranium is cast in ingot form (Section 9).

8.1 EFFECTS OF CLEANING DERBIES PRODUCED IN SLAG-LINED AND DOLOMITE-LINED FURNACE POTS -- E. W. Torok, R. F. Bauer, R. A. St. John, and H. M. Eikenberry

Uranium derbies are presently produced at National Lead Company of Ohio in furnace vessels lined with dolomite. Economic studies indicated an advantage in using recycled slag as a furnace pot liner so a slag-reclaiming plant was installed at National Lead Company of Ohio. (It is presently undergoing "shakedown" tests.)

This report describes the results of tests run to evaluate the derby cleaning processes of pickling, leaching, and chipping. Pickling and leaching techniques are described in Section 8.2 of this report.

In early tests, pickled and unpickled derbies (produced at Mallinckrodt from both National Lead Company of Ohio green salt and Mallinckrodt green salt) were remelted and cast as ingots at the National Lead Company of Ohio. Results indicated no significant difference in the slug reject rates for ingots made from (1) pickled derbies which had been produced in slag liner by Mallinckrodt using Mallinckrodt green salt, (2) unpickled derbies which had been produced in slag liner by Mallinckrodt using National Lead Company of Ohio green salt, and (3) unpickled derbies which had been produced in dolomite liners by National Lead Company of Ohio using National Lead Company of Ohio green salt.¹

Phase I of the Derby Cleaning Program had the objective of comparing ingots made from unpickled derbies produced in slag-lined furnace pots and dolomite-lined furnace pots. These were produced at the National Lead Company of Ohio using National Lead Company of Ohio green salt. Results indicated that the slag-liner derbies should be cleaned before they are remelted.²

In Phase II of the derby cleaning program, the effects of cleaning derbies by a leaching method³ and by a leaching and pickling method were evaluated. Results indicated that cleaning of the derbies produced in slag liner improved the slug to good slug yield⁴ and that a better yield was obtained from ingots produced from three-derby charges than from ingots produced from two-derby charges. The latter, a reversal of previous trends, indicates an adverse effect from the introduction of scrap.

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1 Torok, E. W., Eikenberry, H. M., and Church, A. Jr., Summary Tech. Rpt., p. 89, NLCO-625, April 16, 1956.

2 Torok, E. W., Bauer, R. F., and Eikenberry, H. M., Summary Tech. Rpt., pp. 77-79, NLCO-640, July 18, 1956.

3 Meyer, F. H. and Peters, N. N., Summary Tech. Rpt., p. 89, NLCO-640, July 18, 1956.

4 Torok, E. W., Bauer, R. F., and Eikenberry, H. M., op. cit., pp. 77-89.

~~CONFIDENTIAL~~Phase III of the Derby Cleaning Program

Phase III of the Derby Cleaning Program was then initiated to determine the effect on ingot metal quality of (1) derby cleaning methods, (2) amount of scrap in the remelt charge, and (3) the use of good-appearing versus poor-appearing derbies in the charge to the remelt furnace.

The batch size and processing conditions used in the experimental production of derbies in slag-lined and dolomite-lined pots were as follows:

	Dolomite - Lined Furnace Pots	Slag - Lined Furnace Pots
Green Salt Charge	410 pounds	444 pounds
Furnace Pot	14 inches	15 inches
Side Liner Thickness at the bottom of the pot	5/8 inch	1 - 1/4 inches
Side Liner Thickness at the top of the pot	5/8 inch	3/4 inch
Rockwell Furnace Temperature	1225°F	1250°F

As soon as newly produced derbies were broken out (whether they were produced in dolomite-lined or slag-lined furnace pots), as much slag as possible was chipped from the derbies. The derbies produced in slag-lined furnace pots were then visually inspected and sorted into two groups: good-appearing derbies (little slag on the surface), as shown in Figure 8.1-1 and poor-appearing derbies (slag on the surface), as shown in Figure 8.1-2.

NOTE: Several of the derbies produced in the small slag-lined furnace pots (360-pound green salt charge) for Phase II of the program had so-called "plates" on the bottoms of the derbies.¹ Since the large furnace pots have been put into use for the production of derbies in slag liner, no plates have been found at the bottoms of the derbies.

The derbies were then either charged directly into a crucible of a remelt furnace or sent to the Pilot Plant for cleaning by (1) leaching for 6 hours or (2) leaching for 6 hours and pickling for 1-3/4 hours² prior to melting. See Section 8.2 for a description of the cleaning and the cleaning results.

The process conditions for remelting the derbies were as follows:

1. Each charge was made up of four derbies without any scrap.
2. The eight types of charges melted were:
  - a. Chipped slag-liner derbies of good appearance.
  - b. Leached slag-liner derbies of good appearance.
  - c. Leached and pickled slag-liner derbies of good appearance.

¹ Torok, E. W., Bauer, R. F., and Eikenberry, H. M., op. cit., p. 79.

² Taylor, C. W., Cseplo, S. and Davies, H. J., Summary Tech. Rpt., pp. 89-93, NLCO-640, July 18, 1956.

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FIGURE 8.1-1 Typical Good-Appearing Derbies Made in 15-Inch Slag-Lined Furnace Pots

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FIGURE 8.1-2 Typical Poor-Appearing Derbies Made in 15-Inch Slag-Lined Furnace Pots

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- d. Leached slag-liner derbies of poor appearance.
  - e. Leached and pickled slag-liner derbies of poor appearance.
  - f. Chipped dolomite-liner derbies (control).
  - g. Leached dolomite-liner derbies.
  - h. Pickled dolomite-liner derbies.
3. The operating conditions for remelt described below were carefully followed:
    - a. A vacuum pressure ranging from 100 to 15 microns Hg was obtained after the charges had melted.
    - b. The power level was held at 120 kw until an optical pyrometer reading of 2550° F was obtained. Then the power was cut back to 50 kw and held at that level for 20 minutes, after which the heat was cast.
    - c. Helium was added to the furnace four minutes after the heat was cast.
    - d. All ingots were cropped and sampled for the determination of density and for chemical analysis.
    - e. All ingots were rolled to the specified size.

A total of 412 derbies were reduced in 15-inch slag-lined furnace pots, classified as good or poor, and remelted into 103 ingots. The general appearance of the derbies produced in slag-lined furnace pots was good; only 68, or 16.5 per cent, were classified as poor. In addition, 384 derbies were reduced in 14-inch dolomite-lined furnace pots and were remelted into 96 ingots. The derbies produced in dolomite-lined furnace pots were not separated into good and poor categories.

A summary of the densities, chemical analyses, and slug yields of the ingots cast during Phase III of the derby cleaning program is given in Table 8.1-1. These data can be compared with similar data from reductions using two-derby and three-derby charges.¹

TABLE 8.1-1
CHEMICAL ANALYSES AND SLUG YIELDS (PHASE III INGOTS)

	Slag Liner Derby					Dolomite Liner Derby			Total
	Good Appearing			Poor Appearing		Chipped	Leached	Pickled	
	Chipped	Leached	Leached & Pickled	Leached	Leached & Pickled				
No. of Ingots	26	27	33	9	8	30	29	37	199
Avg Density (g/cc)	18.923	18.930	18.889	18.897	18.869	18.921	18.940	18.899	—
Avg Nitrogen (ppm)	81	83	43	87	49	85	83	55	—
Avg Carbon (ppm)	471	447	699	612	795	467	399	666	—
Relative Slug Yield* (%)	-10.32	-9.75	-2.05	-10.01	-4.82	-6.55	-2.56	0	—

* The best average slug yield was considered 0%. The other values show how far below this average the other yields fell.

NOTE: The best slug yield for these 4-derby heats was 5 per cent better than the best yield obtained for 2-derby and 3-derby heats.

¹ Torok, E. W., Bauer, R. F., and Eikenberry, H. M., op. cit., pp. 84, 88.

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Conclusions

1. The slug yield from ingots produced from four -derby charges is better than the yield for those produced from a charge of two derbies and scrap or from three derbies and scrap.
2. For derbies produced in both slag-lined and dolomite-lined furnace pots, cleaning of derbies prior to recasting results in a higher slug yield.
3. Leaching of derbies results in a lower carbon content, and pickling of derbies results in a lower nitrogen content. Leaching followed by pickling does not appear to lower the carbon content.

Future Work

A fourth phase of the derby cleaning program is being initiated. In this phase, all-virgin-derby charges will be used. The leaching cycles will be varied, and no derbies will be pickled. The derbies will be visually inspected and divided into two groups: good and poor.

8.2 METHOD OF CLEANING DERBIES PRODUCED IN SLAG-LINED AND DOLOMITE-LINED FURNACE POTS – S. Cseplo and C. C. Fogel

Background information on this project and information on the effect of derby cleaning on metal quality can be found in Section 8.1 of this report. A facility for water leaching and acid pickling uranium derbies is described in an earlier quarterly report.¹

Described below is the cleaning (in the Pilot Plant) of derbies produced in slag-lined pots and dolomite-lined pots. The cleaning methods included water leaching-acid pickling, acid pickling, and water leaching. The derby weight losses resulting from leaching and pickling are given, as well as analyses of the leach water, the pickle solution, and the sludge.

The major objective of this project is to develop the most economical method of removing MgF_2 slag from uranium derbies. The objectives of the work reported here were:

1. To hold the fluoride level of the pickling and leaching liquors below 200 parts per million so that the liquor may be used as a feed to the Refinery with no additional processing,
2. To develop a method that will give a low uranium dissolution percentage while accomplishing the major purpose, ridding the derby of MgF_2 . Uranium that is dissolved must be recycled – either to the Refinery or (if the fluoride content exceeds 200 parts per million) to the uranium recovery plant.

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¹ Taylor, C. W., Cseplo, S., and Davies, H. J., Summary Tech. Rpt., pp. 89-93, NLCO-640, July 18, 1956.

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Water Leaching – Equipment and Procedure

Two leaching tanks were installed in the Pilot Plant. Each tank has three removable trays and is capable of handling 24 derbies (eight derbies per tray) in one tank-batch. A steam coil in the bottom of the tank supplies heat for boiling the water. The lid is fitted with a heat-exchanger to reflux the condensed steam to the leach tank.

The derbies, as received from the Metals Production Plant, were placed on open grid trays and their positions were recorded. Leaching times were specified by the Metallurgical Department. The derbies were covered with leaching water, which was brought to boiling temperature and held at that temperature for the required time. All steam boil-off was condensed and refluxed to the leach tank. The derbies were removed from the leach water and given a water rinse (the rinse water being drained back into the leach tank). Then the derbies were dried with live steam and weighed. After each batch was leached, a sample of the leach water was taken and was analyzed for uranium, fluoride, and pH.

The water in the leach tanks was changed either when the sludge in the bottom of the tank built up to the bottom tray or at the end of the month (before inventory).

Acid Pickling – Equipment and Procedure

Acid pickling was carried out in the equipment normally used for continuously dissolving massive scrap uranium pieces in nitric acid. The piping for this equipment was arranged so that the equipment could be used for either operation, depending on the setting of the valves. Two trays holding four derbies each were built to accommodate eight derbies for one pickling cycle.

The loaded racks were lowered into a pickling solution containing 25 to 50 per cent nitric acid and held at 160°F. Pickling time was 1-3/4 hours. The derbies were rinsed by being sprayed with water for approximately one minute, and then were given a second rinse by being immersed in 170°F water. They were then removed from the tank and any loose material remaining on the derbies was removed with live steam. The derbies were then dried and weighed. Samples of the pickling acid, the first water rinse, and the second water rinse were taken and analyzed for fluorides, uranium, and acid concentration.

The pickling acid was changed when the acid concentration dropped below 4.55 N (25%) HNO₃. Uranium concentration at this acid concentration was approximately 200 g/l. The second-rinse water was changed when its uranium content reached 2.4 g/l.

Results and Discussion

A total of 1172 derbies were processed in the Pilot Plant in the work reported here. Table 8.2-1 shows the average weight loss for each type of derby in each process.

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TABLE 8.2-1

**WEIGHT LOSSES OF DERBIES SUBJECT TO
LEACHING, PICKLING, OR BOTH**

Treatment	No. of Derbies	Range of Wt Loss (lb)	Average Wt Loss (lb)	Wt Loss* (%)
Dolomite - Liner Derbies				
Leached 6 Hours	306	0 to 23.5	3.0	1.0
Leached and Pickled	30	10 to 17.0	12.6	4.2
Pickled	159	10 to 19.5	14.3	4.8
Slag - Liner Derbies				
Leached 6 hours	197	0 to 9.5	1.3	0.39
Leached 12 hours	88	0.5 to 10.5	2.65	0.85
Leached and Pickled	141	7.5 to 37.0	14.6	4.6
Pickled	12	13 to 15.5	14.4	4.4
Nonprogrammed Derbies (Selected, low-quality derbies)				
Leached 6 hours	233	—	7.42	2.5

* This includes uranium metal particles, MgF_2 slag, and black oxide.

For both the slag-liner derbies and the dolomite-liner derbies, acid pickling produced the cleanest derbies. Twelve-hour leaching of slag-liner derbies gave more than twice as much weight loss as did the six-hour cycle.

As a result of processing approximately 350 slag-liner derbies, the uranium content of the leach water increased from 0.0005 to 0.002 g/l, the pH dropped from 9.4 to 8.8, and the fluoride content increased from <20 to 100 ppm.

As a result of processing approximately 200 dolomite derbies, the uranium content in the leach water showed no definite increase, but varied from batch to batch. Uranium content varied from 0.0006 to 0.4 g/l. The pH dropped from 9.8 to 9.4, and the fluoride content increased from <20 to 250 ppm.

Approximately 72 slag-liner derbies and 72 dolomite-liner derbies were leached separately, and a sample of the sludge from each group was taken for analysis. Results are given in Table 8.2-2.

~~CONFIDENTIAL~~TABLE 8.2-2**ANALYSIS OF SLUDGE**

Sludge From:	U (%)	F (%)	Ca (%)	Mg (%)	Spectrographic Analysis (ppm)					
					Al	As	B	Bi	Co	Cr
Dolomite - Liner Derbies	65.9	2.14	0.36	5.99	1000	<100	<100	<60	<10	300
Slag - Liner Derbies	59.1	1.46	0.09	7.26	12000	<100	<1000	<60	<10	300

Sludge From:	Spectrographic Analysis (ppm)									
	Cu	Fe	Mg	Mn	Ni	P	Pb	SiO ₂	Sn	V
Dolomite - Liner Derbies	<100	400	>6000	100	150	<100	<10	240	10	<100
Slag - Liner Derbies	<100	250	>6000	20	40	<100	<10	1000	10	<100

Evidently, most of the MgF_2 hydrolyzed. If the proportion of fluoride content to magnesium content had been the same in the sludge as in MgF_2 , the fluoride content of the sludge from dolomite - liner derbies would have been 9.5 per cent and that for slag - liner derbies would have been 11.5 per cent. The ratio of MgF_2 to uranium in the sludge would then have been 0.24 to 1 for dolomite - liner derbies and 0.32 to 1 for the slag - liner derbies.

The fluoride content of the nitric acid pickle solution varied from 20 to 510 ppm while the uranium content varied from 36 to 227 g/l. The fluoride content of the water from the initial one - minute rinse averaged about 100 ppm at a uranium content of 28 g/l, while the fluoride content of the final rinse water averaged 20 ppm.

8.3 CONTINUOUS REDUCTION OF URANIUM TETRAFLUORIDE – O. R. Magoteaux, V. G. Minutolo, and C. A. Neu, Jr.

A step in the uranium production process is the batch reduction to derby metal of uranium tetrafluoride (green salt) blended with granular magnesium metal. These batch operations are costly and have low production rates.

Therefore, a project was started to develop a continuous reduction process that will produce metal suitable for remelting into acceptable ingots in the Metals Production Plant. This project is in the equipment setup stage, but a few scoping runs have been made.

The process utilizes a graphite cylinder as a reaction vessel (Fig. 8.3-1 and 8.3-2). The uranium tetrafluoride - magnesium mixture is introduced through an opening near the cylinder top, a continuous reaction is maintained within the reactor, and molten uranium metal and slag are poured through an opening at the reactor bottom.

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FIGURE 8.3-1 Assembled Reactor, Showing Coil, Insulation, Charge Chute, and Extension Sleeve

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FIGURE 8.3-2 Section View of Assembled Reactor

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In the previous quarterly,¹ it was stated that remaining work included the evaluation of process variables, the determination of optimum reduction conditions, the development of equipment, and the development of a satisfactory pouring technique. To be more specific, the following were yet to be determined or developed when the work reported here was started:

1. Optimum per cent excess magnesium in the charge,
2. Optimum charging rate to achieve a greater fluidity of product (and thus improve separation efficiency),
3. A technique for lessening contamination of the metal by the graphite reactor vessel,
4. A pour control device that will permit intermittent pouring.

Progress is reported below.

Equipment Modifications

External heating facilities and insulation conditions for the reactor vessel were improved by installing a new induction coil and by sintering zirconia ram between the vessel and coil. The reactor vessel size was reduced, resulting in a shorter preheat cycle and allowing tests to be performed with less feed consumption. The inside diameter is now tapered from 9 inches at the top to 6 inches at the bottom, and the outside diameter is 11 inches. (The reactor last reported² had an 11-inch ID, top to bottom, and a 16-inch OD.)

A hole in the extension sleeve (graphite) atop the reactor permits a steel charge chute to be inserted. Fiberfrax is placed around this sleeve, and a zirconia plate is placed on top of the sleeve. This arrangement permits better charging and retards contamination of the products by convection of the air within the reactor.

The suitability for intermittent casting of a slide-type pour control was evaluated. This control was found to be unreliable. As an alternative, a knockout-type pour control is now being used, but because this type of pour control limits the process to a batch operation, other methods (pet-cock, stopper-rod, siphon or self-slag, and melt-plug) are being investigated. So that they may be evaluated, these methods have been incorporated into designs of new reactor vessels.

UF₄ - Mg Charge

Calcium metal was first used for scoping reductions,³ and later, magnesium metal was substituted. The feasibility of a process in which magnesium is used was proved⁴ on a pilot scale.

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¹ Magoteaux, O. R., Minutolo, V. G., and Neu, C. A., Summary Tech. Rpt., pp. 73-77, NLCO-640, July 18, 1956.

² *ibid.*

³ Magoteaux, O. R., Minutolo, V. G., and Wuller, G. E., Summary Tech. Rpt., pp. 81-85, NLCO-625, April 16, 1956.

⁴ Magoteaux, O. R., Minutolo, V. G., and Neu, C. A., *loc. cit.*

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FIGURE 8.3-3   **Left:** Massive Metal Cast Into $3\frac{1}{2}$ -Inch-Diameter Insulated Graphite Molds
                              Right: Massive Metal Which Remained In Reactor After Reduction

Very recently, compacting of green salt-magnesium ($\text{UF}_4 - \text{Mg}$) was accomplished on a Komarek-Greaves rotary-type briquetting press. This press produces a pillow-shaped briquette 1-1/4 inches square by 5/8 inch thick. It is estimated that a pressure of 30 tsi was used. Thus far, an output of 2300 pounds per hour has been accomplished at a roll speed of 6.5 rotations per minute.

Process Studies

The briquetted $\text{UF}_4 - \text{Mg}$ remaining from that prepared earlier¹ was used primarily to develop a satisfactory pour control, but was also used in preliminary tests to determine the minimum charge rate that will produce molten products in the present reactor. Charge rates of 13.1, 25.0, and 37.5 pounds of briquetted $\text{UF}_4 - \text{Mg}$ per minute were used. It was found that the highest charge rate produced the best separation of slag from metal and resulted in the highest casting yields (as high as 92.1 per cent by weight of uranium charged). In these tests, it was significant that the

¹ Magoteaux, O. R., Minutolo, V. G., and Wuller, G. E., *loc. cit.*

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temperature of the reactor vessel increased considerably (120°F) when the high charge rate was used and only slightly (50°F) when the intermediate charge rate was used. The temperature decreased when the low charge rate was used. Maximum temperatures for the 13.1, 25.0, and 37.5 lb/min charge rates were 2400°F , 2560°F , and 2590°F , respectively. A high temperature is desired in order to increase fluidity and thus improve slag-metal separation.

Slag and metal made in these tests were allowed to liquefy for 15 minutes and were then poured into insulated graphite molds having 3-1/2-inch inside diameters (Fig. 8.3-3).

From these tests, it was concluded that a charge rate of greater than 25 pounds per minute must be used in the present size reactor.

During the past quarter, the following improvements have been achieved:

1. As a result of the use of the new induction coil and the stabilized zirconia insulation, the preheat time of the reactor vessel has been decreased and plugging of the pour hole has been reduced.
2. Metal-slag separation in the mold was better than in previous runs.
3. Slower reaction rates, less vapor evolution and higher casting yields were achieved by the use of UF_4 - Mg briquettes in the place of uncompact UF_4 - Mg mixtures.

Future Work

1. Process variables are to be further evaluated to establish the optimum conditions for reduction.
2. Reductions will be made using briquettes prepared in a rotary-type press.
3. Various refractory materials will be applied as coatings in order to eliminate contamination of the metal by the graphite reactor vessel.
4. Various pour control techniques for the intermittent pouring of the products will be evaluated.

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9. URANIUM METAL CASTING PROCESS

Uranium metal in the form of derbies, along with reject slugs, rolling mill scrap, and briquetted chips, is charged into a crucible for melting in a vacuum induction furnace. There, the metal is melted, brought to a specified temperature, and poured into a mold which is positioned beneath the crucible. The metal solidifies in ingot form. After breakout, the unsound, high-impurity metal at the top of the ingot is cropped and sampled.

9.1 MELTING AND CASTING OF URANIUM - 10 WT % NIOBIUM ALLOY - S. L. Reese and S. O. Samoriga

Considerable experimental casting of 10 weight per cent uranium-niobium alloy has been done at National Lead Company of Ohio to supply material for nuclear reactor experiments.¹ This alloy is reported to have very good corrosion resistance in 640° F water. The presence of significant amounts of carbon or oxygen in the alloy is reported to be detrimental.

The purpose of the work performed this quarter was to correlate the improved ingot casting practice² with the quality of the extruded bars produced from the ingots. The criterion for quality of extruded bars was niobium analysis. This is a continuation of the study reported in the previous quarterly report;³ essentially the same melting conditions were used.

Method and Results

Recent work included 107 melts made in graphite crucibles in a bottom-pour induction furnace. Both alloying melts and remelts were included. After the ingots were cropped, they were analyzed at top and bottom for niobium and carbon content and then were extruded to 1/2 -inch by 3 -inch bars by the customer. The bars were cut into short lengths and the ends of individual pieces were analyzed for niobium. The casting and extrusion results for these ingots appear in Table 9.1-1.

TABLE 9.1-1

EFFECT OF TYPE OF MELT ON EXTRUDED BAR YIELDS

No. of Ingots	Type of Melt	Ingot Analysis Avg Wt % Nb		Carbon in Ingot				Extruded Bars In-Spec.* (%)
				Top of Ingot		Bottom of Ingot		
		Top	Bottom	Avg	Range	Avg	Range	
9	Low-carbon Virgin	10.5	10.4	375	230-595	310	220-435	100 (4 Ingots only; 5 not yet reported)
51	High-carbon Virgin	10.2	9.9	704	310-2200	706	360-1145	
47	Remelt	10.5	9.8	896	210-2810	760	345-1175	76

* Analytically acceptable, based on customer niobium analyses reported to date.

1 Palmer, W. E. and Reese, S. L., Summary Tech. Rpt., pp. 91 - 94, NLCO-625, April 16, 1956.

2 Reese, S. L. and Samoriga, S. O., Summary Tech. Rpt., pp. 101 - 104, NLCO-640, July 18, 1956.

3 *ibid.*

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The reported carbon analyses are those of shipped ingots which have in many cases been re-cropped to bring them within a 9.2 to 10.8 weight per cent niobium specification. The top crops often have high niobium and carbon contents. The carbon values on the low-carbon heats (from wafer samples) average approximately 200 ppm less than the carbon values on the other two groups of ingots (from drillings obtained with carbide-tipped drills).

The 100 per cent yield for the extruded bar from low-carbon virgin metal ingots is indicative of the homogeneity of the low-carbon melts. The niobium varied less than 0.5 per cent over the entire length of extruded bar on three of the four low-carbon ingots extruded and analyzed to date. In contrast, a variation of 2.5 per cent in niobium content was not uncommon from many of the high-carbon and remelt ingots, which generally were higher in impurities. The carbon content of the high-carbon ingots also varied over a wide range.

Discussion

The phase diagram (not shown) for uranium-niobium alloy indicates a rather wide solidification range at 10 weight per cent niobium and a general increase in the temperature of solidification as the niobium content increases. Almost without exception, however, the periphery of the ingot, which solidifies first, is lower in niobium content. The center line of the ingot is higher in niobium content. The top of the ingot, freezing last, is highest in niobium. The exact mechanism of this reverse segregation phenomenon is not known, but a number of contributing factors have been determined:

The rate of solidification contributes much to the manner and extent of the segregation. A superheated or hot-mold melt, where freezing is slow, gives extensive vertical segregation, i.e., the niobium has sufficient time to float out. When there is not an excessive superheat in the metal, pouring into a hot-topped mold lessens the vertical segregation but results in a moderate horizontal gradient in niobium content. A quick freeze results primarily in horizontal segregation, and shrinkage cavities generally occur.

With our melting practice, in which a hot-topped mold is used, horizontal segregation has been as much as three weight per cent from edge to center. One virgin ingot and one remelt ingot were split longitudinally and analyzed for niobium segregation. The average horizontal segregation from edge to center in the virgin ingot was 0.5 weight per cent, ranging from 0 to 1.1 weight per cent; the average for the remelt ingot was 2.0 weight per cent, ranging from 0.5 to 3.0 weight per cent. Data on special low-carbon ingots are being obtained by the customer. There is little gross vertical segregation except for the top 3 to 4 inches of the ingot, whose niobium content is 11 to 13 weight per cent.

Segregation, observed as floating-out (probably in the form of oxides and carbide), has been observed in the crucible. In the recently produced heats, the metal was agitated in the crucible to minimize this tendency. Crucible residue from two typical agitated heats contained 17 and 20 per cent niobium, and the respective carbons were 0.8 and 1.3 per cent.

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On the basis of the observations described above (especially those regarding the small section at the top of the ingot which contains a high content of niobium), it is thought that rapid segregation of some of the niobium is occurring, along with slower, less extensive segregation of most of the alloy. The material which separates rapidly is believed to consist of impurities such as carbon and oxygen which have combined with niobium and are essentially insoluble in the metal at temperatures near the solidification temperature. It has been shown that niobium scavenges carbon from the melt, since alloy repeatedly remelted maintains a nearly constant carbon content of 500 to 1000 ppm, whereas the carbon content of the top, high-niobium section often exceeds 2000 ppm and has been found to be as high as 5000 ppm. It has been reported that the oxide follows the same pattern, but since the oxygen content of the alloy has not been determined, this has not been confirmed.

Since the uranium-niobium system is one of complete solubility in this range in the gamma and liquid phases, gross segregation should not occur in ingots to the degree found. Only a mechanism such as the formation or presence of insoluble, low-density niobium compounds would explain the segregation.

A possible mechanism of horizontal segregation is the formation of "pockets" (small areas high in niobium) in the ingot. Evidence of pocket formation has appeared repeatedly in sections of extruded bar. The center sections often contain more than 11.2 per cent niobium, and the end sections contain 9 per cent niobium. The location of the high-niobium pockets is not constant. The pockets may be caused by bridging, which stops the upward flow of niobium and its compounds. A concentration of niobium compounds could well raise the freezing temperature at a given point in the molten ingot center and contribute to freezing-across, which would result in a high-niobium area.

The analytical results reported for extruded bar made from ingots cast from low-carbon heats indicate that less pocketing and less segregation occur where the carbon level is low (less than 400 ppm). One ingot, made with niobium from a different manufacturer, gave an indication of some pocketing on initial extruded bar analyses. Higher oxide content is being investigated as a possible cause.

This work verified not only that sound ingots can be produced that have uniform ingot niobium analyses, but that the melting techniques developed offer the prospect of making completely homogeneous metal from low-carbon uranium and niobium melt stock in one casting step. The induction melting process is a relatively simple one-step process and should be useful for large-scale uranium-niobium alloy production.

Future Work

Further work is needed in order to determine the mechanics of segregation more completely so that homogeneous metal may be consistently produced in sound ingots of economical size.

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10. RECOVERY OF URANIUM FROM SCRAP MATERIALS

The Uranium Recovery Plant at National Lead Company of Ohio is responsible for the recovery of uranium from various scrap materials.

In the hydrometallurgical circuit, the uranium is recovered from hydrochloric acid leach solution by precipitation with ammonia. Coprecipitated fluoride is removed by calcination of the uranium "diuranate" cake.

Other scrap recovery processes involve oxidation, direct nitric acid dissolution, etc.

10.1 DIURANATE CALCINATION TESTS – A. B. Kreuzmann and E. O. Rutenkroger

During operation of the National Lead Company of Ohio Recovery Plant, fluoride removal from the diuranate product has been accomplished by high-temperature calcination in a Herreschoff type furnace. Previous diuranate calcination tests which were conducted in the laboratory¹ demonstrated the effect of (1) calcination temperature, (2) calcination time, (3) the presence of inert gases, (4) bed depth, and (5) the use of a fluidized bed on the rate of fluoride volatilization from this material.

A series of three plant tests was conducted to evaluate the effects of calcination time and temperature on fluoride removal in the Herreschoff roaster, which measured nine feet in diameter and had six hearths. The wet diuranate material was extruded onto the top hearth of the furnace by means of a Moyno pump and was moved over the various hearths by the action of the furnace rabble arms. During the first test, the furnace was maintained at approximately 1500°F, with the diuranate material being retained at temperature for 90 minutes. The second test was conducted at a calcination temperature of approximately 1700°F and with a retention time at temperature of 115 minutes. In the third test, the furnace temperature was maintained at 1700°F, while the rabble arm drive was altered to produce a retention time at temperature of 210 minutes. Each of the tests was conducted over a 12-hour period, with samples of the diuranate feed and calcined product taken at hourly intervals during the test.

A summation of the data obtained from each test is shown in Table 10.1-1. The results of these tests showed that calcination of diuranate at 1500°F for approximately 90 minutes was effective in removing 60 per cent of the contained fluoride. Increasing the calcination temperature to 1680°F and the retention time, at temperature, to 115 minutes increased the fluoride volatilization to 83 per cent. Further increases in retention time (to 210 minutes) at temperature of 1680°F did not improve the fluoride volatilization over the 83 per cent previously obtained.

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¹ Whitman, A., *The Removal of Fluoride from Ammonium Diuranate Filter Cake in a Fluidized Bed Furnace*, FMPC-515, December 23, 1954.

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TABLE 10.1-1

DIURANATE CALCINATION TESTS (12-HOUR TESTS)

Test No.	Calcination Temp* (°F)	Total Retention Time in Furnace** (min)	Estimated Retention Time at Temp (min)	Diuranate [†] Feed to Furnace				Diuranate Ash [†]			Fluoride Volatilized (%)
				H ₂ O (%)	U ^{††} (%)	F ^{††} (%)	Cl ^{††} (%)	Wt (lb/hr)	U (%)	F (%)	
1	1520	144	90	57.8	48.9	5.4	0.33	361	53.0	2.33	60
2	1680	138	115	57.3	46.4	6.0	0.18	246	52.2	1.16	83
3	1680	252	210	58.3	46.6	6.4	0.25	285	51.1	1.21	83

* Temperature is an average of the bottom three hearths for Test 1 and of the bottom four hearths for Tests 2 and 3.

** The retention time was determined by rabbling out the furnace at the end of each test and dividing the weight of material obtained by the average lb/hr of material obtained during the test.

† All analyses are averages of hourly samples taken throughout the tests.

†† On a dry basis.

10.2 RECOVERY OF URANIUM FROM CARBON CAKE - A. B. Kreuzmann

The uranium values must be recovered from the carbon cake which is obtained when certain Refinery feed slurries are filtered. If a leaching method can be developed that will leave less than 0.2 per cent uranium in the residue, the leached residue can be discarded to the tailings pit. Washing and leaching techniques were described in the previous quarterly report.¹

Processing of carbon cake for recovery of uranium was started in the National Lead Company of Ohio Recovery (Scrap) Plant. The water-washing technique used was: washing the carbon cake at 25°C for 2 hours at a 2 to 1 weight ratio of water to cake. Analysis of the washed residues indicated that the lots of material which were processed were not homogeneous with respect to insoluble uranium, the washed residues from various lots assaying from 1 to 4 per cent. Washed samples of the carbon cake material yielding high-assay residues were treated in the laboratory with 3N, 6N, and 15N nitric acid, demonstrating in each case the amenability of the residual uranium to nitric acid dissolution.

Subsequent lots of materials have been processed in the plant, with 3N nitric acid used as the leaching medium. The resulting residues, washed on the filter, assayed 0.3 per cent uranium or less.

¹ Kreuzmann, A. B., Summary Tech Rpt., pp. 107-108, NLCO-640, July 18, 1956.

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10.3 DISSOLUTION IN NITRIC ACID OF URANIUM FROM URANIUM-NIOBIUM ALLOYS - E. O. Rutenkroger, B. C. Dumas, and T. F. Rupert

Uranium-niobium scrap was produced during recent casting of uranium-niobium alloy ingots. It is essential that the uranium and niobium be separated so that the uranium can be returned to the process streams. The ultimate goal of this project is to recover all of the uranium contained in the scrap and, preferably, to recover the niobium also.

Preliminary tests are reported in the previous quarterly report.¹

During the past quarter, a series of laboratory experiments was conducted to study the effects of temperature and acid concentration on the dissolution in nitric acid of uranium from uranium-niobium alloys. Thirty-five to forty-gram samples of uranium-niobium alloys which were estimated to contain 10 to 15 per cent niobium were dissolved in 7.8N and 15.7N nitric acid for periods up to 96 hours and at temperatures ranging from 26°C to 90°C. Results of these studies (shown in Table 10.3-1) indicate that temperature has a marked effect on the amount of uranium dissolved in 15.7N nitric acid over a 96-hour period. Treatment of samples with 15.7N nitric acid for 96 hours at 26°C and for 48 hours at 90°C resulted in uranium dissolutions of 30 and >99.9 per cent, respectively. Two samples were treated with 7.8N nitric acid at temperatures of 70°C and 90°C for periods of 96 hours. Both of these trials resulted in dissolution of >99.9 per cent of the uranium.

TABLE 10.3-1

RECOVERY OF URANIUM FROM URANIUM-NIOBIUM ALLOY BY NITRIC ACID DISSOLUTION

Trial No.	Wt Alloy Used (g)	HNO ₃		Digestion		Residue			U Dissolved (%)
		Vol (ml)	N	Temp (°C)	Time (hr)	Wt (g)	U (%)	Nb (%)	
1	37.8	300	15.7	26	96	34.5*	63.0	13.2	30
2	38.7	300	15.7	50	96	14.4*	43.5	31.0	81
3	36.0	300	15.7	70	48	10.6*	36.2	36.8	87.5
4	35.5	300	15.7	90	48	5.8	0.17	62.4	>99.9
5	38.9	300	7.8	70	96	—	0.11	77.4	>99.9
6	38.5	300	7.8	90	96	8.7	0.13	81.3	>99.9

* Residues were burned at 1200°F prior to analysis.

¹ Dumas, B. C., Summary Tech. Rpt., pp. 106-107, NLCO-640, July 18, 1956.

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During the initial phases of one trial, it was observed that a mild explosion occurred in the reaction vessel. In an effort to study the unstable character of this system, several additional controlled experiments were conducted in which samples of uranium-niobium alloy were lowered carefully into hot concentrated nitric acid (8N and 15.7N) from a remote position. It was noted that explosions of varying intensities could be produced by allowing the metal to strike either another piece of metal or the base of the reaction vessel. On occasion, the explosion produced was of sufficient violence to blow most of the acid from the vessel, and on other occasions the vessel (a 250-ml round-bottom glass flask) was blown apart. In several other experiments, samples of uranium-niobium alloy were lowered into nitric acid, allowed to react for a short period (1 to 5 min), withdrawn from the reaction vessel, and subjected to a strong electric discharge (Tesla Coil) which produced an explosion which was accompanied by a bright flash. Both of these explosions were photographed with a movie camera; however, development of this film is not complete at this time.

Due to the potential hazard involved during dissolution of uranium-niobium alloys in nitric acid, a series of experiments are being conducted to study the efficiency of uranium dissolution in nitric acid after the uranium-niobium material has been burned at 1200° F. Results obtained thus far have shown that treatment of the calcine with 15.7N nitric acid resulted in dissolution of 92 to 96 per cent of the uranium. It was also noted that in the range studied (30° to 90° C), the dissolution temperature had little or no effect on uranium dissolution.

Future work will be done on the recovery of uranium from uranium-niobium alloy scraps which have been calcined.

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11. THORIUM PROCESS DEVELOPMENT

In the process of manufacturing massive thorium metal, thorium oxide is hydrofluorinated to thorium fluoride, and then the thorium fluoride is mixed with zinc chloride and calcium metal and is reduced by a thermite-type reaction to a thorium-zinc alloy. The thorium-zinc alloy is heated under vacuum to distill off the zinc (thus forming thorium sponge), after which melting, casting, and scalping steps are required in order to produce sound, pure thorium metal. Melting and casting are accomplished by welding pieces of derby to form consumable electrodes (primary electrodes), then arc-melting the thorium into 5-inch-diameter water-cooled copper crucibles, scalping the resulting 5-inch-diameter ingot in order to remove impurities, and arc-melting the 4-1/2-inch-diameter consumable electrodes (secondary electrodes) into 7-inch-diameter copper crucibles.

11.1 CALCIUM REDUCTION OF THORIUM OXIDE – S. Cseplo, C. C. Fogel, and C. W. Taylor

A project was initiated to demonstrate the Sylvania process for calcium reduction of thorium oxide to thorium metal powder. Previous small-scale tests at Sylvania had indicated a process which potentially would meet National Lead Company of Ohio needs but would not require a fluoride conversion plant as does the existing oxalate process.

The following items must be demonstrated before the process can be used for producing thorium:

1. Adequate purity level of the thorium powder,
2. The feasibility of pressing thorium powder into electrodes,
3. The feasibility of melting the electrodes into solid metal, and
4. The practicality of the process on a production scale.

NOTE: Although the pressed forms were called electrodes, they were not used as such in this study.

The over-all procedure, as adapted to National Lead Company of Ohio processing equipment, consists of the following steps:

1. Blending of a thorium oxide – calcium chloride – calcium metal charge,
2. Reduction of thorium oxide to metallic powder in an electrical resistance furnace,
3. Separation of the thorium powder from impurities by a leaching and washing procedure,
4. Forming electrodes of the thorium powder in a hydraulic press, and
5. Melting of the electrodes in a vacuum induction furnace, followed by casting in cylindrical shape.

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These steps are illustrated in Figures 11.1-1 and 11.1-2 (although the steps shown in Figure 11.1-2 were not adhered to in all of the experimental work reported here).

Charging and Reduction

The materials, in the proportion of one part of thorium oxide, 0.40 part of calcium chloride, and 0.454 part of calcium metal, were blended in a twin-shell blender which had been purged with argon gas. (See Tables 11.1-1 and 11.1-2 for analyses of initial materials.) After the materials were blended for 30 minutes, the material was tamped into an argon-purged reduction pot. The lid was bolted on, the pot was placed under one-pound argon pressure, and the entire assembly was placed in a glo-bar furnace. In all of the runs, the pots were cold when loaded and placed in the furnace.

TABLE 11.1-1

CHEMICAL ANALYSIS OF ThO₂

Runs 1 - 13 (Inclusive)		Runs 14 - 17 (Inclusive)	
Drum 1	87.6% Th 0.046% C 0.14% H ₂ O	Drum 10	87.5% Th 0.01% C 0.23% H ₂ O

TABLE 11.1-2

SPECTROCHEMICAL ASSAY* OF CHARGE MATERIALS

	ThO ₂ (Runs 1 - 13)	Charge Material ThO ₂ (Runs 14 - 17)	CaCl ₂	Ca**
Al	<10	<10	10	6
B	<0.2	<0.2	<1	2
Be	<1	<1	—	—
Bi	<2	<2	—	—
Ca	<200	<200	—	—
Cd	<0.2	<0.2	<1	<1
Co	<1	<1	<6	<6
Cr	4	10	<6	10
Cu	2	10	<6	<6
Fe	25	35	<6	20
Mg	4	6	4000	2000
Mn	<1	2	8	<6
Mo	<1	<1	—	—
Ni	4	12	<6	<6
P	<40	<40	—	—
Pb	5	6	<6	<6
SiO ₂	<20	<20	<12	80
Sn	<1	<1	—	—
V	<10	<10	—	—
Zn	<10	<10	<6	<6

* All results are ppm.

** Screen analysis was 99 per cent -4, +40.

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FIGURE 11.1-1 Calcium Reduction of Thorium Oxide (The Furnace Charge Consists of the Following Constituents: Thorium Oxide – 1 part, Calcium Chloride – 0.40 part, and Calcium Metal – 0.454 part.)

FIGURE 11.1-2 Basic Flowsheet: Thorium Powder Leaching (Shows Alternative Methods of Sludge Treatment)

The temperature was brought up to 1742°F (the reaction temperature) during a heat-up period of several hours. The temperature was held at 1742°F for a period of two hours to insure complete reaction.

In Runs 1 to 9, small 4-inch reduction pots of 15-1/2-pound capacity were used to produce 7.35 pounds of thorium metal powder in each reduction; in Runs 10 to 13, 16, and 17, a 10-inch pot of 116-pound capacity was used to produce 58 pounds of thorium metal powder in each reduction; and in Runs 14, and 15, a 14-inch pot of 226-pound capacity was used to produce 114 pounds of thorium metal powder in each reduction. The initial two runs (Runs 1 and 2) were made in 4-inch steel pots, while Runs 3 to 9 were made in 4-inch stainless steel pots. The stainless steel pots were used for two reasons:

1. To avoid iron and carbon contamination from the steel pot (Table 11.1-3).
2. In order to make possible the use of dilute acid for leaching purposes.

Leaching and Washing

The reduction product is a single fused mass of grayish color. Leaching procedures for individual runs are described in later paragraphs.

The method of treating the material after leaching was (1) addition of an excess of water, (2) agitation, (3) allowing the slurry to settle, and (4) decanting off the supernatant liquor. This was repeated once, and enough dilute nitric acid was added to bring the pH of the slurry down to 1.0. The slurry was agitated for one-half hour and the liquor was adjusted again to a pH of 1.0 to insure complete lime neutralization. The material was filtered and the thorium powder was washed twice with 25 gallons of cold water. The washings were tested with silver nitrate to insure that chloride removal had been complete.

The residues from the 4-inch pots were all leached in essentially the same way, except that Run 5 used an acid leach rather than a water leach. Since this method resulted in excessive thorium losses in the decant and filtrate liquors, it was not used again. In Runs 3 and 4, a jet leaching apparatus was used whereby the pot was turned upside down and the hard residue was cleaned out of the pot by means of a jet nozzle under pump pressure. Since the average time for cleaning out a pot by means of agitation and water soaking was about 14 hours, the jet leaching method (whereby the pot was cleaned in only three hours) seemed preferable.

Runs 10 through 13, made in a Type 430 stainless steel 10-inch-diameter pot, yielded thorium powder weighing 55 pounds. Runs 10 through 12 were leached out by the use of the agitation and water-soak method described above. The average leach time with this method was 48 hours. In Run 13, a jet nozzle cleaning apparatus was used that was similar to the jet nozzle system used in Runs 3 and 4. By this method, the leach time was reduced from 48 hours to 15 hours.

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TABLE 11.1-3

CHEMICAL ASSAY OF THORIUM METAL

Run	Th (%)	ThO ₂ (%)	H ₂ O (%)	Tap Density (g/cc)	Bulk Density (g/cc)	C (ppm)	N (ppm)	Fe (ppm)	Cl (ppm)
1		0.29	0.21	2.902	2.299	1950	100		70-80
2	96.1	0.24	0.30	2.951	2.393	2680	15		52
3		0.54	0.17	2.222	1.707	1795	115		70-80
4		0.76	0.21	2.767	2.128	1450	115		70-80
5	94.2	0.26	1.17	2.1	1.6	2895	370		70-75
6	87.7	0.36	10.37	2.6	1.4	1665	115		70-75
7	98.4	0.24	0.29	3.1	2.3	865	110		115-120
8	96.6	0.71	1.36	2.9	2.3	1605	60		115-120
9	98.0		0.16	3.1	2.2	930	65		100-105
1-9*	98.9	0.22	0.11	3.4	2.7	1090	90	1400	
10	86.7		0.31	3.0	2.1	1925	60	410	120-125
10**	91.2	0.29	0.14	2.7	2.1	1500	70	410	-
11	99.0	0.12	<0.10	3.0	2.5	1100	110	1050	-
12	98.9	0.18	0.26	3.1	2.4	895	80	1340	-
13	99.3	0.49	<0.10	3.0	2.3	695	305	360	17,000
13**	97.7	0.8	1.33	2.9	1.74	800	70	585	10,630
14	99.4	0.3	0.24	3.4	2.72	680	225	354	4,895
15	99.5	<0.01	0.20	3.13	2.44	480	65	204	5,345
14, 15*	99.3	0.42	0.20	3.3	2.7	655	330	178	90
16	94.0	0.3	0.94	4.18	3.18	860	340	343	25,950

* Composite of runs noted.

** Represents material that required a 2nd acid treatment after previously being dried.

Runs 14 and 15, made in a 14-inch steel pot equipped with a Type 446 stainless steel liner, yielded 107 pounds of thorium powder. Leaching was accomplished by means of the jet apparatus used in Run 13, except for a variation in jet nozzles. Several nozzles were tried, ranging from a pipe cap having a single 1/8-inch hole to a Schutte-Koerting spray nozzle. Leach time varied from 36 to 40 hours on each run.

Runs 16 and 17, in which a Type 446 stainless steel pot of 10-inch diameter was used, yielded 55 pounds of thorium metal powder. Leaching was accomplished as before by the use of the jet cleaning apparatus, with a leach period of 22 hours.

The yields obtained between charging of the ThO₂ and the leached and washed product are shown in Table 11.1-4.

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Separation of Thorium Powder from Chloride, Acid Salts, Metal Salts, and Water

The method of treating the resultant sludge was essentially the same on all runs, the only difference being the final method of powder concentration. After the powder was twice washed with water and the supernatant liquor was decanted in order to get rid of most of the calcium chloride flux, enough water and nitric acid were added to neutralize all of the calcium oxide present. After agitation and settling, the acidic liquor was decanted off and the powder was concentrated, either by further washing and decantation or by filtration and washing. Filtration seemed to be preferable, since concentration by decantation was laborious and time-consuming.

Regardless of the method of final powder concentration, the powder was washed with water until the final liquor had a pH of 7.0. This was done to insure complete removal of any residual acid or metal salts. The resulting wet powder was dumped into stainless steel trays and was dried in a heated air oven at 90° to 100° F.

The resulting dry powder from Runs 1 to 16 did not seem to be pyrophoric or to exhibit any dangerous properties. However, during the acid neutralization step of Run 17, severe fuming and other evidences of powder reactivity were exhibited. The acidic liquor and powder slurry then was filtered normally on a one-foot by one-foot stainless-steel-plate-and-frame filter, but after a few minutes, a hole appeared in the filter cloth, making it necessary to dump the press before the water wash step. During the dumping of the press, the wet thorium powder exploded and burned. Because of the danger of fire from the thorium fines, each batch of thorium powder was stored in one-gallon metal cans under an argon atmosphere.

Samples of thorium powder that showed high iron analyses were examined, and it was found that such samples were contaminated with iron particles. A sample of powder from Run 12 was magnetically separated twice and submitted for analysis. A similar sample was screened at 100 mesh, and the -100 mesh material was magnetically separated twice and submitted for analysis. Analysis of the various powders (tabulated below) showed a tenfold reduction in iron content, proving that the major contamination had been free iron particles in the powder. The jet nozzle leaching was thereupon instituted as a substitute for the mechanical operation previously used.

IRON CONTENT OF THORIUM POWDER (RUN 12)

Material	Fe (ppm)
Run 12 powder, as processed	1340
Run 12 powder, magnetically separated twice	130
The same Run 12 powder, screened at 100 mesh, and the 100-mesh fraction further magnetically separated twice	120

Most of the thorium powder produced by this method was shown to have a particle size distribution that was approximately 97 per cent -100 mesh. Table 11.1-5 shows the size distribution of the powders from Runs 1 through 12. Dry screening of the powder was stopped because of the possibility of dust explosions from the fine fractions of the powder.

TABLE 11.1-4

SUMMARY OF THORIUM RUNS

Run No.	Type of Pot	ThO ₂ (lb)	CaCl ₂ (lb)	Ca (lb)	Time to Reduction Temp (hr)	Time at Reduction Temp (hr)	Vol Shrinkage Resulting from Reduction (%)	Method of Leach	Leaching Time (hr)	Method of Powder Concentration	Yield (%)	Loss - Decant Plus Fines (%)
1	Steel (4" Diam)	8.37	3.37	3.75	4-1/2	2	-	Agitation and Water Soak	48	Filtration on Buchner Funnel	100+	-
2		8.37	3.37	3.75	1-1/2	2	-		48	Filtration on PVC Plate and Frame Filter	89.3	-
3	Stainless Steel (4" Diam)	8.37	3.37	3.75	2	2	40	Jet Nozzle	3	Filtration on Buchner Funnel	34	-
4		8.37	3.37	3.75	2	2	46		24	Filtration on PVC Plate and Frame Filter	77.6	-
5		8.37	3.37	3.75	1	2	48	Agitation and Nitric Acid (1.5M)	8		33*	-
6		8.37	3.37	3.75	2	2	3		14		81.6	-
7		8.37	3.37	3.75	1-1/4	2	11		15		93.3	-
8		8.37	3.37	3.75	1-1/2	2	33		21		81.2	-
9		8.37	3.37	3.75	1-1/2	2	31.5		14	Decantation	79.2	-
10		62.5	25	28.38	2	2	33	Agitation and Water Soak	48		93.5	-
11	Stainless Steel (Type 430) (10" Diam)	62.5	25	28.38	2	2	33		45	Filtration on 1' x 1' Plate and Frame Filter	108	-
12		62.5	25	28.38	2	2	43		54	Decantation	93	1.2
13		62.5	25	28.38	2-1/2	2	Unknown	Jet Nozzle	15		79	1.3

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TABLE 11.1-4 (Cont'd)

SUMMARY OF THORIUM RUNS

Run No.	Type of Pot	ThO ₂ (lb)	CaCl ₂ (lb)	Ca (lb)	Time to Reduction Temp (hr)	Time at Reduction Temp (hr)	Vol Shrinkage Resulting from Reduction (%)	Method of Leach	Leaching Time (hr)	Method of Powder Concentration	Yield (%)	Loss - Decant Plus Fines (%)
14	Carbon Steel (14" Diam)	122	48.8	55.4	3 - 1/2	2	37	Jet Nozzle	36	Decantation	78	0.412
15	W/Stainless Steel (Type 446) Liner				4 - 1/2		41		40		76	-
16	Stainless Steel (Type 446)	62.5	25	28.38	17**		44		22	Filtration on Plate and Frame Filter	79	-
17†	(10" Diam)				4 - 3/4		50		35			

* Excessive thorium losses in the decant and filtrate liquors were caused by using an acid leach rather than a water leach.

** A Fuse burned out.

† Material was destroyed by fire during the filtration operation.

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FIGURE 11.1-3 Thorium Powder Electrodes

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TABLE 11.1-5

Run	On 60 (%)	On 100 (%)	On 150 (%)	On 200 (%)	On 250 (%)	On 325 (%)	- 325 (%)
1 to 9	1.2	3.3	5.3	11.2	18.1	14.4	46.5
10	18.0	6.3	7.8	19.3	17.7	13.8	17.1
11	0.7	2.2	9.5	14.2	21.3	22.2	29.9
12	0.9	2.2	10.0	17.4	17.2	17.0	35.3

Pressing of Electrodes; Melting

Electrodes of varying diameters and lengths were made by the following method: The powder from Run 10 was tamped into one-inch-ID rubber tubing, the ends were capped with rubber stoppers, and the rubber tube assembly was dropped into a perforated steel tube. The entire tube assembly was dropped into the oil chamber of a 40,000-psi hydraulic press and the lid was bolted on. The press was hand-operated to its maximum pressure and then the pressure was released. The assembly was taken out of the oil and was wiped free of any excess oil, and the rubber stoppers and tubing were stripped off. A straight electrode, 3/4 inch in diameter and 3 inches long and weighing about 180 grams, was produced. Eight more electrodes were made and a trial melting and casting was performed. No derby was formed because of crucible and refractory material failure at 2600° F.

Eight more electrodes, pressed from the thorium powder produced by Run 11, had final dimensions of 7/8-inch diameter and a 5-3/4-inch length (Figure 11.1-3). These electrodes had an average weight of 390 grams. The eight thorium electrodes from Run 11 were placed in a graphite crucible, washed with a beryllium oxide coating, and placed in a small vacuum induction furnace. The electrodes showed severe off-gassing at 2000° F. Melting of the thorium electrodes started at 3000° F, with final melting and pouring at 3500° F. A small cylinder of solid thorium metal was produced. The cylinder of thorium metal was sectioned and a hardness test was made. The metal had a Brinell hardness of 135, and the critical impurity levels for ThO₂, Fe, and C (Tables 11.1-3 and 11.1-6) were approximately equal to the impurity levels in metal produced in the existing Thorium Plant. This phase of the project is completed.

Conclusion

The Sylvania process for producing thorium metal powder from thorium oxide has been successfully demonstrated.

TABLE 11.1-6

SPECTROCHEMICAL ASSAYS* OF THORIUM METAL

Run	Al	B	Be	Bi	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Mo	Ni	P	Pb	SiO ₂	Sn	V	Zn
1	<10	1.0	<1	<2	500	<0.2	<1	10	20	>600	10	15	2	10	<40	5	120	<1	<10	<10
2	<10	<0.2	<1	<2	400	<0.2	<2	6	6	25	60	12	1	300	<40	10	<20	1	<10	<10
3	<10	6	<1	<2	700	0.2	1	75	15	>600	15	300	1	40	<40	>100	80	1	<10	<10
4	20	1	<1	<2	500	<0.2	<1	200	30	>600	40	200	2	100	<40	100	160	<1	<10	<10
5	<10	1.5	<1	<2	500	4	2	600	60	>600	60	400	4	350	<40	40	40	1	<10	20
6	<10	<0.2	<1	<2	>4000	<0.2	<1	60	>200	300	200	30	<1	5	<40	10	<20	<1	<10	<10
7	30	<0.2	2	<2	4000	0.4	2	150	>200	>600	40	60	2	200	<40	4	<20	<1	<10	<10
8	<10	<0.2	<1	<2	1200	0.2	2	300	>200	>600	80	350	>20	200	<40	4	20	<1	<10	<10
9	80	0.4	<1	<2	1500	0.4	2	350	>200	>600	100	80	2	250	200	45	100	1	<10	<10
1-9**	15	<0.4	2	<2	600	<0.2	1	60	200	>600	50	100	4	100	<40	6	<20	5	<10	40
10	<10	<0.2	<1	<2	>4000	<0.2	<1	15	>200	90	80	5	1	<2	<20	15	<20	<1	<10	<10
10†	<10	<0.2	<1	<2	>4000	<0.2	<1	12	>200	65	100	4	<1	2	<40	6	<20	<1	<10	10
11	<10	<0.2	<1	<2	1500	<0.2	<1	200	150	>600	30	100	<1	6	<40	6	<20	<1	<10	<10
12	15	<0.2	<1	<2	2500	<0.2	<1	200	20	>600	30	15	<1	40	<40	6	<20	<1	<10	<10
13	20	0.4	<1	<2	1000	<0.2	<1	80	10	>600	40	100	>20	40	<40	10	60	<1	<10	<10
13†	40	0.2	<1	<2	1500	<0.2	<1	80	10	700	40	20	4	85	<40	2	30	2	<10	<10
14	40	0.6	<2	<2	800	<0.2	<1	20	10	150	100	10	5	20	<40	6	30	<1	<10	<10
15	<10	0.2	1	<2	600	<.2	<1	10	8	215	15	10	3	25	<40	1	20	<1	<10	<10
14, 15**	<10	0.2	<1	<2	600	<0.2	<1	15	15	550	30	15	1	30	<10	2	<20	<1	<10	<10
16	120	1	1	<2	800	<.2	2	80	30	400	20	50	40	60	<40	6	1200	10	<10	<10

* All results are ppm.

** Composite of runs noted.

† Represents material that received a 2nd acid treatment after previously being processed and dried.

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11.2 PRODUCTION OF THORIUM INGOTS BY THE PRESSED-ELECTRODE ARC-MELT ROUTE - H. H. Baker

High-purity thorium can be produced by arc-melting consumable electrodes, the latter being formed by sawing the massive derby into strips and butt-welding these strips under inert atmosphere (Fig. 11.2-1). A low yield during electrode fabrication is caused by (a) the production of sawdust and small pieces unsuitable for welding and (b) oxidation due to cooling of the weldment in air. Only a 56.2 per cent over-all process efficiency is achieved when 7-inch-diameter ingots are fabricated from dezincodized derbies. Earlier efforts¹ to decrease the percentage of scrap formed when consumable electrodes are fabricated have been directed toward (1) allowing the derby to solidify in cylindrical shapes or (2) shaping the derby by either extrusion or forging. These methods have not been suitable for thorium electrode fabrication. Cylindrical shapes could not be completely dezincodized, and shaping the derby by extrusion or forging proved impractical because of the friable nature of the derby.

A solution to this problem was looked for among the techniques used in processing other metals. The fabrication of primary electrodes of reactive metals such as zirconium and titanium is accomplished by pressing the sponge nodules in a 2-inch by 2-inch cross sectional die. The scrap, or off-grade material, is blended with the sponge prior to pressing.

Work at the Bureau of Mines Station, Albany, Oregon,² resulted in optimum conditions being established for the pressing of primary electrodes from zirconium sponge. A comparison of hardness values of thorium and zirconium indicated that less pressure would be required for thorium than for zirconium. This method appeared to be applicable to thorium electrode fabrication.

In order to determine the feasibility of pressing primary thorium electrodes and to establish the quality levels of ingots, it was decided to produce two ingots by this route. The dezincodized derbies were produced at the National Lead Company of Ohio; electrode fabrication and arc-melting were done offsite; and subsequent ingot evaluation was performed at National Lead Company of Ohio.

Method (Fig. 11.2-2) and Equipment

Derbies were crushed into small pieces and pressed into 2-inch by 2-inch by 10-inch compacts.³ The compacts were butt-welded, using a 1/4-inch-diameter, 2 per cent thoriated tungsten electrode under an inert-arc atmosphere. For the butt welding, the welding tank was evacuated to 60 microns pressure and backfilled with argon to 27 inches Hg vacuum. Welding was done with a current of 275 amperes at 20 volts.

The primary melting of the consumable electrode was done in a 5-inch-diameter copper cup as follows: The furnace was evacuated and backfilled to 25 inches Hg with a mixture of 4 parts of argon to one part of helium. The power setting was 1000 amperes at 30 volts. The resultant

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1 Baker, H. H. and Magoteaux, O. R., *Summary Tech. Rpt.*, pp. 101-114, NLCO-577, October 17, 1955.

2 Beall, R. A., Borg, J. O., and Wood, F. W., *A Study of Consumable Electrode Arc Melting*, BM-RI-5144, August, 1955.

3 Baker, H. H., *Summary Tech. Rpt.*, pp. 123-124, NLCO-625, April 16, 1956.

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FIGURE 11.2-1 Old Process: Flowsheet, Showing Process Efficiency (Seven-Inch Thorium Ingots are Fabricated from Consumable Electrodes. The Consumable Electrodes are Fabricated by Sawing Derbies into Pieces which can be Welded to Electrode Shape. Note: The Percentage Values Represent the Process Efficiencies at Each Step.)

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FIGURE 11.2-2 Small-Scale Test: Flowsheet, Showing Process Efficiency (Seven-Inch Thorium Ingots are Produced from Electrodes Fabricated by Pressing Crushed Derbies. Note: The Percentage Values Represent the Process Efficiencies at Each Step.)

~~CONFIDENTIAL~~ **FIGURE 11.2-3**

Proposed Large-Scale Method: Flowsheet, Showing Process Efficiency (Seven-Inch Thorium Ingots are Produced from Electrodes Fabricated by Pressing Crushed Derbies. Note: The Percentage Values Represent the Process Efficiencies at Each Step.)

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primary ingots were scalped. Approximately 4 per cent of the thorium was removed in order to remove volatiles occluded near the metal surface. The primary ingots were then butt-welded to form the secondary electrodes. The welding technique was the same as that described for primary electrodes, with the exception that the amperage was increased to 375.

The secondary melting was done under the same type of atmosphere and pressure as was the primary melting. The arc was started at a power setting of 1800 amperes and 35 volts, was gradually increased to 2500 amperes, and was held until a pool was obtained. Then the furnace was evacuated to 28 inches, the amperage was raised to 5800, and maintained until 5 inches of meltable electrode remained. At this point, the amperage was reduced to 5000. It was further reduced in increments of 1000 amperes for each inch of electrode melted until an amperage of 2000 amperes was reached. The last 2 inches of electrode was melted at 2000 amperes. This technique minimizes primary pipe in the ingot.

Flowsheets

Figures 11.2-1, 11.2-2, and 11.2-3 are flowsheets showing process efficiencies and scrap losses generated in fabricating electrodes from dezincd thorium derbies. Figure 11.2-1 is a flowsheet showing the old method of sawing, followed by inert gas-arc welding. Figure 11.2-2 is a flowsheet based on the small-scale test data obtained when electrodes were fabricated by the crushing-pressing method. Figure 11.2-3 is a proposed flowsheet for a large-scale crushing-pressing method.

The over-all efficiencies of the three processes are:

Process	Over-all Efficiency* (%)
Old Process	56.2
Pressing crushed derbies (small-scale)	79.3
Pressing crushed derbies (large-scale)	85.4

* Dezincd derby to finished ingot.

Conclusion

It is concluded that thorium electrodes for electric arc-melting can be fabricated more efficiently by a crushing-pressing route than by the presently used sawing and inert gas arc-welding route.

100-100

100-100

12. NEW PROCESSES AND SPECIAL PROJECTS

12.1 OPERATION OF ADU (AMMONIA-URANIUM PRECIPITATE) PILOT PLANT (See also Sections 12.2 and 12.3) – G. M. Reinhart, T. J. Collopy, and H. S. Brech

Batch thermal denitration of uranyl nitrate (to form orange oxide) often gives rise to problems of product uniformity and contamination. There is evidence that the rate of reaction of the orange oxide in subsequent reduction and hydrofluorination steps is slower than the rate of certain other uranium compounds. If a chemical denitration process can be developed, a continuous, low-temperature operation can be put into practice to yield a purer and more uniform product. If a higher degree of reactivity is attained, higher capacity and lower cost in the following screw reductors and hydrofluorinators will result.

Laboratory studies have defined the conditions (Section 12.2 of this report) necessary to produce ADU which is easily filterable. (ADU is a precipitate formed by the reaction of uranyl nitrate solution with ammonium hydroxide.) They have also demonstrated the rapidity with which ADU reacts with H_2 and HF. The objective of this work was to prepare, in small-scale continuous equipment, ADU which was comparable to the laboratory product.

A schematic diagram of the equipment used is shown in Figure 12.1-1. Fifty-five-gallon shipping containers were located on the floor above the other equipment and reactants were fed by gravity to the precipitator. UN (uranyl nitrate) solution was heated batchwise in an open tank, and the flow rates of it and ammonium hydroxide were controlled by needle valves and indicated by rotameters. The precipitator was made of a two-liter stainless steel beaker which had a 2-inch by 1/2-inch concentric reducing fitting in its bottom. A 1/2-inch plug cock regulated the outflow rates to maintain a pool of 0.2 to 0.5 gallon in the precipitator during continuous runs. The surge tank was an insulated 25-gallon tank with a flat bottom which was slightly inclined toward the discharge. A 12-inch by 18-inch-diameter Eimco rotary vacuum filter was used without modification. A polyethylene filter cloth gave good service when properly installed.

Batch precipitations were made under conditions as nearly as possible like those used in the laboratory work. Uranyl nitrate solutions were maintained at about 160 g/l uranium by measuring and adjusting the specific gravity. The same measurement was made on the ammonium hydroxide and the volume of this reagent was adjusted so as to maintain a constant weight input of NH_3 . Because of the absence of a precipitator heater, the reactions were carried out at 130° to 140°F, compared to 150°F in the laboratory work. All batch reactions resulted in precipitates which settled rapidly and filtered easily, duplicating, in these respects, the material produced in the laboratory. There was no difficulty in maintaining the desired final pH of 9.7 ± 0.1 . About 100 pounds of filter cake were produced in this manner for use in studies of its suitability in the manufacture of moving-bed reactor pellets.

A few preliminary continuous precipitations were made, and in the range investigated (pH 3 to 8), a good correlation was found in pH and NH_3/U weight ratio relationships between these continuous runs and the batch runs (Fig. 12.1-2). A short precipitator retention time (1 to 2 minutes) was

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FIGURE 12.1-1 Schematic Diagram: ADU Pilot Plant

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FIGURE 12.1-2 ADU Precipitation

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used in order to avoid post-precipitation reaction. The resulting small volume of reacting materials promoted local action around the points of addition of the reactants and made control of pH very difficult. Settling and filtration characteristics of this product were poor, as compared to those of the batch precipitate.

Analysis of the washed filter cake averaged (on a wet basis) 1.5 to 2.0 per cent NH_3 , 1.2 to 3.6 per cent NO_3 , 41 to 47 per cent U, and 34 to 55 per cent loss on heating to 102°F .

An attempt was made to reproduce the filterability of batch precipitate at the same time the amount of ammonium hydroxide used was reduced. The uranyl nitrate solution was acidified with nitric acid prior to neutralization so that a large amount of ammonium nitrate was present. The results of this effort to replace ammonium hydroxide with nitrate were inconclusive.

Plans for the future include the preparation in the Pilot Plant of quantities of ADU suitable for testing in the moving bed reactor.

12.2 AMMONIA PRECIPITATION AND FILTRATION STUDIES FROM URANYL NITRATE SOLUTIONS — P. S. Gentile, T. J. Collopy, and D. A. Stock

This project is currently under investigation because of a need for a process to replace batch thermal denitration of uranyl nitrate solution. The process must (1) be continuous and (2) produce a feed for conversion to green salt that is more reactive and economical than the feed now used.

When ammonium hydroxide is added to a solution of uranyl nitrate, a precipitate (ADU) is formed that may be used as a feed for the conversion-to-green-salt process. The objective of this investigation during the past quarter was to determine the conditions for producing an easily filterable precipitate. The laboratory investigation has demonstrated that the following conditions will give a filterable uranium cake:

A pH of 9.8 before filtration.

Addition of the ammonium hydroxide to the uranyl nitrate solution (in preference to addition of the uranyl nitrate solution to ammonium hydroxide).

The use of uranyl nitrate containing approximately 160 g/l uranium.

The use of concentrated ammonium hydroxide (28% NH_3)

A precipitation temperature of 150°F ,

Minimum aging prior to filtration,

A stirring rate sufficient to maintain the precipitate in homogeneous suspension, and

A rate of agitation which will minimize "localized" pH changes.

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The results of an evaluation of filter cloths showed that Nylon cloth gives the best filtration rate and precipitation retention and has the best resistance to abrasion.

Detailed laboratory data are included in a recent topical report.¹

12.3 LABORATORY INVESTIGATION OF THE PELLETING, REDUCTION, AND HYDROFLUORINATION OF AN AMMONIUM DIURANATE - TYPE PRECIPITATE - G. G. Briggs, D. C. Bonfer, R. C. Abbott, and J. D. Drew

During recent months, work has progressed on the preparation and evaluation of "ammonium diuranate" (ADU) as a feed material for the production of green salt. Previous thermobalance tests in the laboratory have indicated that the reduction and hydrofluorination reactivities of ADU can greatly surpass those of pellets prepared from pot denitrated oxide.² It is believed that this high reactivity can be utilized advantageously to increase conversion to UF_4 in the moving bed reactor. The immediate objective is to prepare a sufficient quantity of the material in pellet form for reduction and hydrofluorination tests in the moving bed reactor.

The term "ADU" refers to the precipitate formed when ammonium hydroxide is added to an aqueous solution of uranyl nitrate. Attempts to characterize this material at National Lead Company of Ohio and at other sites³ indicate that the precipitate is not the single true compound expressed by the formula, $(NH_4)_2U_2O_7$. The material, when washed and dried, contains a much lower percentage of ammonia than is indicated by the above formula. A small percentage of nitrate is present. The material also contains water of hydration which is gradually removed by prolonged heating at temperatures of about 212°F. The dried powder is light yellow, is finely divided, and has a tap density of about 1.3 grams per cubic centimeter.

The specific objectives of the work reported were: (1) to investigate methods of preparing pellets from ADU which possess sufficient strength for handling and processing in a moving bed type operation, and (2) to measure the reaction rates during the hydrofluorination of UO_2 produced from these pellets in the thermobalance. The work on the second objective has not yet been completed.

Materials and Method - Pelleting

ADU for the studies, in the form of an unwashed wet filter cake, was supplied by the Pilot Plant group which had prepared a quantity of the material (Section 12.1 of this report) for preliminary pelleting tests in the MBR extrusion equipment. Some of the wet cake was reslurried and filtered

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1 Gentile, P. S. and Collopy, T. J., *Summary Tech. Rpt.*, NLCO-645, August 15, 1956.

2 Briggs, G. G., Votaw, J. W., DeMarco, R. E., Richards, D. E., Abbott, R. C., and Bonfer, D. C., *Summary Tech Rpt.*, pp. 72-79, NLCO-625, April 16, 1956.

3 Ewing, R. A., Kiehl, S. J. Jr., and Bearse, A. E., *Investigation of Ammonium Uranates*, BMI-1115, July 19, 1956.

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in the laboratory to remove soluble ammonium nitrate, which is a by-product of the precipitation reaction. The washing was repeated twice, and the final filter cake was then dried at 212°F. The cake was then ground to powder. A sample analyzed 2.20 per cent NH_3 , 1.45 per cent NO_3 , and 72.89 per cent uranium. The tap density of the powder was 1.3 grams per cubic centimeter.

Pellets were prepared in the shape of 1/4-inch cubes by (1) adding water to the ADU to form a stiff paste (the weight of water being approximately 50 per cent of the weight of the ADU), (2) spreading the paste in a 1/4-inch layer on aluminum foil, (3) slicing the layer into 1/4-inch cubes with a spatula, and (4) drying the material at 194°F in an oven. The pellets prepared in this manner were very weak. They could be crushed easily by mild pressure. Heating the pellets to 750°F to convert them to UO_3 only slightly enhanced their strength. The UO_3 pellets were then hydrated by warming them in water, and then were dehydrated at 750°F. This treatment hardened the pellets somewhat, but the pellet structure contained many small cracks which probably resulted from strains developed by shrinkage. As a result, the pellets were friable.

In further experiments, it was found that pellets prepared from the unwashed, wet ADU cake possessed considerably more strength than pellets prepared from washed cake (after drying at 212°F and after conversion to UO_3 at 750°F). The presence of the residual ammonium nitrate may have resulted in bonding action when the pellets were dried.

Further improvement in pellet strength resulted when concentrated uranyl nitrate solution was added to the unwashed ADU before pelleting. It was then necessary to partially dry the wet ADU filter cake so that the paste formed after adding the uranyl nitrate solution was stiff enough to be cut into pellets. Uranyl nitrate addition also caused a shrinkage of the pellet structure when the pellets were dried at 212°F.

The uranyl nitrate solution employed in these tests was prepared by dissolving a pot-denitrated UO_3 in 6M nitric acid. The solution was concentrated by heating to a boiling point of 250°F to remove excess nitric acid which, if not removed, would dissolve some of the ADU. The solution was then diluted to a concentration of 624 grams of uranium per liter.

The addition of one part uranium as uranyl nitrate to ten parts uranium as ADU appeared to be optimum in producing pellets which possessed good strength and which did not develop cracks when dried at 212°F and converted to UO_3 at 750°F. A somewhat higher ratio of uranyl nitrate to ADU (1.4 to 10 on a uranium basis) resulted in uneven shrinkage and splitting of many of the pellets during the initial drying phase. On the other hand, pellets produced at the still higher ratio of 1.6 to 10 were greatly densified during heating at 212°F and did not undergo extensive cracking. However, the pastes formed with the relatively high uranyl nitrate additions were viscous and sticky.

It is believed that the uranyl nitrate strengthens the ADU pellets by bringing about contraction of the structures during the early stages of heating and also by its denitration at higher temperatures to form orange oxide, which cements the particles of UO_3 derived from the ADU. During heating of the pellets, the evolution of ammonia was evidenced by its odor. White fumes, presumably of sublimed NH_4NO_3 , were also noticed. At higher temperatures, the brown fumes of NO_2 were evolved.

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Reduction and Hydrofluorination of ADU Pellets and ADU - Uranyl Nitrate Pellets

Samples of (1) pellets prepared from the unwashed ADU and (2) pellets prepared from this material with various additions of uranyl nitrate were reduced to UO_2 in a laboratory tube furnace, and were then hydrofluorinated in a thermobalance. The primary objectives were to observe the effect of high reduction temperature on the subsequent rates of hydrofluorination and to establish the effect of uranyl nitrate additions on the hydrofluorination rate. Table 12.3 - 1 presents data pertinent to the preparation of the pellet samples used.

TABLE 12.3 - 1**COMPOSITION OF PELLETTED PASTES**

Pellet Sample	Wt of Wet ADU (g)	Vol. of Conc.† Uranyl Nitrate Solution (ml)	Vol of Water Added (ml)	Grams U in Uranyl Nitrate/100 grams U in ADU
1	60.0*	0	0	0
2	45.0**	3.7	5.6	9.3
3	45.0**	4.6	4.7	11.5
4	45.0**	5.5	3.8	13.7
5	45.0**	6.4	2.9	16.0

* The ADU used in Sample 1 consisted of unwashed filter cake containing 41.6 per cent uranium.

** The ADU used in Samples 2 through 5 consisted of partially dried unwashed filter cake containing 55.1 per cent uranium.

† U concentration: 624 g/l; specific gravity: 1.81.

Pellets from each of the five samples were heated to 750°F in order to convert them to UO_3 . They were then reduced at 1700°F with hydrogen in a tube furnace. This is considered a high reduction temperature. The reduction actually involved the conversion of U_3O_8 pellets to UO_2 , since the pellets were first heated to 1700°F in nitrogen before the hydrogen was introduced. Hydrogen was passed over the samples for 30 to 40 minutes at 1700°F and the hydrogen flow was continued while the reaction chamber was cooled to 100°F or less. The UO_2 pellets were much smaller than the UO_3 pellets, and a few were cracked.

Sample 5 was the first to be hydrofluorinated in the thermobalance at 1100°F. An attempt to introduce the sample into the reaction chamber at 650°F resulted in immediate oxidation of the pellets, despite the fact that a flow of nitrogen was being maintained. The weight change that occurred indicated that the sample had been 70 per cent oxidized to U_3O_8 . The ease of oxidation of the UO_2 derived from ADU is in strong contrast with the relative inertness of UO_2 pellets prepared from pot-denitrated orange oxide. The latter can be introduced into the reaction chamber with negligible oxidation at 1100°F. Sample 5 was re-reduced with hydrogen to UO_2 while the reaction chamber was

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reheated to 1100°F. Hydrofluorination was then begun, and the reaction proceeded to 98.8 per cent conversion in the extremely short time of 12 minutes.

The above result, although indicative of the very rapid hydrofluorination rate which can be achieved with UO_2 from ADU, did not constitute confirmation that the original UO_2 prepared at 1700°F possessed a similarly high hydrofluorination reactivity, since it is known that cycling UO_2 to U_3O_8 and back to UO_2 can result in enhanced reactivity.¹ (See also Section 6.3 of this report.) The UO_2 pellet structure is also deteriorated by expansion and spalling when the oxidation to black oxide occurs. The latter effect was clearly evident when the sample of green salt pellets was removed from the thermobalance reaction chamber as the pellets had broken into small pieces. (This normally does not occur unless oxidation has taken place.) In addition, the tap density of the green salt powder prepared from the sample was 2.5 g/cc, which is considerably less than the density normally obtained (2.8 to 3.3 g/cc).

The remaining four samples of UO_2 pellets were hydrofluorinated at 1100°F, using a procedure in which each sample was placed in the thermobalance reaction chamber at room temperature and was heated to 1100°F in hydrogen. This procedure resulted in only slight oxidation of the sample while the temperature increased above 600° to 700°F. At approximately 700°F, the hydrogen re-reduced any black oxide which had formed.

The hydrofluorination rates for samples 1, 2, 3, and 4 were also extremely rapid, as is shown by the data presented in Table 12.3-2. The results may be compared with similar data obtained for two samples of UO_2 pellets which were prepared by hydrating pot-denitrated orange oxide and then reducing the pellets at 1600°F. Also, for purposes of comparison, the hydrofluorination results are presented for a sample of UO_2 which was prepared in powder form by reducing (at 1600°F) a sulfated pot-denitrated orange oxide.

The data of Table 12.3-2 indicate that although the hydrofluorination proceeded rapidly to conversion of approximately 95 per cent in all cases, final conversion was relatively slow for those samples which contained higher percentages of uranyl nitrate. Nevertheless, the results show that high reduction temperatures have very little effect on the subsequent hydrofluorination rate of UO_2 derived primarily from ADU.

Tap densities obtained for the UF_4 powder prepared from the ADU-uranyl nitrate pellets ranged from 2.5 to 3.3 g/cc.

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¹ Bard, R. J., *The Activation of Low-Reactivity Uranium Dioxide Particles*, LA-1952, October, 1955.

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TABLE 12.3-2

THERMOBALANCE HYDROFLUORINATION AT 1100°F OF UO₂ PELLETS*
DERIVED FROM ADU, ADU-URANYL NITRATE MIXTURES,
AND POT-DENITRATED UO₃

Pellet Sample	Grams U in Uranyl Nitrate/100 grams U in ADU	Per Cent Conversion to UF ₄ at Indicated Time							
		5 min	10 min	15 min	20 min	25 min	30 min	40 min	50 min
1	0	77.3	96.6	97.9	98.3				
2	9.3	71.2	96.1	97.4	97.9				
3	11.5	71.0	93.4	95.1	95.9	96.4	96.9	97.3	97.8
4	13.7	65.4	93.0	95.2	95.9	96.3	96.6		
5**	16.0	75.5	98.3	98.8					
A†	—	35.0	59.0	73.3	81.0	84.5	86.9	88.8	90.0
B††	—	35.0	59.7	77.3	86.8	91.5	94.0	96.0	96.5
C†††	—	46.1	58.6	—	69.2	72.4	75.9	79.8	83.0

* All ADU samples were reduced at 1700°F for 30 to 40 minutes.

** UO₂ sample 70 per cent oxidized to black oxide and re-reduced prior to hydrofluorination.

† Hydrated pellets prepared from pot-denitrated UO₃.

Water of hydration, 7.3%. Reduced at 1600°F.

†† Hydrated pellets prepared from pot-denitrated UO₃.

Water of hydration, 10.3%. Reduced at 1600°F.

††† Sulfated pot-denitrated UO₃ powder reduced at 1700°F for 30 minutes.

X-Ray Diffraction Patterns

An X-ray diffraction pattern was prepared for the orange oxide prepared by heating an ADU-uranyl nitrate preparation to 750°F. This material contained 16 grams of uranium from uranyl nitrate per 100 grams of uranium from ADU. The pattern was unlike any observed for samples of pot-denitrated orange oxides. Relatively few lines were resolved, indicating small crystallite size or lattice strain. On the other hand, the diffraction pattern obtained for the UO₂ produced from the (ADU-uranyl nitrate source) orange oxide by reduction at 1700°F was indistinguishable from patterns obtained for UO₂ samples prepared from pot-denitrated orange oxide which had also been reduced at 1700°F. The lines of the pattern were sharply defined, indicating a high degree of crystallinity.

Conclusion

The use of uranyl nitrate in the pelleting of ADU for plant-scale work is suggested.

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Summary

1. Pellets of improved strength for moving bed operations can be prepared from ADU by adding concentrated uranyl nitrate solution to the wet paste prepared for pelleting. Laboratory results indicated that the most suitable pellets were produced when the uranium ratio between uranyl nitrate solution and ADU was about one to ten.
2. UO_2 pellets have been prepared from ADU and ADU-uranyl nitrate mixtures at the high reduction temperature of 1700°F . These pellets hydrofluorinate at 1100°F at rates much greater than those observed with UO_2 pellets prepared from hydrated pot-denitrated orange oxide.

12.4 PREPARATION OF ACTIVE UO_2 FROM UF_6 - S. L. Reese, W. E. Palmer, and J. Blasdel

Uranium dioxide is being used for fuel elements in certain nuclear reactors. Much of the reactor requirements are for UO_2 enriched in U^{235} content, and all enriched uranium is initially available in the form of UF_6 .

The standard method of converting the UF_6 to UO_2 is to reduce the UF_6 to UF_4 with hydrogen and to pyrohydrolyze the UF_4 with steam to UO_2 .

The UF_6 can also be converted to UO_2 by reaction of UF_6 gas with steam to produce UO_2F_2 , followed by hydrogen reduction of UO_2F_2 to UO_2 . The UO_2F_2 produced by this process is extremely fine and of low density. Since the surface area of the UO_2F_2 is so great, it should lend itself to almost instantaneous reaction with hydrogen at the proper temperature¹ and should produce UO_2 in a sub-fluidized vertical tube reactor. It is thought that this method will give a purer product and will be cheaper, particularly with slightly enriched UO_2 . In addition, the physical characteristics of the UO_2 might prove to be more advantageous for making reactor fuel elements. A study of this process is being made. A goal is to reduce fluoride content of the UO_2 to 200 ppm.

Summary

The conversion of UF_6 to UO_2F_2 with steam in the UF_6 reduction reactor was found to proceed well at 400°F .

Feeding UO_2F_2 into a 2-inch-diameter by 5-foot-long vertical tube, with preheated hydrogen moving countercurrently, required three passes to produce 98.6 per cent UO_2 . The optimum reactor temperature was determined to be 1400°F .

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¹ Votaw, J. W., Briggs, G. G., DeMarco, R. E., Richards, D. E., Abbott, R. C., and Bonfer, D. C., Summary Tech. Rpt., pp. 55-57, NLCO-625, April 16, 1956.

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Equipment and Method - Production of UO_2F_2

Three lots of UO_2F_2 were processed. One of these was made in the 10-inch-diameter UF_6 to UF_4 reactor¹ with a UF_6 feed rate of three pounds per minute. The steam and UF_6 were fed into nozzles in the top flange of the 17-foot vertical reactor tube, and the UO_2F_2 product fell into a hopper at the bottom of the tank. An excess (about 0.5 lb/min H_2O) of superheated steam at 350°F was introduced with the UF_6 , and light, fluffy, very fine powder was produced. Two small lots were made by the same method in a 5-inch-diameter 6-foot-long vertical tube, except that the flow of UF_6 was about 0.25 lb/min. In one run, the product hopper was cool enough to condense moisture, permitting the particles to cement into larger granules of dense material. The UO_2F_2 has a tendency to be carried off in the off gas because of its low density and must be collected by the off gas cyclone.

Equipment, Method, and Results - Hydrogen Reduction of UO_2F_2

The reaction, $\text{UO}_2\text{F}_2 + \text{H}_2 \longrightarrow \text{UO}_2 + 2\text{HF}$, was carried out in a 2-inch-diameter by 5-foot-long vertical reactor. The UO_2F_2 was fed into the top onto one or more screens to break up the soft agglomerates and spread the powder. The reactor was vibrated to facilitate passage of the powder, which fell at the rate of about two pounds per hour. When more than one screen was used, a small quantity of UF_4 was formed on the upper screen as a result of extended exposure to the HF product from the reaction occurring lower in the tube.

Initially, oxygen was burned in an excess of hydrogen to supply heat and to give steam and hydrogen at 1300° to 1600°F as reactants. The steam was intended to pyrohydrolyze any UF_4 formed from the product HF. This technique was not satisfactory, the product being a mixture of UO_2 and U_3O_8 .

In recent runs, external heat was applied, and preheated hydrogen was moved countercurrently to the falling UO_2F_2 . The fluffy UO_2F_2 was converted to 78.25 per cent UO_2 in one pass, to 96.8 per cent in two passes, and to 98.59 per cent in three passes. The fluoride content was found to be 0.08 per cent in the three-pass products.

A study of reactor temperature indicated 1400°F to be near the optimum, as shown in Table 12.4-1.

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¹ Reese, S. L. and Palmer, W. E., Summary Tech. Rpt., Vol I, pp. 39, 40, NLCO-600, January 16, 1956.

~~CONFIDENTIAL~~TABLE 12.4-1**RELATIONSHIP OF U_3O_8 AND FLUORIDE
CONTENT TO REACTOR TEMPERATURE**

Reactor Temperature (°F)	U_3O_8 (%)	F (%)
1500	0.75	0.07
1400	0.24	0.08
1300	0.36	0.11
1200	3.03	0.21
1100	7.70	3.40

Reactor design and UF_4 formation are problems requiring further study.

**12.5 HIGH-FREQUENCY HEATING OF URANIUM COMPOUNDS – F. M. Teetzel and
J. F. Schonberger**

Many of the production processes and laboratory tests carried out at National Lead Company of Ohio require the heating of uranium compounds in powder form. UO_3 , UO_2 , and UF_4 must all be heated at various times to carry out reactions or make certain tests. Under present procedures, the powders are placed in containers and the containers are heated externally. The powders are subsequently heated by thermal conduction through the walls of the containers and through the powders. The thermal conductivity of uranium powders is very poor; therefore, this system is inefficient, and time-consuming and produces large thermal gradients through the powder. A method of heating uranium powders more rapidly, with temperatures uniform throughout the powder, is desired.

Dielectric heaters (high-frequency heaters) have been used to advantage in industries such as plastics, wood, rubber, and foundry where it is required that materials with poor thermal and electrical properties be heated. The possibility therefore existed that this technique could improve several of the processes at National Lead Company of Ohio.

It was not feasible to approach the problem theoretically because of the lack of knowledge of the physical constants of the powders.

Samples of UO_2 and UO_3 were taken to the laboratory of the Girdler Company, in Louisville, Kentucky, where tests were performed on the material in one of their dielectric heaters. The unit in which the tests were conducted was capable of delivering 7.5 kilowatts of power at a frequency of 16 megacycles with about 16 kilovolts between electrodes. The electrodes were approximately 16 inches square, and the spacing between electrodes was variable so that loads of different sizes could be accommodated.

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Standard procedure for the tests was to put a sample of powder in a Pyrex beaker or in a Vycor evaporating dish and to place it between the electrodes. The power was turned on for a preset interval of time, usually three minutes, and then was turned off automatically. The temperature of the powder bed was measured by probing through the powder with a very small pencil-type thermocouple. During this period, the sample was cooling off, of course, but this was not considered critical in these tests. After the temperature was measured, the sample was replaced between the electrodes and the procedure was repeated.

The tests performed were brief and of an exploratory nature, and so only the following generalized conclusions will be drawn:

1. UO_3 and UO_2 can be heated to temperatures in excess of 800°F by the use of a dielectric heater. 800°F was the limit of the pyrometer. Therefore, no higher temperatures can be quoted, although a sample of UO_3 was heated to red heat.
2. With a properly designed container, the heat generated in the bed of powder is evenly distributed through the bed, and any temperature gradient through the bed is dependent upon the radiant heat lost from the bed.
3. The rate at which a sample of powder can be heated appears to be much higher than the rate obtained by the use of conventional methods.
4. UO_3 apparently undergoes a transformation at a temperature of about 800°F which so alters its electrical properties as to make it a semi-conductor rather than a nonconductor above this temperature.
5. The sample of UO_2 tested gave indications of being a semi-conductor at all temperatures.
6. The rate of temperature rise of UO_3 increased with increasing temperatures.

More work would be required in order to ascertain the limits of usefulness and the practical applications of this heating technique, but, based upon the results of the original tests, the system offers promise of being a great improvement over present methods of heating uranium powder.

12.6 EVALUATION OF THE REACTIVITY TRAIN AS A DEVELOPMENT TOOL -

W. C. Manser, M. D. Snyder, and K. J. Notz

A program has been initiated to investigate, on a laboratory scale, the effect of pot denitration conditions on the "reactivity" of the resultant orange oxides towards hydrogen reduction and hydrofluorination. The work here reported was conducted to determine the feasibility of using a "reactivity" train test to characterize various pot products, with the intention of using this test as a screening procedure in order to reduce the number of samples which are to undergo a complete physical and chemical analysis. Two existing testing trains were modified to permit hydrogen reduction and hydrofluorination under controlled temperatures and gas flow rates. This work was directed toward a high (ca 97%) degree of conversion to green salt, since previous efforts had shown inadequacies in a low (ca 85%) conversion level test.

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Equipment

The apparatus is essentially the same as that described and previously reported.¹ The two reactivity trains each consist of a monel reaction tube 20 inches long and having a 1.5-inch ID. It is mounted horizontally in an electrically heated tube furnace. One end of the tube has a flanged cover to allow insertion of the sample boat. The sample boat is made of monel and is divided into four sample compartments. A hole drilled into one end of the boat permits insertion of the thermocouple well. The equipment is designed so that quantities of nitrogen, hydrogen, and anhydrous hydrogen fluoride, measured by a rotameter, can be passed through a preheater and preheated lines into the reaction tube. The temperature is measured by a chromel-alumel thermocouple and can be controlled within $\pm 20^\circ\text{F}$.

Procedure

Three grams of UO_3 are weighed into each section of the sample boat, giving a sample bed depth of about three millimeters. If two samples are to be treated simultaneously for comparison purposes, they are placed in diagonally opposite compartments. It has been noted that there is a variation in degree of conversion between compartments. The two front compartments (those first exposed to the gas flow) react more completely than do the rear two, and there is an unpredictable variation between the left and right compartments. By combining the samples placed in diagonally opposite compartments, these differences are minimized.

The boat is sealed into the reaction tube and the reaction tube is purged with nitrogen for five minutes, during which time the heaters are turned on. The nitrogen is then replaced by hydrogen and the controller is set for the desired temperature. When the desired temperature is reached, reduction is continued for the specific time. At the end of the reduction period, the temperature is adjusted to the subsequent hydrofluorination temperature. The hydrogen is then replaced by anhydrous hydrogen fluoride and maintained for the desired time. After hydrofluorination, the anhydrous hydrogen fluoride is replaced with hydrogen and the heaters are turned off. The furnace is opened, and the reaction tube is cooled with an external stream of compressed air. When the temperature has dropped below 400°F , the hydrogen atmosphere is replaced with nitrogen and cooling is continued to room temperature.

The sample is removed and ground in an agate mortar. The product is then analyzed for ammonium oxalate insoluble (AOI). AOI is a measure of the uranium oxide content of the green salt.

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¹ Briggs, G. G., Fetner, C. J., and Maddox, R. L., *Summary Tech. Rpt.*, p. 75, NLCO-565, July 15, 1955.

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Selection of Reduction Conditions

It was desired to select the conditions which gave at least 99 per cent reduction with as low a temperature and as short a time as possible. (High-temperature reduction has been investigated and is reported in Section 12.7 of this report.) The degree of reduction was determined after hydrofluorination by analyzing the final product (a mixture of UF_4 , UO_2 and UO_2F_2) for total uranium and U^{+4} . The difference is U^{+6} , which is present as UO_2F_2 (the UO_2F_2 resulting from hydrofluorination of unreduced UO_3). Reductions for 60 minutes at 1200 F gave the desired per cent conversion, and these conditions were therefore adopted as standard reduction conditions for all future hydrofluorination runs. The results of these tests are given in Table 12.6-1.

TABLE 12.6-1

EFFECT OF TIME ON REDUCTION OF UO_3 *

Run No.	Reduction		UO_2F_2 ** (%)	Average (%)
	Time (min)	Temp (°F)		
31	45	1200	1.01	—
32	45	1200	1.32	—
34	60	1200	0.23	0.37 ± 0.29
35	60	1200	0.32	
36	60	1200	0.48	
38	60	1200	0.52	
40	60	1200	0.80	
41	60	1200	0.56	
42	60	1200	0.50	
43	60	1200	0.30	
44	60	1200	0.22	
37	70	1200	0.36	—
39	90	1200	0.22	—

* National Lead Company of Ohio nonsulfated, Lot 3E-16-1027.

** % UO_2F_2 = 1.294 (% total U - % U^{+4}).

Selection of Hydrofluorination Conditions

Table 12.6-2 lists the results of tests conducted to determine the optimum temperature and the approximate time needed to effect a high level of conversion to UF_4 . On the basis of these runs, 1100°F was selected as the standard hydrofluorination temperature.

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TABLE 12.6-2

EFFECT OF TIME AND TEMPERATURE ON THE
HYDROFLUORINATION OF UO_2^*

Run No.	Hydrofluorination		Conversion to UF_4^{**} (%)
	Time(min)	Temp ($^{\circ}\text{F}$)	
36	130	900	92.09
31	60	1000	93.19
32	60	1000	90.89
34	70	1000	94.82
35	130	1000	97.00
41	110	1100	98.24
37	190	1100	98.98
54	180	1100	98.49
55	180	1100	98.48
38	120	1200	97.61
39	120	1200	98.12
42	180	1200	98.28
44	60	1300	96.02
43	90	1300	99.15
45	90	1300	96.39
46	120	1300	97.14
47	120	1300	97.18
40	120	1300	99.15

* National Lead Company of Ohio nonsulfated UO_3 (Lot 3E-16-1027)
reduced under standard conditions (60 minutes at 1200°F).

** $\% \text{UF}_4 = 1.319 [\% \text{U}^{+4} - (0.8815 \times \% \text{AOI})]$

Absolute Precision

Table 12.6-3 gives the reproducibility obtained for each of the reactivity trains. These trains were designed and constructed to be similar in every detail. The gas flow and temperature control were calibrated and adjusted as nearly as possible to be identical. However, small variations in the flow rate of the reactant gases and temperatures may have caused some of the differences in the per cent conversion on replicate runs.

The precision of the reactivity trains was determined by making six replicate runs on one train and seven runs on the other train, using National Lead Company of Ohio nonsulfated UO_3 (Lot 3E-16-1027) under standard reduction conditions (60 minutes at 1200°F) and hydrofluorination for 180 minutes at 1100°F .

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TABLE 12.6-3

PRECISION OF THE TWO REACTIVITY TRAINS UNDER TEST CONDITIONS*

Left Reactivity Train			Right Reactivity Train		
Run No.	AOI (%)	AOS** (%)	Run No.	AOI (%)	AOS** (%)
54	0.99	99.01	55	1.20	98.80
59	0.68	99.32	56	1.19	98.81
61	0.94	99.06	58	0.90	99.10
63	0.75	99.25	60	0.92	99.08
65	0.17	99.83	62	1.01	98.99
67	1.14	98.86	64	0.77	99.23
			66	0.80	99.20
Avg	0.78	99.22		0.97	99.03
Standard Deviation	± 0.31	± 0.31		± 0.16	± 0.16
Limit of Error at 95% Confidence Level	± 0.61	± 0.61		± 0.31	± 0.31
% Limit of Error at 95% Confidence Level	± 78.2	± 0.6		± 32.0	± 0.3

* Reduction: 60 minutes at 1200° F. Hydrofluorination: 180 minutes at 1100° F.

** % AOS = 100 - % AOI.

As shown in Table 12.6-3, the limit of error on the reactivity trains, based on the per cent ammonium oxalate insoluble, varies widely. However, if the precision is determined on the per cent AOS basis, the limit of error is ± 0.3 to ± 0.6 per cent at the 95 per cent confidence level.

Reactivity Ratios

Table 12.6-4 lists reactivity ratios calculated in two ways: AOI basis and AOS basis. It is apparent that the AOI-basis ratios reflect the poor reproducibility of the degree of conversion. On the other hand, AOS-basis ratios tend to minimize real differences between samples. The precision of AOI-basis ratios could probably be improved by hydrofluorinating to a greater per cent conversion. This, however, is undesirable, because any real differences existing between samples become smaller as conversion approaches 100 per cent. Sensitivity of AOS-basis ratios could be increased by converting to a lesser degree, such as 80 or 90 per cent, but such a figure would be valueless, since conversion curves may cross each other. This is shown in Figure 12.6-1. Table 12.6-4 also indicates the "cross-over", in that the reactivity ratio changes from >1 to <1 as hydrofluorination time is increased from 90 minutes to 180 minutes. This shows that only meager information is supplied by a reactivity train test.

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TABLE 12.6-4

**COMPARISON OF AOI RATIOS AND AOS RATIOS USING NATIONAL LEAD
COMPANY OF OHIO SULFATED (S) AND NONSULFATED (NS) ORANGE OXIDES**

Run No.	HF Time (min)	AOI(S) (%)	AOI(NS)	$\frac{AOI(NS)}{AOI(S)}$	$\frac{AOS(S)}{AOS(NS)}$
85	90	1.38	2.67	1.93	1.01
86	90	3.12	4.37	1.40	1.01
89	90	2.43	4.04	1.66	1.02
92	90	3.03	4.49	1.48	1.02
93	90	1.84	2.81	1.53	1.01
Avg		2.36	3.68	1.56	1.01
Std. Deviation		±0.68	±1.08	±0.20	±0.006
95% Conf. Level		±1.33	±2.12	±0.39	±0.01
83	120	1.37	1.63	1.19	1.00
84	120	1.80	2.77	1.54	1.01
87	120	1.29	1.43	1.11	1.00
88	120	1.79	2.27	1.27	1.00
94	120	1.80	1.61	0.89	1.00
95	120	2.14	1.69	0.79	1.00
96	120	1.44	0.70	0.49	0.99
98	120	1.46	1.22	0.84	1.00
Avg		1.63	1.67	1.02	1.00
Std. Deviation		±0.27	±0.59	±0.31	±0.005
95% Conf. Level		±0.53	±1.16	±0.61	±0.01
76	180	1.24	0.48	0.39	0.99
80	180	1.34	0.69	0.51	0.99
81	180	0.98	0.48	0.48	0.99
82	180	1.34	1.09	0.81	1.00
Avg		1.23	0.69	0.56	0.99
Std Deviation		±0.14	±0.24	±0.16	±0.005
95% Conf. Level		±0.27	±0.47	±0.31	±0.01

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FIGURE 12.6-1 Effect of Hydrofluorination Time on AOI Content

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12.7 ULTRASONIC VELOCITY MEASUREMENT IN URANIUM METAL — P. R. Morris

The objective of this study is to develop a method for determining preferred orientation in uranium metal.

Hanford observers have reported a variation in resonant frequency that is associated with changes in average elastic moduli resulting from different types and degrees of preferred orientation. Where a large volume of material is to be examined on a "go-no go" basis, the measurement of the velocity of propagation of an ultrasonic pulse as a means of separating materials having differences in preferred orientation seems to offer certain advantages over resonance techniques.

In the design of an instrument for the separation of materials having differences in velocity of propagation, two considerations limit the choice of frequency to the range, 1 to 5 megacycles:

1. The accuracy of measurement increases with frequency.
2. The upper frequency limit is determined by the inability to transmit through large-grained (beta heat treated) uranium at the higher frequencies (greater than 5 megacycles).

Methods based on the use of a quartz crystal oscillator as a standard have been used by many investigators. The elapsed time between transmitted and received pulses is measured by counting the number of oscillations of the standard in the interval. In this method, the pulse generator is triggered by a signal obtained from the standard, so that the transmitted pulse may be used to start an oscilloscope sweep. Signals from the standard and from the receiver are viewed on the scope, which permits counting the number of oscillations of the standard between transmitted and received pulse. If this method were to be adapted to an automatic machine, the number of pulses produced by the standard would have to be counted by a scaler, which would be shut off at the end of the interval. The error in gating is ± 1 count. To achieve an accuracy of ± 0.1 microsecond, a 10-megacycle standard and scalars which could handle this counting rate would be required. The scaler would also have to be preset and be able to handle about 1000 counts. The circuitry of such a unit would weigh heavily against this method so it was not pursued.

The method selected involves shock excitation of the transmitting crystal and measurement of the time of arrival of the lead edge of the received pulse. An electrical delay line is used as a standard. Measurements of velocity are comparative, not absolute. The equipment consists of a pulse generator and amplifier, an electrical delay line, transmitting and receiving crystals, a water bath, a preamplifier and amplifier, a pulse width discriminating network, two flip-flops, a cathode ray oscilloscope, and necessary power supplies. The use of parallel resonant tank circuits has been avoided in an effort to secure a minimum rise time for the leading edge of the pulse. The output stage which drives the transmitting crystal has a load resistor of 450 ohms. This provides electrical damping for the transmitting crystal and assures a fast rise time. The transmitted pulse is simultaneously impressed on the delay line. At a time slightly preceding the received pulse, the signal from the delay line is used to reset one of the flip-flops and to trigger the oscilloscope sweep.

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The received signal is amplified, used to fire the flip-flop, and presented on the oscilloscope. The signal from the flip-flop is fed into a resistor-capacitor pulse-width discriminating network. The output of this network is used to fire a second flip-flop which can be reset manually. This second flip-flop provides the reject signal.

The time of transit through a beta heat treated 8-inch slug at room temperature is approximately 64 microseconds. The transit time through an alpha rolled slug is approximately 1.5 microseconds longer. These figures are in close agreement with values obtained by resonance measurements, indicating that there is probably negligible velocity dispersion (variation with frequency) over the range, 7000 cycles to greater than one megacycle.

In practice, the time between reset and fire of the first flip-flop is adjusted to 1.5 microseconds for a standard beta heat treated slug. The transit time through slug and water bath is about 80 microseconds. The output of the first flip-flop is then a 1.5-microsecond pulse for the beta treated standard and a 3.0-microsecond pulse for an alpha rolled standard. The instrument had a precision of approximately 0.3 microsecond (± 0.15 microsecond).

The transmitter puts out a 400-volt rectangular pulse of 1-microsecond duration having a 0.1-microsecond rise time. The preamplifier and amplifier taken together have a gain of 10,000 and a rise time of 0.15 microsecond for a 750-microvolt input pulse having a 0.03-microsecond rise time. Type 6AK5 pentodes are used in the flip-flops to obtain reset and fire times of less than 0.05 microsecond. The oscilloscope provides a five-microsecond triggered linear sweep and is used to position and align the crystals. A 2.25-megacycle crystal is used as a transmitter and a 1-megacycle crystal as a receiver. Using frequency-staggered crystals seems to improve the rise time of the unit.

In preliminary tests, results obtained with the instrument have been in close agreement with "Sonotest" results. (The Sonotest is the instrument presently used at Hanford and the National Lead Company of Ohio to distinguish structures.)

In future work this instrument will be evaluated by testing partially transformed material.

Acknowledgment

The author is indebted to V. Morton for his aid in constructing the equipment.

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12.8 WEIGHT RECORDER - J. A. Williamson

Data obtained manually from a thermobalance¹ often contain (1) errors caused by balance fluctuations and (2) timing errors which can not be compensated, since with manual operation, the amount of fluctuation or time error involved is not known. By continuous recording of the weight change, timing errors are minimized and balance fluctuations are actually recorded. Thus, a representative smooth curve of the actual weight change can be drawn through the recorded trace. Continuous recording also shows any sudden rate of weight changes (such as phase changes) which might be missed by manual data-taking methods.

The Mettler "Gram-atic" analytical balance on the thermobalance (Fig. 12.8-1) was modified so that a linear variable differential transformer (LVDT) could be used to continuously detect the balance beam position. The LVDT was mounted inside the weighing compartment of the balance on a Lucite stand which straddles the balance pan. The core of the LVDT was suspended from a hook at the top of the bridle of the balance pan. The top of the Lucite stand was made adjustable so that the relative position of the LVDT and its core can be varied. This allows the recorder to be zeroed with the balance at zero milligrams position. Since 100 milligrams of the balance reading is obtained by optical projection of the beam position, the output of the LVDT as the core rises and falls is proportional to the optical part of the balance reading.

Since interaction of the LVDT and the core produces a magnetic downward pull on the balance pan which is proportional to the voltage output of the transformer, the span of the projected scale of the balance is decreased. In order to increase the projected scale span to its original value of 100 milligrams, larger balance "sensitivity adjusting weights" were substituted and adjusted to the proper position.

The output of the LVDT is fed to an A. C. recorder which can be calibrated directly over a 100-milligram range. The recorder used is a Brown Instrument Company strip chart recorder which was modified by the Schaevitz Engineering Co.² to incorporate their Type 60 AD-3 amplifier and Type 100S-L LVDT. The LVDT is used as the recorder balancing element. A micrometer screw positions the core of the recorder LVDT. The core is driven by the balancing motor through the pen drive cable. With the input leads of the recorder shorted together, the system becomes a null-seeking system in which the pen balancing motor drives the core to a position representing the electrical center or null position. The recorder balancing LVDT can be zeroed by means of a zero shifter knob extending below it. This moves the core with respect to the LVDT. With the input leads of the recorder connected to the secondary or output of the measuring LVDT mounted in the balance, the system now becomes a null balance system in which the recorder balancing LVDT core moves in accordance with that of the measuring LVDT. The ratio of the movement of the two LVDT cores is dependent upon the position of the "pen sensitivity" potentiometer mounted in the amplifier.

¹ Williamson, J. A., *Summary Tech. Rpt., Vol. II, pp. 68-70, NLCO-601, January 16, 1956.*

² Schaevitz Engineering Co., Camden, New Jersey, *Operating Instructions Schaevitz Recorder System, Serial No. 12-54-1.*

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FIGURE 12.8-1 Thermobalance, Prior to Installation of Differential Transformer and Lucite Stand.

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The pen sensitivity is used to calibrate the recorder at the full-scale point desired. As the pen sensitivity is increased, the gain of the recorder amplifier should also be increased. The gain control is adjusted to the maximum value possible which does not result in hunting or oscillating of the pen.

The weight recorder has performed satisfactorily. Data obtained with this unit may be found in a recent quarterly report.¹ The system is linear within ± 0.5 milligram at any point in the 100-milligram range and has held its calibration point over a two-month period.

The limit of 100 milligrams for the scale range is a limit imposed by the balance used. The scale range could be altered by selecting a balance having the proper projection range.

12.9 CENTRIFUGAL CASTING OF HOLLOW FUEL PIECES - E. B. Blasch and J. C. Straub

Recent cost estimates for producing two sizes of hollow fuel pieces by three routes - rolling-drilling, extrusion, and centrifugal casting - showed an economic advantage for the centrifugal casting route. This route has the advantage of a higher net metal yield from charge to finished slug and would eliminate primary fabrication facilities.

Centrifugal casting is performed at National Lead Company of Ohio in a pilot-scale casting machine. The top portion of the casting machine consists of a furnace; below it is the mold chamber, and at the bottom are the drive shaft and motor. An induction coil is used to melt the uranium charge in the furnace (which is maintained at a pressure of about 10 microns). When pour temperature is reached (as determined by means of an optical pyrometer), a stopper rod is raised and the molten uranium pours into a rotating mold which is also under vacuum. The metal is driven into the mold cavities by centrifugal force. For the casting of hollow fuel pieces, there is a core in each mold cavity. The core is supported at both ends. Figure 12.9-1 shows the mold used in this work, with the cope removed to show the gating pattern.

For hollow castings to be suitable as fuel elements, the concentricity of the hole with the outside circumference must be kept within close tolerances. In the past, hollow castings² have been centrifugally cast to moderately close dimensional tolerances (0.010 to 0.015). The ultimate objective of this work is to cast a piece having a concentricity between its OD and ID of less than 0.005 inch and thus to minimize machining.

In an attempt to cast a "precision hollow" fuel element, several heats were run. The concentricity of the castings from two heats were evaluated. Results show that at the end of the casting nearest the mold periphery the eccentricity varied from less than 0.001 inch to 0.007 inch, with an average

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¹ Notz, K. J. *Summary Tech. Rpt.*, pp. 33-39, NLCO-640, July 18, 1956.

² Blasch, E. B., Straub, J. C., and Guay, A. E., *Summary Tech. Rpt.*, pp. 129-137, NLCO-625, April 16, 1956.

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FIGURE 12.9-1 Mold Setup for Hollow Slug Production, Showing Gating and Core Support. Cope Half has been Removed.

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of 0.004 inch. The gate end of the castings, however, showed a greater variation, the average being 0.015 inch and the range 0.005 inch to 0.034 inch. This was probably caused by movement of the cope ring during pouring. Work is in progress to eliminate this movement.

Future investigations will include studies of alternative sleeve materials and process variables for the purpose of achieving a more consistent product. A large production type unit capable of casting larger quantities of metal is being designed.

12.10 PREPARATION OF URANIUM SHOT – H. A. Kraus and S. L. Reese

The interest in using uranium shot in "matrix" compositions with immiscible metals inspired a program to develop a process whereby experimental quantities of shot may be produced. Also, there is an interest in shot (1) in paste fuel experiments, (2) as matrix shielding, and (3) as a possible alloying component in arc-melting. The several methods of producing shot which have been evaluated were reported in recent quarterly reports.^{1,2} The runs were carried out in the existing Pilot Plant vacuum induction furnace.

The spinning disk method has given the best yields of nearly spherical shot. In this method, the molten uranium is bottom-poured onto a spinning refractory disk in an atmosphere of helium gas. The yields with the present equipment have been low because the horizontal free travel of shot is only 17 inches and a large part of the shot does not have sufficient time to solidify before it reaches the furnace wall. Even with this limitation, yields of shot have been as high as 70 per cent. To overcome this limitation, a large vacuum tank (Fig. 12.10-1) was designed and fabricated for the specific purpose of making shot. During the past quarter, the large shot tank was completed. The free travel of shot in this new unit will be approximately six feet. This unit will be available for the production of experimental or semi-production quantities of shot as needed. It should be readily adaptable for the production of enriched or alloyed shot. With the new tank, yields of over 90 per cent usable shot from the metal charged can reasonably be expected.

The experimental runs³ made with the Pilot Plant vacuum induction furnace prove that the shot size is inversely proportional to the disk peripheral speed. An eight-inch-diameter disk at 1000 rpm yielded 61 per cent 10 to 30-mesh shot. At 1400 rpm, 70 per cent of the shot produced was in the 20 to 40-mesh range. When the disk speed was increased to 1800 rpm, over 60 per cent was in the size range of 40 to 60-mesh.

A series of runs in which the disk speed will be varied from a few hundred rpm to more than ten thousand rpm are planned for the new shot tank. From the information obtained, a curve showing the relationship of disk speed to particle size will be drawn. Results obtained to date indicate that this may approximate a straight-line relationship.

1 Kraus, H. A. and Reese, S. L., *Summary Tech. Rpt.*, pp. 137-144, NLCO-625, April 16, 1956.

2 Kraus, H. A. and Reese, S. L., *Summary Tech. Rpt.*, pp. 109-110, NLCO-640, July 18, 1956.

3 *ibid.*

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FIGURE 12.10-1 Shot Tank. The Furnace is Shown on the Top of the Tank. A Manhole in the Side of the Tank not Shown Allows Access to the Disk and Motor Assembly. A Flanged Opening at the Bottom of the Tank Allows Removal of the Shot.

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FIGURE 12.10-2 Etched Cross Sections of Typical Shot (10X)

The physical characteristics of the shot are as follows: The surface has a metallic luster with very little evidence of oxidation. Particles are nearly spherical. Some of the shot have small center cavities (Fig. 12.10-2), although this effect is too small to show up when the over-all true density of the shot is compared with that of solid uranium. The bulk density of the shot averages approximately 11.6 g/cc (which is 61 per cent of the true density of the individual shot particles).

Chemically, the shot retains the properties of the original metal. Spectrographic analyses show no pick-up of impurities in the shotting process.

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12.11 THE MEASUREMENT OF DENSITY OF URANIUM METAL BY RADIATION ABSORPTION – J. P. Scheuer and P. R. Morris

Density determinations are currently made by hydrostatic weighing techniques. Samples for this purpose are sawed from uranium ingots prior to fabrication into fuel elements. The principal source of error lies in the sampling process, which fails where the distribution of inclusions and shrinkage cavities in the ingot is of a heterogeneous nature. A nondestructive density determination applicable to finished slugs would have advantages over the ingot density determination. Since ingot defects are elongated during the fabrication process, there is a smaller sampling error when density determinations are made on slugs.

Equipment and Method

An instrument produced by the Ohmart Corporation is used to determine slug density¹ by measurement of the intensity of radiation passing through the slug. This is the first evaluation of the precision and bias of this instrument.

A full-scale meter deflection of 3×10^{-12} ampere indicates a density of 19.00 grams per cubic centimeter, while zero deflection represents a density of 18.70. Standard slugs having densities of 18.71 and 18.93 grams per cubic centimeter, as determined by hydrostatic weighing, are used to set the zero and gain of the micro-microammeter to read 0.1×10^{-12} ampere and 2.3×10^{-12} ampere, respectively.

After the instrument has been standardized with the two slugs provided, the density of an unknown slug is determined by placing the slug in the test fixture and noting the deflection on the micro-microammeter. Each 1×10^{-12} ampere deflection represents an increment of 0.1 gram per cubic centimeter. The density increment obtained in this manner is added to 18.70 grams per cubic centimeter, and the result is corrected for the diameter² of the piece being measured.

Two hundred and ninety-four slugs were tested by this method, and the results were compared with those obtained by hydrostatic weighing of the whole slug.

Data

A plot of frequency versus density (Fig. 12.11-1) shows the density distribution (as determined by hydrostatic weighing) of the 294 slugs tested. The Ohmart density determination, corrected for diameter effect, averaged 0.0046 gram per cubic centimeter higher than those obtained by hydrostatic weighing of the slug. The 95 per cent confidence interval on this bias is 0.0046 ± 0.0028 gram per cubic centimeter. The 95 per cent confidence limit on the reproducibility of an individual determination

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1 Polson, C. E. and Scheuer, J. P., Summary Tech. Rpt., pp. 62-72, FMPC-437, July 15, 1954.

2 Hesselbrock, H. W. and Scheuer, J. P., Summary Tech. Rpt., Vol II, pp. 51-54, NLCO-601, January 16, 1956.

FIGURE 12.11-1 Frequency Distribution of Slug Densities (Hydrostatic Weighing Method)

(precision) with the Ohmart instrument is ± 0.037 gram per cubic centimeter. By comparison, the 95 per cent confidence limit on the reproducibility of an individual determination for the method of hydrostatic weighing applied to a whole slug is ± 0.008 gram per cubic centimeter.

Sources of Error

The instrument has a tendency to drift in humid weather, necessitating frequent standardization, sometimes at less than 1/2-hour intervals. At times, the drift has been so great as to prevent use of the instrument. This drift is thought to be associated with contact potentials and leakage paths in connectors.

If a density change of 0.30 gram per cubic centimeter produces a change of 3×10^{-12} ampere, and if the cell output may be assumed to be a linear function of the radiation striking the cell, then for the balanced condition, the output of each cell is approximately 2×10^{-10} ampere. The open circuit voltage of the cell is of the order of 1.5 volts. The cell resistance under these conditions is of the order of 10^{10} ohms.

In extremely humid weather, it is reasonable to expect connector leakage resistances on the order of 10^8 ohms. The order of magnitude of this effect has been verified by experiment. The leakage resistance of the Type 21-467 cable is approximately 3×10^{-13} ohm-ft, so that the effects of cable leakage may be neglected.

The most likely source of trouble lies in differences in work function between the elements of a connector and the leakage path between these elements. Such a difference constitutes a source of electromotive force whose internal resistance is equal to the leakage resistance. A potential difference of 5×10^{-5} volt with a leakage resistance of 10^8 ohms would result in a current of 5×10^{-13} ampere. The magnitude of these effects lies well within the realm of possibility and would serve to explain the observed errors.

Future Work

Evacuated connectors are being designed in an effort to reduce surface leakage associated with high humidity. Introduction of these connectors is expected to improve the stability of the instrument.

Acknowledgments

The authors are indebted to H. W. Hesselbrock for his help in obtaining the data, and to G. F. Jennings and A. Church for analysis of the data.

13. ANALYTICAL DEPARTMENT - "WET CHEMICAL" DEVELOPMENT

13.1 STUDIES ON BLOCKSON URANOUS PHOSPHATE - D. Valent and B. Gessiness

Samples of Blockson Uranous Phosphate have been received during the past quarter for assay. The analysis was made by the standard volumetric procedure employed by the National Lead Company of Ohio Ores Laboratory. No difficulties were encountered in the assay of this material.

Determination of Moisture Loss Values

It is interesting to note that loss values obtained by the New Brunswick Laboratory (NBL) at 110°C for phosphate materials follow a similar pattern to those obtained by this laboratory, compared with daily fluctuations in relative humidity.

Figure 13.1-1 indicates the loss pattern obtained at NBL for two typical lots of Blockson Uranous Phosphate in an uncontrolled atmosphere.

Figure 13.1-2 represents the fluctuation of a sample of Texas City Phosphate Concentrate in the uncontrolled atmosphere of the National Lead Company of Ohio laboratory versus an air-conditioned laboratory. Note the higher loss values obtained and the appreciable fluctuation in relative humidity in the air-conditioned laboratory.

Figure 13.1-3 represents the loss patterns (for a sample of Blockson Uranous Phosphate) obtained at National Lead Company of Ohio in an uncontrolled atmosphere and in a dry argon atmosphere at near-zero humidity. Note that the loss values obtained in the argon atmosphere become stabilized after ten days of drying, whereas in the uncontrolled atmosphere the fluctuations appear to be endless.

The observations made by NBL coincide with those observed at National Lead Company of Ohio - namely, that the routine drying procedure is inadequate for the attainment of equilibrium moisture values for phosphate materials.

Ignition Studies

Studies on the behavior of Blockson Uranous Phosphate were made in order to determine its hygroscopicity at elevated temperatures. The analysis of the particular sample chosen for this study is shown in Table 13.1-1:

FIGURE 13.1-1 Blockson Uranous Phosphate: Loss at 110°C and Relative Humidity; Comparison of Two Lots in an Uncontrolled Atmosphere at the New Brunswick Laboratory

FIGURE 13.1-2 Texas City Phosphate Concentrate: Loss at 110°C and Relative Humidity; Comparison of Routine Procedure and Drying in an Air-Conditioned Laboratory

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FIGURE 13.1-3 Blockson Uranous Phosphate: Loss at 110°C and Relative Humidity;
Comparison of Routine Procedure and Dry Argon Atmosphere

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TABLE 13.1-1

ANALYSIS OF BLOCKSON URANOUS PHOSPHATE

	Per Cent
Uranium (Calc as UO_2)	46.4
Loss at 110°C	10.7
Phosphate (Calc as P_2O_5)	21.0
Sodium (Calc as Na_2O)	5.4

The material was ignited at 1000°C (1830°F) and was found to be hygroscopic. Duplicate three-gram samples exhibited a total loss of 14.09 per cent at 1000°C . The material was cooled and weighed after 30-minute periods of ignition; the weight remained constant after 90 minutes of ignition. However, the material gained weight to the extent of 1.85 per cent after a two-hour exposure to the atmosphere. A gain of 6.79 per cent was recorded after an over-night exposure of the samples. Meanwhile, duplicate samples placed in the desiccator as a control showed a total gain in weight of 0.1 milligram (0.003%). When the samples were first removed from the furnace, they appeared to be molten and grey in color. As the sample exposed to the air absorbed moisture, it became yellow, increased in bulk, and finally became powdery. The ignited material dissolved in 10 per cent sulfuric acid as readily as a sample of the material that had not been ignited.

Samples of this material were also ignited at 1200°C (2200°F); at this temperature, the material did not exhibit hygroscopicity. The total loss recorded for three-gram samples was 14.57 per cent. After one hour, the weight of the sample exposed to the air increased 0.7 milligram; the control sample (in the desiccator) gained 0.3 milligram. After 36 hours, a total gain in weight for the exposed samples was 4.7 milligrams (0.16%) and for the control sample it was 0.3 milligram (0.01%). This material too had a molten appearance and was dark grey when removed from the furnace; the exposed sample developed a yellow crust but did not increase in bulk. Furthermore, the sample was difficultly soluble in 10 per cent sulfuric acid. The addition of nitric acid increased the dissolution rate only slightly.

These studies indicate that the hygroscopic nature of the material precludes a precise moisture determination under random, uncontrolled atmospheric conditions. Hence, the assay of this material on an as-received basis, without the application of a correction for moisture loss, should be considered.

13.2 DETERMINATION OF TRACES OF WATER-SOLUBLE OIL IN AQUEOUS SOLUTIONS - R. Prall and E. A. Brown

In a study of the contamination of Refinery feed, a number of aqueous samples were submitted for oil analysis to determine whether or not residues from the metal machining operations were the contaminants. (Texaco C water-soluble oil is used in the metal machining operations in the form of an oil-water emulsion.) Methods for the determination of this oil in aqueous solutions were not available, and a study was undertaken to establish a satisfactory method.

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A modification of the fluorometric method of Benjamin¹ was found to give satisfactory results in the range of 10 to 200 ppm. The method, as employed for oil determinations, is briefly as follows:

1. The oil is extracted with two 25-ml portions of carbon tetrachloride.
2. The combined extracts are evaporated to a volume of 5 to 10 ml, filtered, and adjusted to a volume of 15 ml with the solvent.
3. The fluorescence is measured on the Fisher Nefluoro-Photometer, the No. 425 filter being used as the primary color filter and the No. 530 + being used as the secondary filter. (The filters used were furnished with the instrument.)
4. The concentration of oil in the sample is determined by reference to a calibration curve prepared from oil in carbon tetrachloride standards.

Droplets of oil were observed in samples containing more than 100 ppm of oil, which necessitated that precautions be taken during sampling. The results obtained by carrying aqueous uranyl nitrate and nitric acid through the procedure will be found in Table 13.2-1.

TABLE 13.2-1

**RECOVERY OF OIL FROM URANYL NITRATE-
NITRIC ACID SOLUTIONS***

Standard No.	Oil Added (ppm)	Oil Found (ppm)
1	17	18
2	43	40
3	86	83
4	210	260

* The 0.3N HNO₃ solutions contained 6 g/l U.

Although the method is not specific for water - soluble oil, satisfactory results may be obtained on uranyl nitrate solutions in the range of 10 to 200 ppm.

**13.3 DETERMINATION OF UREA IN URANYL NITRATE SOLUTIONS - B. Hutzelman and
E. Brown**

A study was undertaken to develop a satisfactory method for the determination of urea in uranyl nitrate solutions. This work was part of the exploratory program to use urea as a stripping agent in the solvent extraction process (Sections 3.3 and 3.4 of this report).

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¹ Benjamin, H., *Ind. Eng. Chem., Anal. Ed.*, **16**, 331 (1944).

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Difficulties were encountered with the spectrophotometric method¹ in which p-dimethylamino-benzaldehyde is used as a chromogenic agent. Nitrates were found to interfere with the color development and to give erratic results. The urease method² was not satisfactory because uranium and other heavy metal ions "poison" the conversion of urea to ammonia and carbon dioxide by the enzyme. A quantitative separation of large amounts of uranium from the urea was not practical.

The method of Gertner and Ivekovic³ was found to give satisfactory results on aqueous uranyl nitrate solutions. In this procedure, the urea is oxidized to CO₂ and NH₃ by persulfate. The CO₂ is absorbed on ascarite and weighed. The results obtained on standards containing 100 mg of urea averaged 96.6 per cent recovery. Although the method is not specific for urea, satisfactory results were obtained on purified aqueous uranyl nitrate solutions that were 1 to 8 molar in urea.

13.4 DETERMINATION OF FLUORIDE IN NITRIC ACID - P. Hallbach and E. A. Brown

A modification of the spectrophotometric method⁴ for fluoride has been in use in this laboratory for the determination of microgram concentrations of fluoride in a number of plant materials. The method is normally used after a preliminary separation of the fluoride by the Willard-Winter distillation procedure.⁵ This distillation step separates the fluoride as silica tetrafluoride from a number of interfering anions. However, any nitrates or nitric acid present in the sample accompanies the fluoride in the distillation step and tends to change the relationship. The variations in the absorption curves with changes in the nitrate concentration are shown in Figure 13.4-1. The variations in the calibration curve found with changes in the nitrate content of the sample seriously limit the usefulness of the method.

A satisfactory calibration relationship may be obtained by adding a fixed amount of nitric acid to the fluoride standards. A typical curve obtained by adding fluoride to 10 milliliters of 15.7M nitric acid is given in Figure 13.4-2. The samples, in turn, may be adjusted to the same nitric acid concentration as the standards by the direct addition of fluoride-free nitric acid.

Satisfactory results were obtained by using this modified procedure for the determination of fluoride in nitric acid in the concentration range of 1 to 20 ppm.

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1 Watt, G. W. and Chrisp, J. D., *Anal. Chem.*, **26**, 452 (1954).

2 *Official Methods of Analysis*, Association of Official Agricultural Chemists, p. 372 (1955).

3 Gertner, A. and Ivekovic, H., *Z. Anal. Chem.*, **142**, 36 (1954).

4 Horton, A. D., Thomason, P. F., and Miller, F. J., *Anal. Chem.*, **24**, 548 (1952).

5 Willard, H. H. and Winter, O. B., *Ind. Eng. Chem., Anal. Ed.*, **5**, 7 (1933).

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FIGURE 13.4-1 Effect of Nitric Acid on Fluoride Standards Containing 30 μg Fluoride

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FIGURE 13.4-2 Calibration Curve for Fluoride in Nitric Acid

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13.5 DETERMINATION OF SULFATE IN ORANGE OXIDE – E. Tieman, E. Frank, and B. Gessiness

A method has previously been developed for the determination of sulfate in orange oxide for the range of 100 to 600 micrograms of sulfate per grain sample of UO_3 .¹ The procedure is based on the extraction of the uranium from a 3N nitric acid solution of the sample with a tributyl phosphate - carbon tetrachloride solution and subsequent turbidimetric determination of the sulfate in the aqueous phase.

The current work was initiated to determine whether the sulfate can be determined by this method if the sulfate concentration is less than 100 micrograms. A sample of orange oxide submitted by the Analytical Quality Control group was chosen as a UO_3 standard; a sulfate value was determined by the analysis of numerous five - gram and ten - gram samples of this material. The precision and average "base" value obtained for this sample are shown in Table 13.5-1.

TABLE 13.5-1

**DETERMINATION OF SULFATE VALUE FOR STANDARD
SAMPLE OF ORANGE OXIDE**

Sample Weight (g)	Optical Density*	SO_4 ($\mu\text{g/g}$)
5.0036	0.053	9.3
5.0071	0.056	9.8
5.0039	0.053	9.3
5.0015	0.053	9.3
10.0019	0.099	8.7
10.0015	0.103	9.1
10.0005	0.104	9.2
Average		9.2

* The optical density was measured at a wave length of 375 millimicrons in 5 - cm cells vs a reagent blank.

A stock solution was prepared which contained one gram of the standard orange oxide per 10 milliliters of solution. Varying amounts of a standard sulfate solution were added to 10 - milliliter aliquots of the stock solution, and the total sulfate concentration was determined. The results of this work are summarized in Table 13.5-2.

¹ Gerhardt, E. and Gessiness, B., Summary Tech. Rpt., p. 141, NLCO-577, October 17, 1955.

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TABLE 13.5-2

DETERMINATION OF SULFATE IN SPIKED 10-ml ALIQUOTS
OF STOCK UO_3 SOLUTION

Experiment No.	Optical Density*	SO_4 ($\mu\text{g/g}$)		
		Added to 10 ml Stock Soln	Found	Calculated
1	0.100	72.5	88.0	81.7
2	0.097	72.5	85.4	81.7
3	0.097	72.5	85.4	81.7
4	0.091	67.0	80.1	76.2
5	0.093	67.0	81.8	76.2
6	0.084	67.0	73.9	76.2
7	0.089	67.0	78.3	76.2
8	0.062	43.4	54.6	52.6
9	0.064	43.4	56.3	52.6
10	0.065	43.4	57.2	52.6

* The optical density was measured at a wave length of 375 millimicrons in 5-cm cells vs a reagent blank.

The results indicate that a sulfate concentration as low as 50 micrograms per final volume of 50 milliliters can be determined quite accurately, and that the procedure is dependable for routine use. Furthermore, the precision for concentrations greater than 50 ppm is within the limits usually obtained for turbidimetric work.

An additional improvement has been made in the turbidimetric determination of sulfate in orange oxide. It has been found that the precision of the determination can be greatly increased by back-washing the aqueous extracts with carbon tetrachloride, thereby eliminating droplets of tributyl phosphate which affect the accurate measurement of the turbidity. Results obtained on 5-gram and 10-gram samples indicate excellent precision, even at concentrations below 50 ppm sulfate. A final report summarizing the recommended umpire procedure for sulfate has been prepared and distributed to other AEC laboratories cooperating in the G.A.C. program.

13.6 EFFECT OF WET SCREENING ON ORANGE OXIDE PARTICLE SIZE - W. Ellis and E. Brown

In this laboratory, the wet screen test is used to determine the particle size of orange oxide. In this method, the sample is placed on the top sieve and washed through each successive sieve with a stream of water. The material retained on each screen is dried and weighed.

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In view of the possible hydrolysis of the sample during the test, which could alter the particle size, a study was undertaken to evaluate the extent of hydration of the sample. Six production samples of 100 grams each were selected for this study. The fractions retained on each sieve were dried for 30 minutes at 110°C to remove surface moisture. The fractions were then analyzed for water by use of the combustion train method.¹ The results will be found in Table 13.6-1.

TABLE 13.6-1

**WATER IN ORANGE OXIDE BEFORE AND
AFTER WET SCREENING**

Sample No.*	Water (%)			
	Original Sample Before Screening	>40	<40, >80	<80, >325
1a	1.28	1.35	1.28	1.22
1b		1.24	1.19	1.21
2a	1.67	1.01	0.90	0.98
2b		0.92	0.89	1.01
3a	0.84	0.87	0.80	0.79
3b		0.83	0.59	0.83
4a	1.00	0.99	1.03	0.96
4b		1.00	1.10	1.01
5a	0.67	0.74	0.46	0.56
5b		0.79	0.58	0.60
6a	1.25	0.92	1.15	0.88
6b		0.77	0.97	0.92

* a and b are duplicate determinations of the same sample

Since the moisture content of the individual fractions is no greater than that obtained on the original sample before screening, it is apparent that hydrolysis does not occur during the wet screen test. The time of contact of the sample with the wash water (approximately 5 minutes) apparently does not bring about hydration of the material and the particle size does not appear to change. The results obtained with the wet screen test for orange oxide in which kerosene was used as a wash liquid (no data given here) were found to compare favorably with results obtained when water was used as a wash liquid.

¹ Rodden, C. J., "Analytical Chemistry of the Manhattan Project," p. 280, McGraw-Hill, New York, 1950.

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13.7 SOLUBILITY OF UO_3 IN A SATURATED SOLUTION OF AMMONIUM OXALATE -

R. W. Harries, G. Riechmann, and F. Jenkins

The degree of solubility in a 6 per cent ammonium oxalate solution of the product UO_3 produced by the Denitration Plant was determined. It was desired to learn whether the presence of UO_3 in UF_4 would significantly increased the ammonium oxalate insoluble (AOI) results.

Three UO_3 samples, each of approximately 2.0 grams, were weighed and transferred to 200 milliliters of boiling saturated ammonium oxalate solution. After addition, the solution was allowed to continue to boil for a period of 15 minutes, which is the normal time for digestion during an AOI determination. The solution was filtered through a tared sintered-glass crucible of medium porosity and the insoluble residue was washed with alcohol and ether. The dried residue and the crucible were weighed and the following data were obtained:

Sample No.	Sample Wt (g)	Residue Wt (g)	Residue (%)	Soluble UO_3 (%)
1	1.9982	0.0106*	0.53	99.47
2	2.0338	0.0154*	0.76	99.24
3	2.0301	0.0270*	1.33	98.67

* Most of the residue consisted of black material (probably U_3O_8) and small pieces of a yellow material (probably UO_3 that did not dissolve).

It is evident from the results that UO_3 is very soluble in hot saturated ammonium oxalate solution and should not interfere in the AOI determination.

13.8 EVALUATION OF TWO METHODS FOR THE DETERMINATION OF URANYL OXYFLUORIDE IN URANIUM TETRAFLUORIDE -

A. E. Carter, M. Jursik, and F. E. Jenkins

An evaluation of two methods for the determination of uranyl oxyfluoride in uranium tetrafluoride is in progress. Uranyl oxyfluoride, generally referred to as the water-soluble material in uranium tetrafluoride, is normally calculated from the hexavalent uranium as follows:

$$\% \text{ Total U} - \% \text{ U}^{+4} = \% \text{ U}^{+6}$$

$$\% \text{ U}^{+6} \times 1.294 = \% \text{ UO}_2\text{F}_2$$

In an effort to establish more precise values, an analytical method for directly determining the amount of UO_2F_2 in UF_4 is desired. Two methods were suggested for this determination. Briefly, the two methods are:

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1. Determination of Methanol-Soluble UO_2F_2 in UF_4 (Umpire method suggested by New Brunswick Laboratory)

The green salt sample is ground and is digested with methanol, and the soluble uranium is filtered and determined colorimetrically with sodium peroxide in alkaline solution. The soluble uranium is assumed to be UO_2F_2 .

2. Determination of Water-Soluble UO_2F_2 in UF_4 ¹

The green salt is ground and is digested with H_2O , and the soluble uranium is filtered and determined colorimetrically with sodium peroxide in an alkaline solution. The soluble uranium is assumed to be UO_2F_2 .

A group of four samples was selected to be analyzed. All equipment was standardized and the UF_4 samples were ground for one hour, using a mechanical mortar and pestle. The results of the determinations are shown in Table 13.8-1.

TABLE 13.8-1

DETERMINATION OF UO_2F_2 IN UF_4 BY DIFFERENT METHODS

(Mechanically Ground Samples)

Sample No.	UO ₂ F ₂ (%)				Calculated*
	Method No. 1 (alcohol)		Method No. 2 (water)		
	Analyst 1	Analyst 2	Analyst 1	Analyst 2	
NBL	1.12	1.19	1.87	1.97	1.84
Standard 7656	1.10	1.17	1.90	1.99	
NLO	1.21	1.21	1.89	1.91	1.79
Analytical Control	1.22	1.24	1.87	1.86	
MCW	0.53	0.58	0.95	0.97	1.71
Co-op 85435	0.54	0.55	1.04	1.06	
MCW	0.41	0.51	0.87	1.02	1.20
Co-op 86687	0.39	0.49	0.90	1.04	

* Based on determinations of total U and tetravalent U; calculated from the equations at the beginning of this section.

¹ Rodden, C. J., Current Procedures for the Analysis of UO_3 , UF_4 , and UF_6 , TID-7003, February, 1956.

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The values obtained for Method No. 2 (using a mechanically ground sample) agreed with the calculated values in three of the four instances. The Mallinckrodt Chemical Works sample 85435 was reground mechanically in air for two more hours and portions of the sample were taken at the end of the second and third hours and retested. The effect of the prolonged grinding of the green salt on the UO_2F_2 results is shown in Table 13.8-2.

TABLE 13.8-2

**EFFECT OF PROLONGED GRINDING OF UF_4
IN AIR ON WATER-SOLUBLE UO_2F_2**

Sample	UO_2F_2 (%)			
	1 - hr Grind	2 - hr Grind	3 - hr Grind	Calculated Value
MCW Co-op 85435	0.96	1.44	1.90	1.71
	1.05	1.48	1.89	

It is concluded that grinding time is a critical factor in the water-soluble method of determining UO_2F_2 .

Further studies are recommended in which grinding time will be compared with per cent water-soluble uranium. Also, studies will be made in order to determine whether prolonged grinding in the absence of air affects the portion of the UF_4 that is soluble in water. The length of grinding time and the type of laboratory equipment used must be standardized.

The alcohol-soluble method appears to be less suitable than the water-soluble method for determining UO_2F_2 in green salt.

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14. ANALYTICAL DEPARTMENT - SPECTROCHEMICAL DEVELOPMENT

A large majority of the spectrochemical analyses performed were of a plant control nature, but much analytical assistance was also given to development type samples emanating from other departments within the Technical and Production Divisions.

14.1 CHEMICAL SEPARATION OF RARE EARTHS FROM URANIUM MATERIALS -

M. G. Atwell and C. E. Pepper

Reactor-grade uranium must be analyzed for some of the rare earth elements (Dy, Eu, Er, Gd and Sm) because of the high neutron cross sections of these elements. Since these rare earth elements are present in small amounts, a chemical separation to concentrate them is required prior to a quantitative analysis.

Until recently, pentaether was used at National Lead Company of Ohio as the organic extractant in the separation of the rare earth elements from uranium. However, due to poor quality of pentaether and lack of a reliable source, substitution of tributyl phosphate (TBP) as the extractant for uranium was introduced.

During this quarter, the inherent losses at the various steps of the chemical extraction of the rare earths were investigated. Since these losses could not be detected by the use of spectrographic methods, rare earth losses were determined by four procedures utilizing radioactive $\text{Eu}^{152-154}$. Each procedure is briefly described below:

National Lead Company of Ohio TBP-Kerosene Method (Method A)

This procedure consists essentially of three extractions with 33-1/3% TBP - 66-2/3% kerosene mixtures to remove the uranium from nitrate solutions. After the extractions, an 8-hydroxyquinoline extraction is made in order to remove the so-called common impurities (Fe, Ni, Cr, Al, etc.). The separated rare earths in solution are precipitated with NH_4OH and filtered, and the residue is ignited to the oxide.

National Lead Company of Ohio 100% TBP Method

This procedure is almost identical to Method A, except that 100 per cent tributyl phosphate (TBP) is used as the organic extractant.

~~CONFIDENTIAL~~New Brunswick Laboratory Method¹

The New Brunswick Laboratory uses four successive TBP extractions to remove the uranium from a chloride solution. A NaOH precipitation and a hexamine precipitation are then made, in order to remove the residual common impurities not removed in the uranium extractions.

National Lead Company of Ohio TBP-HCl Method

This procedure is a modification of the New Brunswick method. It essentially eliminates the NaOH and hexamine precipitations by substituting an 8-hydroxyquinoline extraction to remove the residual impurities not retained by the TBP.

Results and Discussion

In Table 14.1-1 are shown the losses at each step of the four procedures mentioned above.

TABLE 14.1-1
COMPARISON OF RARE EARTH SEPARATION PROCEDURES

	National Lead Company of Ohio Methods			New Brunswick
	TBP - Kerosene (% Eu ¹⁵²⁻¹⁵⁴)	100% TBP (% Eu ¹⁵²⁻¹⁵⁴)	TBP - HCl (% Eu ¹⁵²⁻¹⁵⁴)	Method (% Eu ¹⁵²⁻¹⁵⁴)
First TBP Extraction	7.0	0.8	0.4	0.1
Second TBP Extraction	6.1	10.4	0.1	1.6
Third TBP Extraction	4.3	8.1	0.4	0.5
Fourth TBP Extraction	—	—	0.1	0.1
Kerosene Wash	—	L 0.1	—	L 0.1
NaOH Precipitate Filtrate	—	—	—	L 0.1
NaOH Precipitate Filter Paper	—	—	—	0.5
NH ₄ OH Precipitate Filtrate	—	—	—	0.2
NH ₄ OH Precipitate Filter Paper	—	—	0.1	0.1
8-hydroxyquinoline Extraction	1.2	4.3	2.1	—
Chloroform Wash	L 0.1	L 0.1	L 0.1	—
Filtrate from Quinolate Precipitate	L 0.1	L 0.1	L 0.1	—
Hexamine Precipitate	—	—	—	8.7
Filtrate from NH ₄ OH Precipitate	—	0.6	L 0.1	0.1
Rare Earth Residue	81.0	76.1	96.4	87.8
Total Recovery	99.60	100.3	99.6	99.7

L — less than

¹ Rodden, C. J., *Current Procedures for the Analysis of UO₃, UF₄, and UF₆*, p. 105, TID-7003, February, 1956.

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It is obvious that the New Brunswick method of using TBP with chloride solution is superior to the other procedures in the removal of uranium. However, large final "rare earth" residues obtained by use of the New Brunswick method motivated the introduction of the modifications listed in the National Lead Company of Ohio TBP-HCl procedure. The small (less than 2.0 mg) rare earth residues and the high rare earth recovery obtained by the use of National Lead Company of Ohio TBP-HCl method were significant factors in establishing this method as the routine rare earth separation procedure at National Lead Company of Ohio.

14.2 DETERMINATION OF RADIUM IN K-65 MATERIALS - W. W. Beyer and N. L. Poling

National Lead Company of Ohio is required to maintain a material balance on radium received in the Q-11 ores and on the final residue after removal of the uranium (the latter being referred to as K-65 material).

The analytical method used by National Lead Company of Ohio is the same as that reported by Hudgens, Zyskowski, Nelson, and Meyer.¹ Measurements, in this method, employ a high-pressure ionization chamber with a commercial vibrating-reed electrometer read-out. The K-65 material is packed in 12-milliliter-capacity glass vials. These vials are sealed to prevent loss of the radon gas. After a growth period of forty days, the vials are at radioactive equilibrium and the activity of the 1.8-Mev gamma ray is proportional to the radium content of the vial. The ionization produced within the high-pressure chamber by the Bi^{214} (radium C) gamma ray is recorded and compared with radium standards. The gross assays must be corrected for sample gamma ray attenuation.

The problem thus far has been to accurately determine the gamma ray absorption of the sample material in the vials. The work reported here consisted of a statistical treatment of new and old gamma ray absorption measurements.

Gamma ray attenuation, although not varying greatly with respect to small variations in sample bulk density, has been the single correction factor of pronounced consequence. Exact knowledge of the attenuation is required for successful assaying by the high-pressure ionization chamber technique. At the present time, National Lead Company of Ohio lacks sufficient data to soundly establish this attenuation factor.

With the assumption that the gamma ray attenuation does vary with bulk density, single attenuation determinations were plotted against bulk density. The data was accorded a least squares adjustment. From this adjusted curve, corrections were made for the K-65 samples assayed. A comparison of National Lead Company of Ohio's assays with assays by New Brunswick Laboratory and by Massachusetts Institute of Technology is shown in Figure 14.2-1. A bias is noted for activity levels of less than 200 milligrams of radium per ton. The medium deviation for National Lead Company of Ohio assays of less than 300 milligrams radium per ton is 1.06 per cent high. Maximum deviation for a single assay is 2.9 per cent. However, the National Lead Company of Ohio sample assays for K-65 materials agree, within the limits of error obtained, with NBL and MIT values.

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¹ Hudgens, J. E., Zyskowski, C., Nelson, L., and Meyer, R., Quart. Prog. Rpt. for the Period Ending March 31, 1955, p. 61, NBL-107, June, 1955.

FIGURE 14.2-1 National Lead Company of Ohio Radium Assays of K-65 Residues, Compared to New Brunswick Laboratory and Massachusetts Institute of Technology Assays

This bias at low levels may indicate uncertainty in the lower valued radium solution standards. Also, the attenuation factors for the radium solutions may not be accurate. The solution standards and the sample gamma attenuation are to be investigated further during the next quarter.

14.3 SPECTROGRAPHIC IMPURITY ANALYSIS OF URANIUM-NIOBIUM ALLOY – C. A. Haberle and C. E. Pepper

National Lead Company of Ohio is currently producing uranium alloy metal which contains approximately 10 per cent niobium. A spectrographic procedure for determining the metallic impurities present in the final uranium-niobium alloy was required.

The procedures for the preparation of oxide samples from the alloy material and the associated spectrographic analysis of the oxides have previously been reported.^{1,2} This method has been routinely used at National Lead Company of Ohio for approximately six months.

Some difficulty was experienced in obtaining good precision and accurate iron and nickel results when compared to wet chemical values. Investigations soon indicated that samples received as metal punchings (rather than as metal drillings and millings) produced acceptable spectrographic analytical results. All samples now are received as metal punchings of approximately 1/4 inch diameter and 1/8 inch thickness. The reasons for analytical variations being caused by difference in the original sample form are not known at the present time.

Typical comparative analyses for iron and nickel in the uranium-niobium alloy are shown in Table 14.3-1. Results listed are averages of duplicates. Spectrographic values are visual estimates.

TABLE 14.3-1

COMPARATIVE ANALYSIS OF URANIUM – 10 PER CENT NIOBIUM METAL

Sample	Nb (%)	Iron*		Nickel*	
		Spec**	Wet Chem	Spec**	Wet Chem
A	10.4	125	118	45	46
B	10.7	85	99	37	32
C	10.5	85	93	36	29
D	10.8	110	110	35	31
E	10.3	135	122	75	83
F	9.3	165	128	40	37
G	10.5	85	85	35	44
		$\bar{x}$ 113	108	$\bar{x}$ 43	43

* Values in ppm based on uranium – 10 per cent niobium metal

** Spectrographic determinations

1 Haberle, C. A. and Pepper, C. E., Summary Tech.Rpt., pp. 171 - 172, NLCO-625, April 16, 1956.

2 Haberle, C. A. and Pepper, C. E., Summary Tech.Rpt., pp. 153 - 154, NLCO-640, July 18, 1956.

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In Table 14.3-2 are listed the elements and the present reportable low limits for impurities determined spectrographically in uranium-niobium alloy materials.

TABLE 14.3-2**LOW LIMITS* OF DETECTION FOR IMPURITIES IN URANIUM-NIOBIUM ALLOY**

Ag	0.4	Co	2	Mn	2	Si	20
B	0.4	Cr	6	Mo	40	Sn	2
Be	6	Cu	2	Ni	20	V	20
Bi	2	Fe	10	P	40	Zn	20
Cd	0.4	Mg	10	Pb	2		

* Values in ppm based on uranium - 10 per cent niobium metal.

Analytical data from control samples are now being accumulated and will be given a statistical treatment.

The introduction of densimetric techniques for the analysis of boron, chromium, copper, iron, manganese, and nickel in uranium-niobium metal, using these spectrographic methods, is currently in progress.

14.4 SPECTROGRAPHIC IMPURITY ANALYSIS OF URANIUM-MOLYBDENUM ALLOY MATERIALS - E. R. Barker and C. E. Pepper

The National Lead Company of Ohio is producing quantities of uranium - 7.5 per cent molybdenum alloy and uranium - 1.5 per cent molybdenum alloy. A spectrographic method has been developed to permit the impurity analysis of this alloy material.

The previously reported spectrographic method for the analysis of uranium - 7.5 per cent molybdenum alloys, in which AgCl was used as a carrier material,^{1,2} is no longer used. A carrier mixture of graphite and gallium oxide has been successfully substituted, improving the analyses of 18 impurity elements in the uranium-molybdenum alloy.

Ten per cent graphite, when mixed in the sample oxide, suppresses an estimated 80 to 90 per cent of the molybdenum spectra, thus almost completely eliminating any spectral interference from molybdenum. Five per cent gallium oxide, added to the graphite and sample oxide, effectively distills out the common impurity elements, while successfully suppressing excitation of the uranium.

1 Barker, E. R. and Pepper, C. E., Summary Tech. Rpt., pp. 172-173, NLCO-625, April 16, 1956.

2 Barker, E. R. and Pepper, C. E., Summary Tech. Rpt., pp. 154-155, NLCO-640, July 18, 1956.

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The spectrographic procedure routinely in use at National Lead Company of Ohio for the analysis of the two uranium-molybdenum alloys is described below:

Sample Preparation

1. Approximately two grams of uranium-molybdenum alloy is dissolved in HNO_3 , evaporated to dryness, and ignited to the oxide at 850°C for at least one hour.
2. Mixture of 425 mg of the oxide, 25 mg Ga_2O_3 , and 50 mg of SP-1 graphite for a period of five minutes in a Crescent Wig-L-Bug.

Spectrographic Conditions

1. Spectral Region: 2250-3500 A (2.5 A/mm).
2. Photographic Emulsion: SA-I.
3. Slit Width: 20 microns.
4. Current: 14 amperes d.c. (dead short).
5. Electrode: 0.625 inch long by 0.250 inch diameter (pedestal type).
6. Crater: 0.281 inch long by 0.156 inch diameter.
7. Carrier: 10% graphite and 5% Ga_2O_3 .
8. Charge: 100 mg.
9. Exposure: 53 seconds, with 7-second pre-arc.
10. Plate Development: 4 minutes in D-19.

Results

Samples presently are visually compared to standard plates for alloys containing 7.5 per cent and 1.5 per cent molybdenum. All values are expressed as ppm, based on uranium alloy containing 7.5 or 1.5 per cent molybdenum. The current reportable low limits in the spectrographic analysis of the uranium-molybdenum alloys are shown in Table 14.4-1.

~~CONFIDENTIAL~~TABLE 14.4-1**LOW LIMITS* - U-Mb ANALYSIS**

Al	6
Ag	0.1
B	0.4
Be	6
Bi	1
Cd	0.4
Co	1
Cr	4
Cu	1
Fe	6
Mg	1
Mn	6
Ni	6
P	20
Pb	1
Si	6
Sn	1
Zn	6

* Values in ppm based on U-Mb metal.

The introduction of densimetric techniques for the analysis of boron, chromium, copper, iron, manganese, and nickel is under investigation in an effort to produce quantitative analytical results.

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