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SPECIAL
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SUMMARY TECHNICAL REPORT
FOR THE PERIOD
JANUARY 1, 1956, TO MARCH 31, 1956

EDITED BY
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CONTENTS

1. ABSTRACT

The activities of the Technical Division of the National Lead Company of Ohio are reported for the period of January 1, 1956, to March 31, 1956.

2. SUMMARY

3.1 The Canadian Gravity Concentrate recently received at NLO should be blended with other uranium concentrates in such a manner that the uranium derived from the Canadian concentrate does not constitute more than 1/31st of the total uranium content of a digest batch. This is necessary to bring the fluoride and chloride contents of the blend within specification and provide satisfactory uranium recovery.

3.2 Unblended samples of Pronto uranium concentrate (which contains 1 to 3 per cent thorium and 50 to 65 per cent uranium) were digested and the resultant slurries were extracted in a two-inch-diameter pulsed perforated-plate column. A scrubbed organic product containing 5000 ppm thorium, on a uranium basis, was obtained. Roasting the Pronto concentrate did not preferentially reduce the acid solubility of the contained thorium.

4.1 A 3/1 blend of South African ore/Black Oxide was processed under "low acid flowsheet" conditions in the Pilot Plant extraction columns, with low uranium losses in the raffinate.

4.2 In one-stage batch extraction tests, urea and triethanolamine showed promise of being good stripping agents for the re-extraction of uranium in a UNH-TBP-HNO_3 system.

4.3 In a laboratory investigation concerned with the re-extraction of uranium in a UNH-TBP system, the stripping properties of ammonium citrate, ammonium acetate, acetic acid, and citric acid were superior to those of water, with ammonium citrate and ammonium acetate being superior to acetic acid and citric acid.

4.4 The resistance to corrosion was determined for several proposed materials of construction and for the materials presently used in the Refinery. These materials were tested in various concentrations of boiling nitric acid.

5.1 In thermobalance determinations, Port Hope pot scale (orange oxide) had a significantly higher hydrofluorination rate than did bulk powder from the same pot denitrations, Port Hope product powder, or NLO sulfated UO_3 powder.

5.2 Thermobalance tests indicated that dissolution and redenitration of Port Hope orange oxide exhances the reactivity of UO_2 produced at a reduction temperature of 1650°F. No change was observed in hydrofluorination reactivity when the temperature employed to produce the UO_2 was 1200°F.

5.3 The absolute densities of samples of Port Hope and NLO orange oxide were determined by a differential pressure measurement.

6.1 A twin-drum dryer for the drying of extraction raffinates has been installed in the Acid Recovery Area. Low rates of corrosion of the chromium-plated cast iron drums have been experienced.

6.2 Good corrosion resistance was shown by a laboratory size chromium-plated cast iron drum dryer unit that was exposed to raffinate concentrate solutions. The raffinate solutions were byproducts remaining after extraction of uranium from nitric acid-digested uranium ores.

7.2 In a thermobalance, uranyl fluoride in powder form was successfully reduced by hydrogen to UO_2 at a temperature of 1400° F. A final conversion to UO_2 of 98 per cent was achieved. At lower temperatures, reduction proceeded very slowly.

8.1 The reduction and hydrofluorination of NLO sulfated UO_3 and of Port Hope UO_3 were studied in plant-scale tests. For NLO sulfated UO_3, increasing the reduction reactor main screw speed while using steam injection in the reduction reactor increased the UF_4 assay and permitted the AOI specification to be met. When redenitrated Port Hope UO_3 was used, the AOI specification was met by lowering the set temperature of the first hydrofluorination reactor and using a substantially lower feed rate.

9.1 It was concluded that the existing moving bed reactor system is not amenable to the processing of starch-UO_3 pellets.

9.2 In Pilot Plant tests, NLO sulfated UO_3 was continuously mixed and nodulized in the Bonnot pug mill at NH_4OH concentrations of 0 to 5 per cent.

9.3 Hydrofluorination rates were determined with a thermobalance using pellet samples of UO_2 which had been prepared at various reduction temperatures from UO_3 pellets containing 7.3 and 10.3 per cent water of hydration. The results indicated that the loss of hydrofluorination reactivity caused by increasing the reduction temperature was less severe for the pellets which had been more completely hydrated.

9.4 Ammonium diuranate pellets were successfully converted to green salt in a thermobalance by various reactions involving the thermal decomposition of the ammonium diuranate, hydrogen reduction, and hydrofluorination with anhydrous HF. The reduction and hydrofluroination reactions are completed rapidly when these reactions are carried out separately at temperatures not exceeding 1200° F. Simultaneous reduction and hydrofluorination at 1200° F is a satisfactory alternative method.

10.1 Uranium tetrafluoride was reduced continuously to uranium metal in a small open reactor. Calcium was used as the reductant in this reduction, but magnesium and sodium, which are more economical, are also to be evaluated as reductants.

11.1 In a study utilizing uranium made from a comparatively few lots of green salt, pickling of MCW derbies made from MCW green salt reduced the slug rejection rate considerably. Ingots made from pickled derbies had lower nitrogen contents than did ingots made from unpickled derbies.

11.2 Sound, reasonably homogeneous niobium-uranium ingots (nominal, 10 w/o niobium) were cast. The use of top-pouring induction furnaces for remelt improved homogeneity and gave smaller niobium losses than did bottom-pouring furnaces.

12.1 Equipment is being developed for the production of uranium washers: Uranium ingots are being rolled to produce plate that would meet the thickness specification for washers. Methods of heat treating the uranium plate are being studied and washers are being punched on both progressive and compound dies.

13.1 High-fluoride-content ammonium diuranate was successfully processed to a high-grade uranium concentrate of low fluoride content. The phosphate precipitation process was used in this large-scale operation. (p. 113-16).

13.2 In plant and laboratory tests, MgF_2 slag was successfully processed by a phosphate precipitation technique to a uranium concentrate having a low fluoride content. (p. 116-18

Th Sn Ti Zr Mg Cr Zn Cu Co Ni

13.3 Thorium, tin, titanium, zirconium, magnesium, chromium, zinc, copper, cobalt, nickel, and Pb lead were not as effective in inhibiting fluoride volatalization from a nitric acid solution as was aluminum.

13.4 Sources in the literature indicate that the reaction that occasionally occurs during the treating of uranium with nitric acid can be attributed to one or both of the following mechanisms: (1) Hydrogen evolution, followed by reaction of hydrogen and oxygen or (2) the reaction of uranium metal with nitrogen oxides.

13.5 Laboratory evaluation showed that oxidation of grinder sludge in a closed retort was feasible only after the water and soluble oil were removed by distillation. Oxidation of the sludge, with an oil residue present, caused minor explosions.

14.1 The optimum pressure for fabricating thorium electrodes was found to be 30 tsi. Resistivity was not critical in the range of 10 to 46 tsi pressure.

15.1 Microporosity in thorium slugs is indicated by a slightly decreased back-reflection on the Reflectoscope.

15.2 Voids (¼ inch and larger) have been located in niobium-uranium ingots by the use of a Kelvin-Hughes Mark V Flaw Detector.

15.3 Hollow fuel elements have been cast in the centrifugal casting machine at NLO. By beta treatment followed by a high alpha anneal, grain refinement of these unalloyed fuel elements to the range of 0.1 millimeter has been achieved.

15.4 Uranium shot was prepared in a helium-filled tank, utilizing rotating disks made of graphite, porous carbon and zirconia. Flat and concave shapes were tested. A flat zirconia rotating disk gave yields of 20 to 40 per cent in a small shot-tank.

15.5 The relationship between salt bath composition and the amount of hydrogen absorbed by uranium metal in heat treatment is further substantiated.

16.1 Both chloride and fluoride were added to a sample, which was then subjected to a fluoride determination. From 88 to 102 per cent of the chloride added was recovered from the distillate from the fluoride determination.

16.2 Excellent recovery was obtained in the coulometric determination of chloride in standard samples.

16.3 A Port Hope method was used for detecting trace amounts of thorium in standard samples of orange oxide. Satisfactory recovery of thorium was obtained.

16.4 A satisfactory procedure for determining niobium in uranium-niobium alloy was developed, based on an Argonne procedure.

16.5 Oxygen in molybdenum was determined by a hydrogen reduction method and a vacuum fusion method, with good agreement of the results.

16.6 A reliable procedure for the determination of arsenic in Port Hope Gravity Concentrate is reported.

16.7 Black oxide standard NY-ST has been re-evaluated, using the standard uranium assay procedure.

16.8 Control samples of South African concentrate were dried at 110° C in a normal atmosphere and in a dry argon atmosphere. Although samples from a given lot of South Aftican concentrate were prepared and sealed at the same time, significant changes in the moisture content were noted during reanalysis of the material over a period of many months. Meanwhile, the as-received uranium assay of this material remained in control. A much higher loss value was obtained in the argon oven. Fluctuations in the argon oven could not be correlated with atmospheric humidity as they can be in the normal atmosphere.

16.9 Molybdenum, nickel, and iron in uranium-molybdenum alloys were determined by various methods.

16.10 Uranium assay of Port Hope Gravity Concentrate was accomplished after the removal of arsenic. Part of the arsenic was removed by treatment with HNO_3 and H_2SO_4 and the remainder was volatilized by adding HCl to the sample and heating it to SO_3 fumes.

16.11 A procedure for the direct turbidimetric measurement of sulfate in the presence of uranyl ion has given satisfactory precision.

17.1 The methods of separating the rare earths from the uranium in Great Bear Lake Gravity Concentrate and Canadian Pronto Ore are described.

17.2 Attempts have been made to prepare a spectrographic standard for uranium-niobium alloy. Complete success has not yet been attained.

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17.3 The spectrographic determination of B, Be, Bi, Cd, Co, Cr, Cu, Fe, Mn, Ni, P, Pb, Si, V, and Zn in uranium-molybdenum alloy is described.

17.4 Beryllium in filter paper samples was determined spectrographically by a modification of the procedure of Cholak and Hubbard.

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3. FEED MATERIAL EVALUATION

3.1 LABORATORY EVALUATION OF CANADIAN GRAVITY CONCENTRATE – C. W. Huntington, E. J. Beer, and T. J. Collopy

On the basis of recent laboratory tests (reported here) and a review of an earlier program,[1] the following recommendations have been made concerning the processing of Canadian Gravity Concentrate:

1. In order to assure complete extraction of uranium and to control the halide content of the feed, the uranium derived from Canadian Gravity Concentrate should not exceed 1/31st of the total uranium content of a digest batch.

2. In order to control the vigorous reaction of the concentrate with concentrated nitric acid and to prevent the formation of free sulfur in the digest slurry, the Canadian Gravity Concentrate should be the last component added to the digester.

3. Since Canadian Gravity Concentrate contains relatively high percentages of rare earth elements and arsenic, the aqueous UNH product and/or orange oxide should be monitored for these elements whenever this concentrate is processed.

NLO recently received a shipment of Canadian Gravity Concentrate for amenability testing. This concentrate was one of the feed materials used in the NLO laboratory and pilot plant program (which was conducted in 1954 in conjunction with Port Hope personnel) to evaluate the digestion and extraction characteristics of a number of typical Canadian feed blends;[2] Specifically, 3-1-1 and 3-1-3 blends of Gravity Concentrate – Mine Leach Precipitate – Beaverlodge Precipitate were evaluated. Tests made during that program showed that the Canadian Gravity Concentrate reacts violently with concentrated acid, with accompanying formation of free sulfur; both characteristics were minimized when the concentrate was introduced last in the digestion procedure. It was also determined that the percentage of unconverted uranium increases with an increase in the proportion of this concentrate in the blends; however, the values of unconverted uranium obtained were within an acceptable range.

A comparison between the analyses of certain major constituents of the current material and a more complete analysis of the earlier material (Table 3-1) indicated that the two shipments should exhibit essentially the same characteristics. A rare earth analysis (Table 3-2) showed a relatively high percentage of rare earth elements in the present shipment.

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[1] *Ryle, B. G., Beer, E. J., Blum, J. F., Collopy, T. C., Huntington, C., Taylor, C. W., and Cseplo, S., Summary Tech. Rpt., p. 1-20, FMPC-404, April 15, 1954.*

[2] *Ibid.*

TABLE 3-1

CHEMICAL ANALYSIS OF CANADIAN GRAVITY CONCENTRATE

Constituent	1954 Shipment*	Present Shipment*	Constituent	1954 Shipment*	Present Shipment*
As	6	11	MgO	3.2	xxx
B	0.01 (ppm)	xxx	Ni	2.60	xxx
CaO	1.0	xxx	PO_4	2.21	2.0
Cl	xxx	0.02	$S^=$	xxx	3
Co	4.36	xxx	SiO_2	9.13	xxx
CO_3	xxx	2.8	SO_4	20.9	20.9
Cu	2.34	xxx	U	10.2	10.
F	xxx	0.2	Rare Earths	xxx	See Table 3-2
Fe	11.75	xxx			

* Per cent on as-received basis, except as noted otherwise.

xxx Not determined.

TABLE 3-2

RARE EARTH ANALYSIS* OF CANADIAN GRAVITY CONCENTRATE

Element	% (as-received basis)	Element	% (as-received basis)
Dy	0.12	Nd	0.12
Eu	0.02	Pr	0.016
Er	0.04	Sm	0.04
Gd	0.06	Tb	0.12
Ho	0.008	Y	0.2
Lu	0.0008	Yb	0.03

* Analysis performed by NLO Spectrochemical Laboratory on a composite of the six lots of the present shipment.

The digestion and extraction characteristics of the concentrate were determined to a certain degree during the earlier program,[1] which utilized 22.5 per cent tributyl phosphate (TBP) as the solvent. The current evaluation, therefore, involved only a laboratory determination of the minimum blend ratio of other feed materials with Canadian Gravity Concentrate that would assure complete extraction in the 33.5 per cent TBP system and at the same time meet feed material specifications with respect to impurities.

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[1] *Ryle, B. G., Beer, E. J., Blum, J. F., Collopy, T. C., Huntington, C., Taylor, C. W., and Cseplo, S., Summary Tech. Rpt., p. 1-20, FMPC-404, April 15, 1954.*

Chloride analyses of the individual lots of the current shipment ranged from 0.014 to 0.028 per cent averaging 0.022 per cent (ore basis). The fluoride range was 0.06 to 0.32 per cent; the average was 0.16 per cent. The uranium assay was approximately 10%. The average values for both halides exceed the NLO feed material specifications of 0.15 per cent Cl and 0.3 per cent F on a uranium basis. It was calculated that a 1 to 3 gross weight blend of Canadian Gravity Concentrate to a high-grade concentrate such as South African Concentrate (60% U) would be required in order to accommodate the maximum fluoride concentration.

Initial laboratory work was performed, therefore, on a 3-1 blend (South African Concentrate – Gravity Concentrate). The components were added alternately to the acid, and no difficulties due to excessive digestion reactivity were encountered. A batch shakeout test was made on a slurry containing 205 g/l U and $3.3\underline{N}$ HNO_3. The results showed that the sixth stage aqueous phase contained 0.29 g/l U. This value considerably exceeds the aqueous raffinate specification (0.02 g/l U) which is used to evaluate laboratory extraction tests.

Since extraction of the 3-1 blend was not complete, a second batch shakeout test was made on a 5-1 blend (South African Concentrate – Gravity Concentrate). The two components were preblended, and the digestion proceeded without extreme fuming and foaming. The extraction procedure was not carried beyond four stages because of the formation of thick emulsions, due to the presence of South African material. The fourth-stage aqueous phase contained 0.077 g/l U, which indicates that satisfactory extraction should be achieved in six stages. Since the proportion of Gravity Concentrate in a 5 to 1 blend is much lower than that used in the pilot plant evaluation of Canadian feed materials,[1] the unconverted uranium values should be well within specification.

South African Concentrate contains approximately 60 per cent uranium, and a 5 to 1 gross weight blend of this material with Canadian Gravity Concentrate (which contains approx. 10 per cent U) corresponds to a 30 to 1 blend on a uranium basis. Thus, in order to assure satisfactory extraction of all uranium values, the uranium derived from Canadian Gravity Concentrate should not exceed 1/31st of the total uranium content of a digest batch.

3.2 PROCESSING OF THORIUM-CONTAINING URANIUM CONCENTRATES – C. W. Huntington, W. C. Manser, J. R. Nelli, J. R. Krekeler, E. J. Fasnacht, R. H. Ellerhorst, D. A. Stock

Thorium bearing uranium concentrates are expected to contain 1 to 3 per cent thorium and 50 to 65 per cent uranium. Since a specification of 50 ppm thorium (maximum) in the orange oxide has been tentatively established, it is necessary that the maximum thorium concentration permissible in the feed slurry for the Refinery extraction system be determined.

Advance samples of Pronto thorium-uranium concentrate have been received for laboratory and pilot plant evaluation. Analysis of one lot of this material showed 66.58 per cent U_3O_8 and 1.08 per cent ThO_2. These samples were subjected to extraction tests and to roasting in an effort to develop methods of separating the thorium from the uranium.

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[1] *Ibid.*

Extraction Tests

Most of the effort expended to date upon the development of processing techniques for thorium-uranium concentrates has been directed toward a determination of the amount of thorium contamination which would be obtained under present Refinery operating conditions if unblended Pronto concentrate were processed at the normal feed slurry concentrations (200 g/l U; 3.0N HNO_3). Batch countercurrent technique has proved cumbersome, since a large number of volume changes are required in order to insure system equilibrium. Batch countercurrent tests were carried through three-volume and five-volume changes; analytical results showed that in both cases the system had not come to equilibrium with respect to thorium distribution.

Subsequent tests were made in the Pilot Plant two-inch-diameter pulsed perforated plate extraction column, which has recently been established as an operating test unit. Initial tests utilized a compound-column (extraction and scrub) system. Flow ratios and the extraction section throughput corresponded to present Refinery operations. Analyses indicated that the system was at equilibrium after two hours. The scrubbed organic product contained 5000 ppm thorium, on a uranium basis.

The two-inch compound column is useful only for scoping or comparative tests, since the system does not parallel the normal process: A relatively short section (10 ft) is available for scrubbing and, contrary to Refinery practice, the scrub section must be organic-continuous. Utilization of the entire (25-ft) column for successive extraction and scrub operations is complicated by the necessity of providing a scrub (BR) recycle to the extraction column. Current work involves an attempt to determine the effect of using a full-length, aqueous-continuous scrub column by (1) making an initial pair of extraction and scrub tests in which a certain scrub recycle concentration is assumed in the preparation of aqueous feed, and (2) repeating the tests on the basis of the actual scrub recycle stream concentrations obtained in the first scrub test. Indications are that a scrubbed organic product containing about 1000 ppm Th will be obtained by this process.

Future work will involve blends of Pronto concentrate with other feed materials.

Roasting of Thorium-Bearing Uranium Concentrates – R. H. Ellerhorst and C. W. Huntington

A laboratory investigation has been made to determine whether any portion of the thorium content of Pronto concentrate can be rendered acid-insoluble by roasting. Samples of the ore were roasted for one hour at 1500°F and 1800°F. Normal digestions, calculated to yield 200g/l uranium in the digest slurry, were then made. The thorium and uranium contents were determined immediately after digestion and again 24 hours later.

The results in Table 3-3 indicate that roasting at 1500°F has little effect on the acid solubility of thorium. Roasting the ore at 1800°F gave a marked decline in the amount of acid-soluble thorium but also caused a portion of the uranium to be refractory.

Digestions under more vigorous conditions (higher temperature) resulted in a slightly higher acid solubility of both uranium and thorium. Results also showed that a post-digestion reaction takes place in both slurries, causing the thorium and uranium concentrations to approach those of the unroasted ore.

It has been concluded, therefore, that insolubilization by roasting is not a satisfactory means of handling thorium in uranium concentrate feed materials.

TABLE 3-3

THORIUM AND URANIUM CONCENTRATIONS IN PRONTO CONCENTRATE SLURRIES

	Sample	U (g/l)	Th (g/l)
1.	Unroasted	197	3.35
2.	Roasted at 1500°F for one hour		
	(a) Analyzed immediately after digestion	200	3.01
	(b) Analyzed 24 hours after digestion	204	3.22
3.	Roasted at 1800°F		
	(a) Analyzed immediately after digestion	137	0.14
	(b) Analyzed 24 hours after digestion	182	2.88
4.	Roasted at 1800°F, digested at 60°C		
	(a) Analyzed immediately after digestion	155	1.06
	(b) Analyzed 3 days after digestion	198	3.11

4. REFINERY PROCESS

4.1 THE LOW-ACID FLOWSHEET INVESTIGATION – S. Cseplo and C. W. Taylor

Because of good preliminary results[1] with a low-acid flowsheet using 33.5% TBP, 66.5% Amsco 125-90w solvent, and a feed assaying 0.5 to 1.5N HNO_3 at an F/O/S ratio of 4.5/9/1, further runs were made in order to evaluate the extraction characteristics of slurry type feeds at low free-acid concentrations. The advantages of using a low free-acid concentration were discussed previously[2] and will not be repeated here.

Summary

Excellent column operation was achieved with a low-acid flowsheet using siliceous -ore feed at ambient temperature; the raffinate losses were low (0.01 g/l U) and the OK liquor product met purity specification. Preconditioning of the feed by digestion in 2.0N HNO_3 at 180° F was found to be essential to preventing emulsions attributed to "soluble silica" in the feed. When lower acidity (0.2N HNO_3) was used for preconditioning, it was necessary to heat the feed and organic streams to 150° F in order to obtain satisfactory column operation. Feed batches were prepared from a 3/1 weight ratio of South African ore/Black Oxide, and were digested at 400 g/l U at 0.2 to 2.0N free nitric acid for three hours at 180° F. Batches were diluted with water (and acid, if required) to 200 g/l U and 0.6 to 1.2N HNO_3 for column feed. The feed/organic/scrub flow ratio was 4.5/9/1.

Operating Conditions

Four runs made under the best conditions found from the previous low-acid runs are summarized as follows in Table 4-1.

Data and Discussion

For Runs 308 and 309, the South African ore and Black Oxide (3/1 weight ratio) ores were digested in 5.8N HNO_3 for one hour at 150° F, resulting in a feed slurry that was only 0.2N in free acid. Additional acid and water were added to bring the final feed slurry up to a concentration of 200 g/l U and 0.6N HNO_3 in Run 308 and 1.2N HNO_3 in Run 309.

Severe emulsification in the extraction column occurred from the start of Run 308 and did not lessen or disappear when pulsing conditions were reduced. It appeared that the feed slurry was of a gelatinous nature, which contributed greatly to the emulsification difficulties. Several hours later, the feed slurry and solvent streams were heated to 150° F and the columns were allowed to come to a temperature equilibrium. Phase inversion occurred near the middle of the column, with the upper portion aqueous-continuous (abnormal) and the lower portion organic-continuous (normal).

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[1] Cseplo, S. and Taylor, C. W., Summary Tech. Rpt., pp. 27-28, NLCO-577, October 17, 1955.
[2] ibid.

TABLE 4-1

OPERATING CONDITIONS FOR THE PILOT PLANT LOW-ACID FLOWSHEET EXTRACTION TESTS

Stream compositions
AF: 200 g/l U (all runs)
$0.6\underline{N}$ HNO_3 at 70°F for 8 hr and
$0.6\underline{N}$ HNO_3 at 150°F for 8 hr (Run 308)
$1.2\underline{N}$ HNO_3 at 150°F (Run 309)
$1.2\underline{N}$ HNO_3 at 70°F (Run 310)
$1.0\underline{N}$ HNO_3 at 70°F (Run 311)

AX: 33.5% TBP, 66.5% Amsco 125-90w
Nonacidified
150°F (Runs 308 and 309)
70°F (Runs 310 and 311)

BS: Deionized water at 70°F

CS: Deionized water at 150°F

Pulse conditions
A column: frequency: 50 cpm;
amplitude: 1 inch
B column: frequency: 35 cpm;
amplitude: 1 inch
C column: jet mixers

Continuous phase
A column: organic
B column: aqueous
C column: organic
D column: organic

Flow Ratios
Feed/Organic/Scrub: 4.5/9/1
Strip-water/Organic: 1.1/1

Flow rates (gph)
AX: 99
AF: 50
BS: 11
CS: 120

Total Throughput (gsfh)
A-column: 800
B-column: 550
C-column: 1095

Solvent cleanup system
Na_2CO_3 wash in mixer-settlers, followed by a water-wash in "D" column.

The run continued with apparent raffinate losses of about 0.7 g/l U until the eighth hour of the run, when the emulsion finally broke and disappeared entirely. The AP saturation during the first part of the run averaged about 120 g/l U, with a BR recycle of about 150 g/l U. The raffinate losses steadily decreased upon the breaking up of the emulsion and at about the twelfth hour of the run, the throughput was increased from 800 gsfh to 920 gsfh. The run continued at this throughput rate for eight more hours before lack of feed caused a shutdown. Raffinate losses during the latter part of the run (Run 308A) averaged about 0.12 g/l U, with an AP saturation of 100 g/l U and a BR recycle of 90 g/l U. Normally, an AP (organic extract) uranium saturation above 110 g/l results in a raffinate loss between 0.2 and 10 g/l U with a $3\underline{N}$ HNO_3 200 g/l U feed batch and 33.5% TBP at the same flow ratios.

Run 309 used the same operational conditions as Run 308. The feed stream was adjusted to a 200 g/l U and $1.2\underline{N}$ HNO_3 concentration and heated to 150°F to see if the additional free acid would give better extraction characteristics. No emulsification difficulties were encountered during the run and check samples of the extraction column raffinate and strip column raffinate showed uranium losses of 0.02 g/l U and 0.01 g/l U, respectively. The AP saturation reached a value of 90 g/l U, with a BR recycle of 30 g/l U. The relatively low AP saturation was caused by leaking feed pumps that allowed dilution water to enter the feed stream, thus diluting the stream and causing a lower saturation than expected.

Since the silica content of the South African ore seemed to be the major cause of emulsification difficulties in the extraction column, the feed batches of South African and Black Oxide (3/1 weight ratio) for Runs 310 and 311 were digested at a concentration of 400 g/l U and $2\underline{N}$ HNO_3 free acid content for a period of three hours at 180°F. The increase of free HNO_3 from 0.2 to $2.0\underline{N}$ during digestion was sufficient to alter the siliceous nature of the ore and to precipitate the soluble silica as the insoluble form. When feed batches were prepared under these conditions and with a water dilution to 200 g/l at $1\underline{N}$ HNO_3, there was a good column startup, (as is experienced in a standard $3.0\underline{N}$ HNO_3 - feed extraction run) with no emulsion difficulties.

The main difference between Runs 309 and 310 was that in Run 309 the feed and organic streams were heated to 150°F to reduce the apparent viscosity effect, whereas in Run 310, both streams were used at room temperature (about 60°F). No emulsification problems were encountered during the run and there were no apparent difficulties with feed pump dilution. The AR loss during the run averaged about 0.011 g/l U, with a CR loss of 0.006 g/l U. The AP density averaged about 0.9650, corresponding to a uranium concentration of 96 g/l U.

Run 311 (using South African and Black Oxide feed batches) was made up to 200 g/l U at $1\underline{N}$ HNO_3, using the same digestion conditions as in Run 310. The purpose was to make an extended run for at least 20 hours to insure continued operation of the extraction columns at equilibrium. The feed slurry assayed 205 g/l U and $1.00\underline{N}$ HNO_3 and the solvent assayed 33.5% TBP and 66.5% Amsco 125-90w. All other conditions were the same as those used for the other runs, with the feed and solvent streams kept at room temperature. Extraction characteristics were excellent, with good operation and no emulsion or any other adverse effects noted. Extraction column raffinate losses averaged about 0.01 g/l U, with the strip-column raffinate loss assaying about 0.01 g/l U. Since attainment of a certain concentration of the final CP product was not essential to the development of the low-acid flowsheet, the strip water was allowed to vary from 110 to 120 gal per hour (an A/0 ratio of 1.1 to 1.2/1) to keep the strip column raffinates low in residual uranium.

The uranium and nitric acid contents of all streams are given in Table 4-2. The spectrographic analyses of the CP product from all the runs (Table 4-3) were excellent, with all contaminants well within the acceptable limits.

TABLE 4-2

STREAM ANALYSES

Stream		Run 308 (70°F)	Run 308A (150°F)	Run 309 (150°F)	Run 310 (70°F)	Run 311 (70°F)
AX	U(g/l)	0.002	0.002	0.003	0.002	0.003
	HNO_3 ($\underline{N}$)	None	None	None	None	None
AF	U(g/l)	198	199	200	200	205
	HNO_3 ($\underline{N}$)	0.6	0.7	1.2	1.2	1.0
AP	U(g/l)	120	100	90	94	85
	HNO_3 ($\underline{N}$)	0.06	0.07	0.2	0.2	0.2
AR	U(g/l)	0.7	0.12	0.02	0.01	0.01
	HNO_3 ($\underline{N}$)	0.5	0.5	1.1	1.0	0.8
BP	U(g/l)	96	94	90	90	81
	HNO_3 ($\underline{N}$)	0.02	0.02	0.04	0.04	0.04
BR	U(g/l)	150	90	30	35	29
	HNO_3 ($\underline{N}$)	0.3	0.6	2.1	1.7	1.6
CP	U(g/l)	62	52	75	70	48
	HNO_3 ($\underline{N}$)	0.02	0.02	0.04	0.02	0.02
CR	U(g/l)	0.006	0.008	0.01	0.006	0.01
	HNO_3 ($\underline{N}$)	None	None	None	None	None

TABLE 4-3

SPECTROCHEMICAL ANALYSES* OF THE AQUEOUS UNH PRODUCT (CP)

Impurity	Analysis**	Impurity	Analysis**	Impurity	Analysis**
Al	<4	Fe	$4^{\dagger\dagger}$	Ni	<2
B	<0.2	Fe	$<4^{\ddagger}$	P	<20
Bi	<1	Mg	$4^{\dagger}$	Pb	<1
Cd	<0.2	Mg	$4^{\dagger\dagger}$	SiO_2	<20
Co	<2	Mg	$3^{\ddagger}$	Sn	<1
Cr	<4	Mn	<4	V	<20
Cu	<1	Mo	<4	Zn	<20
Fe	$6^{\dagger}$				

* ppm on a uranium metal basis

** For Runs 308 to 311, the analyses for all of these elements except Fe and Mg were identical.

† Run 308

†† Run 309

‡ Runs 310 and 311

4.2 LABORATORY INVESTIGATION OF ORGANIC BASES AS STRIPPING AGENTS FOR RE-EXTRACTION OF URANIUM IN A UNH-TBP-HNO_3 SYSTEM – P. S. Gentile and R. H. Ellerhorst

Ten selected organic bases were tested for their ability to re-extract uranium from a UNH-TBP-HNO_3 system.

Procedure

A stock solution of 86 g/l uranium in 33.5 per cent TBP was prepared and the uranium was re-extracted, using aqueous solutions of various stripping agents in one-stage batch shakeout tests. The procedure for the batch shakeout test was as follows:

> To 50 milliliters of the organic uranium solution in a separatory funnel was added 50 milliliters of the stripping solution. The two phases were shaken for five minutes and allowed to settle until complete phase disengagement occurred. The two phases were then sampled and analyzed for uranium.

In all cases, an attempt was made to find the concentration of the stripping agent which would re-extract the uranium in a one-stage batch shakeout while maintaining the uranium in the organic phase within Refinery specifications (0.02 g/l U).

Data and Conclusions

Urea has been shown to be the most promising reagent for increasing re-extraction of uranium. Table 4-4 shows that it has good stripping characteristics, excellent phase disengagement, and in addition, results in liquid phase re-extraction (no precipitation).

Triethanolamine (Table 4-5) also shows promise of being a good stripping agent. Difficulty may be encountered as a result of precipitation occurring at low concentrations of triethanolamine.

Fine stripping properties were shown by 2-aminoethanol (Table 4-6) but also precipitation of the uranium.

Table 4-7 gives the results obtained using hexamethylene-tetramine, glycine, pyridine, aniline, ethylenediamine, ethanolamine and 2,2'iminodiethanol. Saturated solutions of these reagents showed poor stripping properties and also caused precipitation.

TABLE 4-4

BATCH SHAKEOUT TESTS OF URANIUM USING UREA AS A STRIPPING AGENT
(Aqueous/Organic Volume Ratio = 1/1)

Conc. of Urea	Conc. of Uranium (g/l) Aqueous Phase	Conc. of Uranium (g/l) Organic Phase	Phase Disengagement
Saturated Solution	–	0.12	Good
10M	89	0.10	Good
8M	79	0.13	Good
6M	77	0.9	Good
4M	77	3	Good
3M	72	6	Good
2M	66	13	Good
1M	55	25	Good

TABLE 4-5

BATCH SHAKEOUT TEST OF URANIUM USING TRIETHANOLAMINE AS A STRIPPING AGENT
(Aqueous/Organic Volume Ratio = 1/1)

Conc. of Triethanolamine	Conc. of Uranium (g/l) Aqueous Phase	Conc. of Uranium (g/l) Organic Phase	Phase Disengagement	Remarks
4M	76	<0.0005	Fair	
2M	81	0.001	Good	
1M	2.4	0.006	Poor	Pptn of the U occurs

TABLE 4-6

BATCH SHAKEOUT TEST OF URANIUM USING 2-AMINOETHANOL AS A STRIPPING AGENT
(Aqueous/Organic Volume Ratio = 1/1)

2-aminoethanol	Conc. of Uranium (g/l) Aqueous Phase	Conc. of Uranium (g/l) Organic Phase	Phase Disengagement	Remarks
10M	–	<0.001	Poor	Forms a U ppt
8M	29.9	<0.0005	Poor	Forms a U ppt
4M	1.9	<0.0005	Good	Forms a U ppt
2M	0.037	0.003	Fair	Forms a U ppt

TABLE 4-7

BATCH SHAKEOUT TESTS OF URANIUM USING VARIOUS REAGENTS AS STRIPPING AGENTS

(Aqueous/Organic Volume Ratio = 1/1)

Conc. of Reagent	Conc. of U (g/l) Aqueous Phase	Conc. of U (g/l) Organic Phase	Phase Disengagement	Remarks
3M Hexamethylenetetramine	0.6	0.057	Poor	Forms a U ppt
2M Hexamethylenetetramine	0.9	0.18	Poor	Forms a U ppt
1M Hexamethylenetetramine	2.3	0.9	Fair	Forms a U ppt
2M Glycine	79	0.82	Good	
1M Glycine	71	7.6	Good	
1M Pyridine	–	–	Poor	Forms a U ppt
0.2M Aniline	–	–	Poor	Forms a U ppt
1M Ethylenediamine	–	–	Good	Forms a U ppt
1M Ethanolamine	–	–	Fair	Forms a U ppt
4M 2,2'-Iminodiethanol	–	–	Poor	

4.3 LABORATORY INVESTIGATION OF INORGANIC STRIPPING AGENTS FOR RE-EXTRACTION OF URANIUM IN A UNH-TBP-HNO_3 SYSTEM – P. S. Gentile and R. H. Ellerhorst

A program has been initiated to find a new stripping agent that will increase stripping efficiency to a point where a single re-extraction column can be used, thereby releasing an additional column for scrubbing. A preliminary laboratory investigation of various stripping agents[1] having been completed, a number of inorganic reagents were evaluated for stripping characteristics by the use of batch shakeout techniques.

Method

A stock solution of 86 g/l uranium in 33.5 per cent TBP was prepared. The uranium was "re-extracted" from the TBP solution in batch shakeout tests, using aqueous solutions of the various stripping reagents. The procedure for batch shakeout testing was to equilibrate equal volumes of the organic and fresh aqueous solutions. The organic was equilibrated a total of six times with fresh aqueous solutions, and the organic and aqueous phases were sampled after each equilibration. The organic phase was analyzed for uranium, while the aqueous phase was analyzed for pH and uranium.

The stripping agents employed were acetic acid, citric acid, oxalic acid, ammonium acetate, and ammonium citrate. One to six equivalents of the reagents were used in each test, an equivalent being defined as the amount of reagent necessary to convert uranyl nitrate to uranyl acetate or citrate.

Data and Conclusions

In Figure 4-1, the stripping efficiency of 1M acetic acid can be compared with that of water (the presently used stripping agent). Although the number of re-extraction stages required was not reduced by using one equivalent of acetic acid, the use of two or more equivalents of acetic acid (Table 4-8) resulted in a uranium concentration in the first stage that was 15 to 20 per cent higher than that of water.

Citric acid (Table 4-9) did not compare favorably with acetic acid, yielding only a 10 per cent increase in uranium concentration in the first stage.

Ammonium citrate and ammonium acetate had the best stripping properties (Fig. 4-1). Not only could the number of re-extraction stages be reduced (Table 4-10), but the concentration of uranium in the first stage was increased 60 per cent when ammonium citrate is used.

Data are not available on the effect of oxalic acid as a stripping agent, because the use of oxalic acid resulted in precipitation rather than liquid phase re-extraction.

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[1] *Gentile, P. S. and Ellerhorst, R. H., Summary Tech. Rpt., NLCO-600, Vol. 1, p. 31, January 16, 1956.*

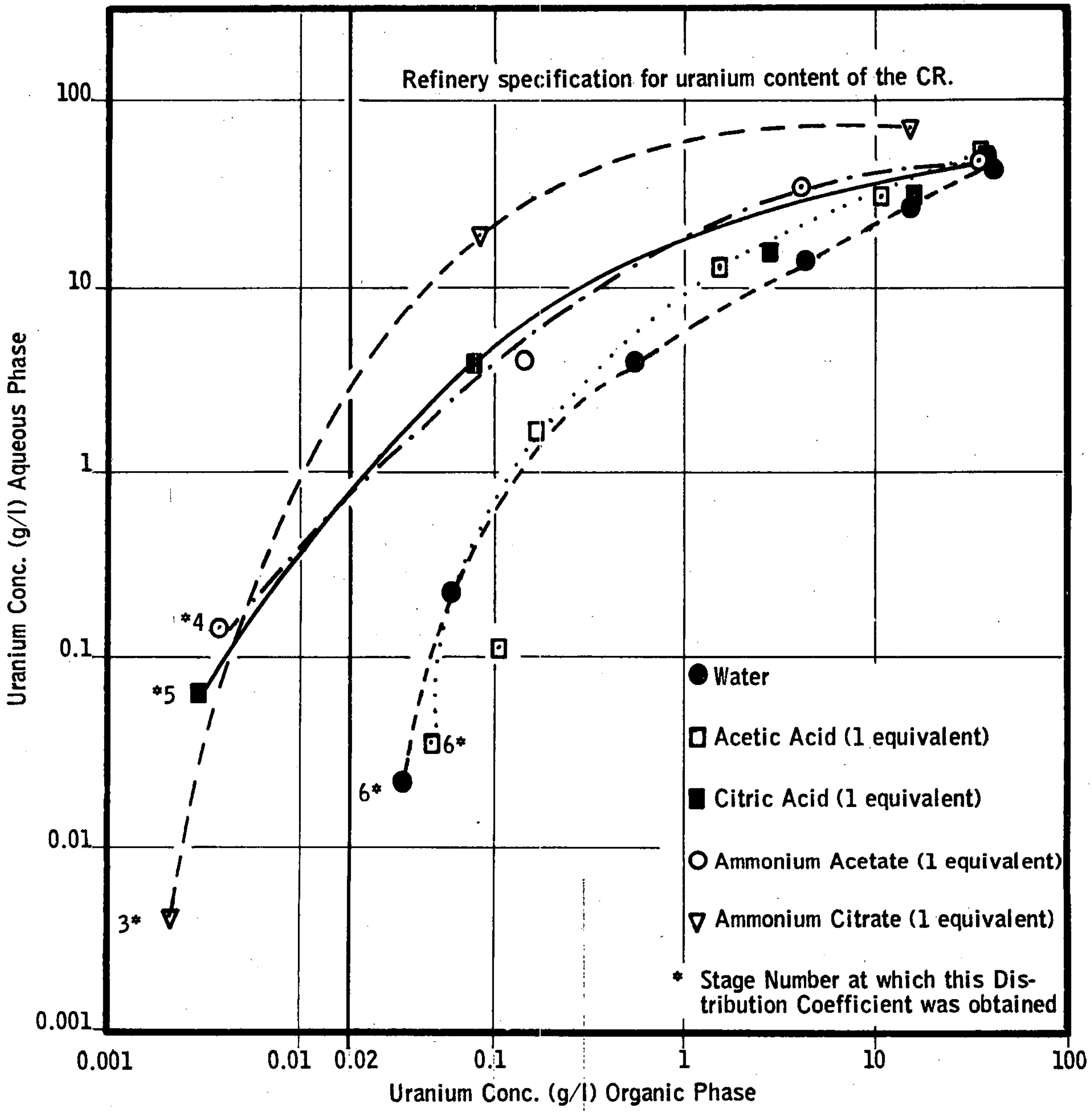

FIGURE 4-1 DISTRIBUTION COEFFICIENTS (A/O) OBTAINED DURING BATCH SHAKEOUT OF UNH-33.5% TBP WITH VARIOUS STRIPPING AGENTS

TABLE 4-8

COMPARISON* OF WATER WITH ACETIC ACID AS THE STRIPPING AGENT

(Batch Shakeout of UNH; Aqueous/Organic Volume Ratio = 1/1)

Stage	Water	Water Containing 1 Equiv** of HAc	Water Containing 2 Equiv** of HAc	Water Containing 3 Equiv** of HAc	Water Containing 6 Equiv** of HAc
			Aqueous Phase		
1E	41.3	45	51	52	52
2E	24.4	28	29	29	29
3E	13.1	12	11	10	10
4E	3.8	1.6	0.99	0.92	0.71
5E	0.23	0.11	0.06	0.059	0.048
6E	0.022	0.034	0.01	0.016	0.016
			Organic Phase		
Feed	84	86	86	86	86
1E	43	39.6	38	37.6	36
2E	17	13	11.5	10	9
3E	4.5	1.5	1.2	0.95	0.57
4E	0.57	0.19	0.08	0.099	0.095
5E	0.064	0.11	0.013	0.026	0.028
6E	0.037	0.054	0.007	0.006	0.005

* All values are reported as U (g/l).

** An equivalent is defined as the amount of reagent necessary to convert uranyl nitrate to uranyl acetate.

TABLE 4-9

COMPARISON* OF WATER WITH CITRIC ACID AS THE STRIPPING AGENT

(Batch Shakeout of UNH; Aqueous/Organic Volume Ratio = 1/1)

Stage	Water	Water Containing 1 Equiv** of Citric Acid	Water Containing 2 Equiv** of Citric Acid
		Aqueous Phase	
1E	41.3	46	44
2E	24.4	27	29
3E	13.1	13.4	14
4E	3.8	2.66	4
5E	0.23	0.067	0.67
6E	0.022	0.015	0.003

TABLE 4-9 (Cont'd)

COMPARISON* OF WATER WITH CITRIC ACID AS THE STRIPPING AGENT

(Batch Shakeout of UNH; Aqueous/Organic Volume Ratio = 1/1)

Stage	Water	Water Containing 1 Equiv** of Citric Acid	Water Containing 2 Equiv** of Citric Acid
		Organic phase	
Feed	84	86	86
1E	43	42	39.6
2E	17	16	17
3E	4.5	3	3
4E	0.57	0.11	0.087
5E	0.064	0.007	0.003
6E	0.037	0.015	<0.0005

* All values are reported as U (g/l).

** An equivalent is defined as the amount of reagent necessary to convert uranyl nitrate to uranyl citrate.

TABLE 4-10

COMPARISON OF AMMONIUM CITRATE, AMMONIUM ACETATE AND WATER AS THE STRIPPING AGENT

(Batch Shakeout of UNH; Aqueous/Organic Volume Ratio = 1/1)

Stage	U in Water (g/l)	pH	Water Containing 1 Equiv* of NH_4AC U (g/l)	pH	Water Containing 1 Equiv* of NH_4 Cit U (g/l)	pH
			Aqueous Phase			
1E	41.3	2.25	48.6	3.50	66	1.90
2E	24.4	2.55	33.1	4.69	16	4.40
3E	13.1	2.75	3.8	5.90	0.004	4.80
4E	3.8	3.12	0.15	6.27	0.001	4.80
5E	0.23	3.80	0.008	6.59	<0.0005	4.80
6E	0.022	4.78	0.0001	6.71	<0.0005	4.80
			Organic Phase			
Feed	84		84		84	
1E	43		37		16.7	
2E	17		4.3		0.083	
3E	4.5		0.16		0.002	
4E	0.57		0.004		0.002	
5E	0.064		<0.0005		<0.0005	
6E	0.037		<0.0005		<0.0005	

* An equivalent is defined as the amount of reagent necessary to convert uranyl nitrate to the uranyl acetate or citrate.

4.4 CORROSION STUDIES FOR THE ORE REFINERY – F. H. Meyer and N. N. Peters

Since March of 1954, materials of construction that may be used in future Refinery Plant service have been tested for resistance to corrosion.

Previous work has been reported in other quarterlies.[1,2,3] During this quarter, studies were directed toward maintaining proper corrosion control over the new materials being installed as part of the Ore Refinery expansion. Samples were generally submitted by Singmaster and Breyer, consultants for the expansion. Many evaluation tests were carried out; 70 per cent boiling nitric acid was used as it was the maximum anticipated corrosive environment. Stainless steels were rejected as unsuitable if a 100-hour exposure test indicated poor resistance of the welds to corrosion and/or a general corrosion rate of more than 30 mils per year.

Other studies carried out during the quarter were directed toward establishing the suitability of new materials of construction for use with nitric acid solutions. Table 4-11 presents data obtained when the resistance of various materials to 70 per cent boiling nitric acid was compared. The volume of solution used was 2000 milliliters in all cases. Duplicate samples (2 by 2-inch coupons) were run in each test. Reaction flasks fitted with refluxing systems were used to contain boiling solutions. It was concluded from the data obtained that all of the other materials tested are inferior to 309Cb and 304ELC stainless steel for 70 per cent nitric acid service.

Figure 4-2 presents graphically the corrosion rates obtained by testing our presently used constructional materials in various concentrations of nitric acid. These data are helpful in determining approximate corrosion rates of the materials of construction at various stages of Ore Refinery processing and in other equipment in which nitric acid solutions are used.

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[1] *Meyer, F. H., Summary Tech. Rpt., pp. 40-46, FMPC-505, January 15, 1955.*

[2] *Meyer, F. H. and Peters, N. N., Summary Tech. Rpt., pp. 52-53, NLCO-565, July 15, 1955.*

[3] *Meyer, F. H., Summary Tech. Rpt., pp. 35-37, NLCO-577, October 17, 1955.*

TABLE 4-11

CORROSION RATES OF MATERIALS IN 70 PER CENT BOILING NITRIC ACID (100-hr TESTS)

Alloy	Wt Loss (MDD)*	Penetration (MPY)**	Producer	Heat No.	CHEMICAL ANALYSIS OF ALLOYS (%)								
					C	Mn	P	S	Si	Ni	Cr	Mo	Other
304 ELC	142	25.7	xxx	xxx	0.04 (max)	1.5 (max)	0.04 (max)	0.04 (max)	1.0 (max)	8 to 11	18 to 21	xxx	xxx
311 SS	3,900	720	Crucible Steel Co.	K 5489	0.16	1.43	0.025	0.011	2.56	24.95	18.88	xxx	xxx
430 SS	960	180	Crucible Steel Co.	120101	0.08	0.41	0.015	0.020	0.49	0.21	17.00	0.07	0.11 Cu
446 SS	370	70	Crucible Steel Co.	142294	0.11	0.43	0.020	0.013	0.42	0.39	23.85	0.97	0.12 Cu
325 SS	21,980	4,050	Crucible Steel Co.	R 559	0.25 (max)	0.60 to 0.90	xxx	xxx	1.0 to 2.0	19.0 to 23.0	7.0 to 10.0	xxx	1.0 to 1.5 Cu
329 SS	157	29.2	Carpenter Steel Co.	xxx	0.08 (max)	xxx	xxx	xxx	xxx	3.75 to 4.5	26 to 28.5	1.35 to 1.65	xxx
16-16-1 SS	1,720	xxx	U. S. Steel	D 1356	0.08	14.6	0.03	0.007	0.30	0.32	17.8	xxx	0.08 Cu
309 SCb	65	12.0	xxx	xxx	0.08† (max)	1.5 (max)	0.04 (max)	0.04 (max)	1.0 (max)	12 to 15	22 to 24	xxx	xxx

* Milligrams per square decimeter per day.

** Mils per year.

† The sum of the columbian and tantalum contents must be at least ten times the carbon content.

xxx Not specified.

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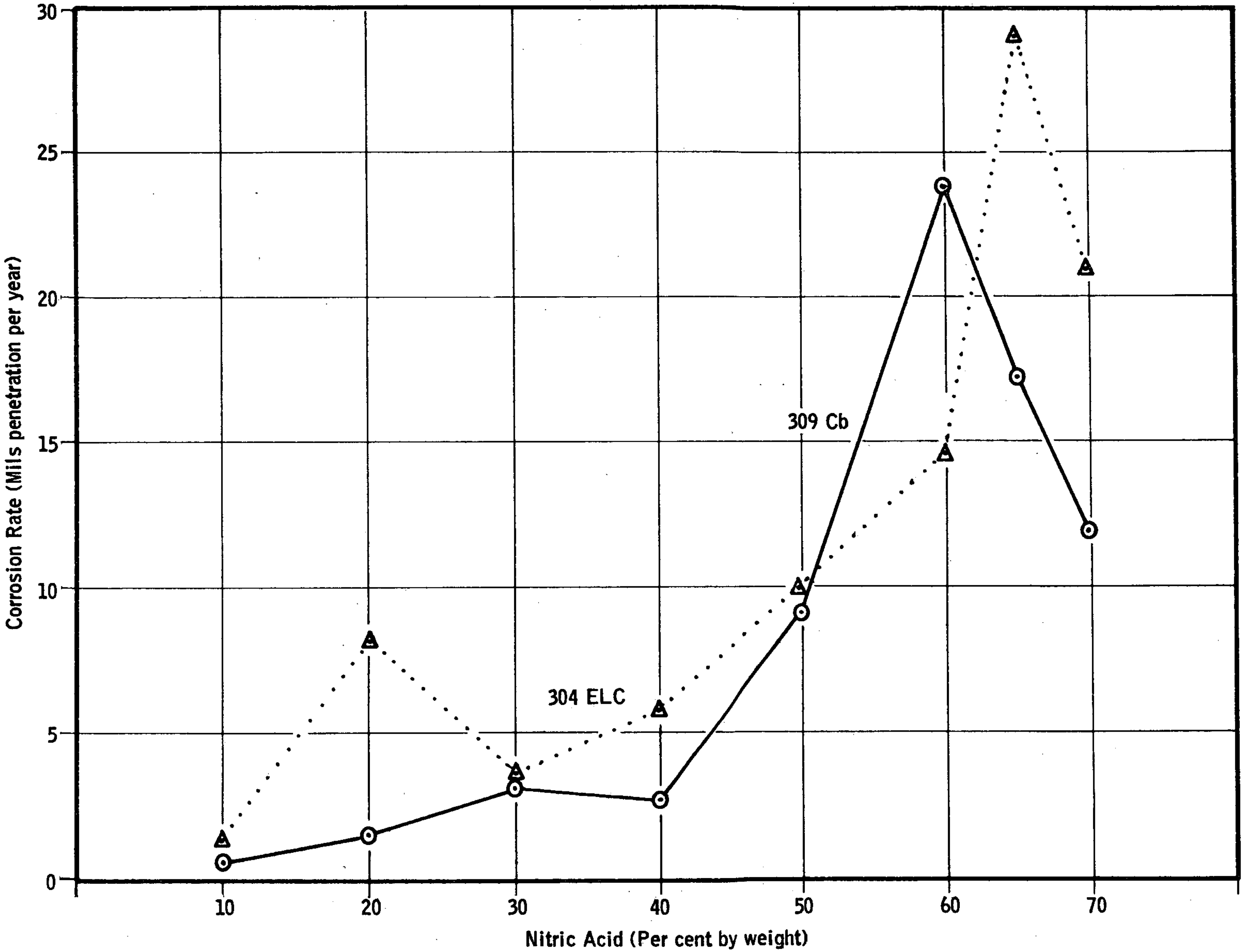

FIGURE 4-2 CORROSION RATES OF STAINLESS STEELS IN BOILING NITRIC ACID SOLUTIONS (EACH VALUE IS AN AVERAGE OF 2 TO 4 SAMPLES)

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5. DENITRATION PROCESS

5.1 REACTIVITY OF PORT HOPE POT SCALE, POT POWDER, AND ORANGE OXIDE PRODUCT – J. W. Votaw, G. G. Briggs, and D. E. Richards

This investigation was undertaken to determine the reason for the low final conversion to green salt exhibited by Port Hope orange oxide during the plant-scale tests at NLO in December, 1955. According to Port Hope, hard scale from the denitration pots represented about 5 per cent by weight of the final UO_3 product. It was considered possible that this portion of the final product was responsible for the low end conversion to green salt.

In January, 1956, therefore, Port Hope supplied samples (Table 5-1) of UO_3 scale and bulk powder from the same denitration pot, plus a sample from a subsequent production lot of UO_3 representative of product material being made at the time the scale and bulk powder were prepared. These samples were scheduled for:

1. Thermobalance reactivity determination
2. Chemical analysis
3. Spectrochemical analysis

In addition, samples were obtained from the same points in the NLO production stream and were scheduled for the same investigation so that they could be compared with the Port Hope materials. To date, only the examination of the Port Hope samples has been completed. Results obtained from examination of the NLO materials will be reported later.

Procedure

All samples were ground to pass a 100-mesh screen. For the thermobalance reactivity determinations, all samples were reduced at 1200°F and then were hydrofluorinated using a temperature programmed from 400° to 1200°F. For comparison, a sample of NLO sulfated "standard" UO_3 powder (Lot 3E-16-706) was run in the thermobalance under the same conditions. The sample weight in all cases was eight grams. The results of these reactivity tests are expressed in Table 5-1. Chemical and spectrochemical analyses are included in Table 5-2.

Results

1. No significant difference in hydrofluorination reaction rates was observed between the NLO "standard", the bulk pot powder, and the final product powder. Indeed, the reaction rate curves for these three samples showed identical abrupt changes of slope at the 55 per cent conversion level. All reached 96 to 97 per cent conversion to green salt in 40 minutes hydrofluorination time.

2. As shown in Table 5-1, a rate of reaction significantly higher than that of the NLO "standard" was obtained from the hydrofluorination of the sample of Port Hope pot scale. Furthermore, no abrupt change of slope was observed in the reaction rate curve. The sample reached 96 per cent conversion to green salt in 22.5 minutes hydrofluorination time.

   To date, no explanation of this high reactivity of the pot scale can be given. Examination of the chemical analysis data reveals a very low nitrate content for the scale, as might be expected, but the nitrate content of the bulk pot powder was at least of the same order. Neither is any significant discrepancy apparent in the spectrochemical analysis.

Further work is planned with these and similar samples of uranium trioxide from different sources. Section 5.3 reports a determination of the absolute density of these Port Hope samples. Also included in this report are (1) a thermobalance study of the reduction and hydrofluorination of recycled Port Hope orange oxide (Section 5.2) and (2) a plant-scale study of the UO_3 to UF_4 process in which recycled Port Hope UO_3 was one of the materials used (Section 8.1).

TABLE 5-1

HYDROFLUORINATION OF PORT HOPE UO_3

Sample Designation	Hydrofluorination Time Ratio* at Indicated Conversion Levels					
	60%	70%	80%	90%	95%	97%
Pot Scale	0.74	0.62	0.60	0.63	0.63	0.69
Bulk Pot Powder	0.85	1.02	1.11	1.12	1.06	1.03
Product Powder	1.04	1.10	1.07	1.04	1.01	1.00

$$* \quad \frac{\text{Time for hydrofluorination of sample to indicated per cent conversion}}{\text{Time for hydrofluorination of standard to indicated per cent conversion}}$$

(The standard is NLO sulfated UO_3, Lot No. 3E-16-706.)

TABLE 5-2

CHEMICAL AND SPECTROCHEMICAL ANALYSES* OF PORT HOPE UO_3

	Pot Scale	Bulk Pot Powder	Product Powder
Ag	1.0	1.0	1.0
Al	<4	<4	<4
As	30	35	30
B	<0.2	<0.2	<0.2
Bi	<1.0	<1.0	<1.0
Cd	<0.2	<0.2	<0.2
Co	<2.0	<2.0	<2.0
Cr	6	<4	6
Cu	40	30	40
Fe	35	20	45
Mg	1.0	<1.0	1.0
Mn	<4	<4	<4
Mo	<4	<4	<4
Ni	12	10	10
P	<20	<20	<20
Pb	4	3	4
SiO_2	<20	<20	<20
Sn	<1	<1	<1
V	<20	<20	<20
Zn	<20	<20	<20
UO_3	99.62%	97.94%	98.29%
NO_3	0.17%	0.52%	1.49%
SO_4	410	320	330
HCl-Insol	0.006%	<0.001%	0.054%
Moisture**	0.20%	1.99%	1.59%

* All values are ppm, except where indicated otherwise.

** "Moisture" is the loss at 760°F in 24 hours. It includes the loss of oxides of nitrogen.

5.2 REACTIVITY OF RECYCLED PORT HOPE URANIUM TRIOXIDE – J. W. Votow, G. G. Briggs, and D. E. Richards

As a result of the failure of Port Hope orange oxide to produce in-specification green salt during the plant-scale tests in December, 1955, it was decided to determine whether or not the reactivity of the original Port Hope material could be improved by redenitration at this site. Consequently, five lots of Port Hope UO_3 (No. 97, 99, 100, 102, and 103) were dissolved at the Pilot Plant and processed through the NLO denitration equipment. The resulting uranium trioxide was used as feed for Experimental Bank 2 in the Green Salt Plant.

Samples from the redenitration run were reacted in the laboratory thermobalance to compare their hydrofluorination reaction rates. The samples used are numbered and described in Table 5-3.

All samples were scheduled for:

1. Determination of hydrofluorination reactivity in a thermobalance.
2. Chemical analysis.
3. Spectrochemical analysis.

The latter two investigations have not been completed and will be reported later.

The variables in the reactivity determination were: the temperature of reduction and the size of sample reacted. All samples were ground to pass a 100-mesh screen.

TABLE 5-3

HYDROFLUORINATION RATE OF UO_2 PRODUCED BY LOW-TEMPERATURE* REDUCTION

Sample No.	Sample Designation†	Hydrofluorination Time Ratio** at Indicated Conversion Levels				
		60%	70%	80%	90%	95%
1	Composite of the 5 Original Port Hope Lots (Lots 97, 99, 100, 102, 103)	0.72	0.77	0.86	0.98	1.06
2	Lot 3F-16-031	0.50	0.64	0.70	0.84	1.04
3	Lot 3F-16-032	0.57	0.73	0.79	0.88	1.09
4	Lot 3F-16-033	0.63	0.84	0.89	1.05	1.11
5	Lot 3F-16-034	0.61	0.72	0.73	0.85	0.98
6	Pot 203 Scale††	0.76	0.77	0.79	0.88	0.97
7	Pot 203 Powder††	0.72	0.75	0.73	0.84	0.95
8	Pot 204 Scale††	0.71	0.77	0.75	0.85	0.97
9	Pot 204 Powder††	0.53	0.74	0.82	0.84	1.16
10	Pot 214 Scale††	0.48	0.59	0.60	0.66	0.74
11	Pot 214 Powder††	0.74	0.82	0.88	1.03	1.17

* Temperature of Reduction 1200°F.

** Time required for sample to reach indicated per cent conversion / Time required for standard to reach indicated per cent conversion

The standard used was NLO sulfated UO_3 (Lot No. 3E-16-706).

† All samples except sample 1 were redenitrated.

†† Samples 6 through 11 were taken from three pots in which Lot No. 3F-16-034 was produced.

Hydrofluorination of UO_2 Produced by Low-Temperature Reduction

Low-temperature reduction of all samples was performed in the thermobalance at a temperature of 1200°F. The weight of reacting powder in each case was eight grams. At completion of the reduction, the samples were cooled under H_2 to 400°F, at which point the hydrogen flow was stopped and HF was admitted to the reaction chamber. The temperature was allowed to rise at the maximum heating rate to a set point of 1200°F. Hydrofluorination was continued until the sample had reached 95 per cent conversion to green salt. Reaction rates of the various samples were compared to that of the NLO sulfated "standard" (Lot 3E-16-706) which had been determined under the same conditions. Results are given in Table 5-3.

With but one exception, the hydrofluorination reaction rates of the eleven samples and the NLO sulfated standard differed little in the range of 95 per cent conversion to green salt. Samples 1, 2, 3, 4, 9, and 11 required slightly longer periods of time to reach 95 per cent conversion than did the standard sample. The other samples required slightly shorter periods of time with the exception of the scale sample from Pot 214, which hydrofluorinated much faster than did the NLO "standard". The high reactivity of another sample of pot scale from a Port Hope denitration pot is discussed elsewhere in this report. No explanation of their high reactivity is advanced at this time.

Hydrofluorination of UO_2 Produced by High-Temperature Reduction

Samples 1 and 5 (Table 5-3) were selected for this group of experiments. Reduction of both samples was carried out in the reactivity train at 1650°F, except for one reduction (Sample 5) at 1800°F. (It was necessary to use the reactivity train for this purpose since it is very difficult to attain a temperature over 1400°F in the reaction chamber of the thermobalance.) In each case, the sample occupied diagonally opposite slots in the reactivity train boat, while NLO sulfated "standard" orange oxide occupied the other two positions. The boat was placed in the train and the temperature was raised under a nitrogen flow to 1650°F. At this point, the nitrogen flow was stopped and hydrogen was admitted to the chamber. Reduction was continued for 10 minutes. The reaction tube was cooled as rapidly as possible to 100°F, using a hydrogen purge, and then the boat was removed. Like materials from the two compartments were combined, ground, and placed in sealed sample bottles.

The hydrofluorination was performed in the thermobalance. A sample of brown oxide (UO_2) was weighed into the reaction pan and placed in the thermobalance at room temperature. The temperature of the thermobalance was raised to 400°F, at which point HF was admitted to the reaction chamber at a flow rate of approximately 1.0 liter per minute. The temperature was then allowed to rise to a set point of 1200°F at the maximum heating rate. Hydrofluorination was continued for 125 minutes. The reaction rate of each sample was compared with that of the NLO "standard" that had been reduced simultaneously with the sample (Table 5-4). The separate experiments included:

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TABLE 5-4

HYDROFLUORINATION RATES OF UO_2 PRODUCED BY HIGH-TEMPERATURE REDUCTION

Exp. No.	Sample No.	Reduction Temperature (°F)	Sample Weight (g)	Hydrofluorination Time Ratio* at Indicated Conversion Levels						% UF_4 at 100 min
				60%	70%	80%	85%	90%	95%	
1.	1	1650	8.0	1.17	1.29	1.69	2.10			84.5
	NLO "standard"	1650	8.0	1.00					1.00	94.9
2.	5	1650	8.0	1.00	1.02	1.07	1.11	1.15		91.4
	NLO "standard"	1650	8.0	1.00					1.00	94.2
3.	5	1800	8.0	1.17	1.17	1.19	1.23			85.0
	NLO "standard"	1800	8.0	1.00				1.00		89.7
4.	1	1650	2.5	1.05	1.16	1.46	1.81			86.0
	NLO "standard"	1650	2.5	1.00					1.00	96.0
5.	5	1650	2.5	0.74	0.84	0.92	1.01	1.13	1.67	94.5
	NLO "standard"	1650	2.5	1.00					1.00	98.6
6.	1	1650	2.5	1.23	1.19	1.13	1.11	1.08		92.3
	5**	1650	2.5	1.00				1.00		93.0
7.	Composite of Port Hope Lots 84-93	1650	2.5	1.20	1.31	1.56	1.72			87.7
	NLO "standard"	1650	2.5	1.00					1.00	98.0

$$* \quad \frac{\text{Time required for sample to reach indicated per cent conversion}}{\text{Time required for standard to reach indicated per cent conversion}}$$

** Lot 3F-16-034 was used as standard for basis of calculations.

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Experiment 1. The hydrofluorination rate of 8-gram samples of Sample 1 and of the NLO standard were compared (1650°F reduction).

Experiment 2. The hydrofluorination rates of 8-gram samples of Sample 5 and of the NLO "standard" were compared (1650°F reduction).

Experiment 3. The hydrofluorination rates of 2.5-gram samples of Sample 5 and of the NLO "standard" were compared (1800°F reduction).

In Experiments 4 and 5, Experiments 1 and 2 were repeated, using 2.5-gram samples of brown oxide produced by 10-minute reductions at 1650°F.

Experiment 6. The hydrofluorination rates of Samples 1 and 5 were compared (1650°F reduction).

Differences in hydrofluorination reactivity between Samples 1 and 5 and the NLO "standard", which were not apparent at low reduction temperatures (1200°F), were evident at a reduction temperature of 1650°F. Data from Table 5-4 (Exp. 1 and 4) indicate that high-temperature reduction produces a much more unreactive brown oxide from Port Hope UO_3 than from NLO sulfated UO_3. Since 1650°F more closely approximates the temperatures reached in the reaction zone of the reduction reactors in the Green Salt Plant than does 1200°F, these data indicate good correlation between experience with Port Hope material in the plant and in the thermobalance.

To check this (Exp. 7), a composite sample of the lots of Port Hope orange oxide which had failed to produce in-specification green salt in plant-scale tests was subjected to a high-temperature reduction in the reactivity train. The sample was then hydrofluorinated in the thermobalance. The resulting hydrofluorination reactivity was compared with that of the NLO sulfated standard reduced at the same time. The hydrofluorination time ratio closely paralleled that of Sample 1 (Exp. 4).

At a reduction temperature of 1800°F, the difference in reactivity between Sample 5 and the NLO "standard" widened appreciably over the difference found at 1650°F reduction (Exp. 3).

Experiment 6 was made in order to check correlation of the reactivity of Sample 1, Sample 5, and the NLO "standard". Although the Sample 5 material showed a slightly greater hydrofluorination rate than did Sample 1, no correlation was obtained. This discrepancy, as yet, has not been explained.

It should be mentioned that increasing the bed depth in the sample pan of the thermobalance produced a lower rate of reaction. Three NLO "standard" samples of 2.5-gram weight averaged 97.5 per cent conversion to green salt, while two NLO "standard" samples of 8 grams each averaged 94.5 per cent conversion at the end of 100 minutes hydrofluorination time.

Conclusions

The data (Exp. 2 and 5) show that dissolving and redenitrating Port Hope material in NLO equipment definitely enhanced the reactivity of the resulting uranium trioxide under the stated conditions of reduction and hydrofluorination.

5.3 ABSOLUTE DENSITY MEASUREMENTS – J. F. Blum

In an effort to evaluate physical properties which may be responsible for or may help one to predict variations in the reactivity of orange oxide, a program has been initiated to measure certain physical properties of UO_2 and UO_3 powders. The objective of this study was to evaluate a differential pressure method for measuring absolute densities. A review of methods employed in measuring the density of solids indicated that the gas-displacement method would be applicable for powdered solids.

The apparatus was essentially the same as that described by Partington.[1] Helium was used as the pycnometer fluid in the pycnometer tube because of its small molecular diameter (which would facilitate its entrance into the small void spaces of porous powdered materials) and because of its relatively low adsorption.

The equipment was initially calibrated with mercury (Table 5-5). Following the calibration, determinations were made on samples of silver nitrate and potassium chloride to determine the accuracy and precision which could be expected on powdered solids. These materials were chosen because previous work had been done on samples of these compounds employing a helium densitometer.[2] The results had indicated that these compounds would make good standards for powdered-solid runs. The results from a series of determinations on $AgNO_3$ and KCl (which were secured from Baker Chemical Company and met A.C.S. specifications of 99.6%) are recorded in Table 5-5.

Before this method was used on orange oxide samples, two factors which would introduce errors into the experimental density results were investigated:

1. The possibility of helium adsorption on the orange oxide powder during density measurements and

2. The effect of particle size on density results.

Samples of NLO orange oxide, Port Hope bulk orange oxide, and Port Hope normal product orange oxide were tested for helium adsorption. The samples were subjected to a helium atmosphere for 17 hours and the volume of gas adsorbed was measured. The results showed no significant gas adsorption in any of the samples over the 17-hour period.

A large sample of NLO orange oxide powder was screened to separate the different particle size fractions. Density determinations were performed on the +40 mesh fraction (U.S. Standard Sieve Series), the −80 mesh to +170 mesh fraction, and the −325 mesh fraction. The results (Table 5-6) show that the measured density did not vary with particle size.

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[1] *Partington, J. R., "An Advanced Treatise on Physical Chemistry", Vol. 3, p. 146, Longmans, Green and Co., New York 1952.*

[2] *Schumb, W. C. and Rittner, E. S., J. Am Chem. Soc., 65, 1692 (1943).*

TABLE 5-5

ABSOLUTE DENSITY MEASUREMENT*

Substance	Measured Density (g/cc)	Precision** (%)	Density[1] (Literature Value) (g/cc)	Density Value† (g/cc)	% Variation of Density from Literature Values
Hg	13.6	±0.8	13.53	–	0.8
$AgNO_3$	4.35	±0.9	4.35	4.349	0.0
KCl	1.96	±1.5	1.98	2.002	1.0

* All densities measured at room temperature (25 ±2°C).
** Each of the values is an average of at least four results.
† As calculated from lattice constant values.

Density determinations were made on Port Hope samples of bulk powder, reactor pot crust, and final product orange oxides. The results, including the per cent precision, are recorded in Table 5-6.

In summary, it can be said that it appears to be feasible to determine real densities of orange oxide samples by a differential pressure measurement. Tests conducted on samples of orange oxide powders have given a ±1 per cent precision. Particle size distribution and helium adsorption have no measurable effect on density results within experimental accuracy.

TABLE 5-6

ABSOLUTE DENSITY OF ORANGE OXIDE SAMPLES

Substance	Measured* Density (g/cc)	Average Deviation	Precision (%)
NLO Screened Powder			
+40 mesh	7.35	±0.05	±0.7
−80 to +170 mesh	7.40	±0.05	±0.7
−325 mesh	7.37	±0.06	±0.8
Port Hope Material			
Reactor pot bulk powder	6.87	±0.03	±0.5
Reactor Pot Crust	7.27	±0.05	±0.7
Normal Product	7.14	±0.04	±0.6

* Average of at least four results.

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[1] *Schumb, W. C. and Rittner, E. S., J. Am. Chem. Soc., 65, 1692 (1943).*

6. NITRIC ACID RECOVERY PROCESS

6.1 DRUM DRYING OF RAFFINATES – E. J. Beer, J. H. Cavendish, and A. Whitman

A series of laboratory tests on the drying of extraction raffinate on a drum dryer have been reported.[1,2] Operation of a semi-works unit has been started in order to evaluate performance with the widest possible range of raffinate feeds and to estimate drum and knife wear rates.

A 24-inch by 36-inch-long atmospheric twin-drum dryer has been installed in the Acid Recovery Area. A heated feed holding tank is supplied periodically with concentrated raffinate from the plant evaporator. This feed is circulated between the holding tank and the dryer feed pan by a LaBour centrifugal pump. Additional circulation, provided by a by-pass between the pump and holding tank, serves to keep the raffinate solids in suspension. The dryer is operated with splash feed in the conventional manner. The dried product is collected in drums and stored for future calcination. To avoid dilution of the nitric acid off-gases, the entire system is enclosed in a stainless steel housing.

Preliminary studies have shown the rapid knife blade wear that had been predicted from laboratory tests. The durability of both Stellite and precipitation-hardened stainless steel is being investigated. Both laboratory corrosion tests (Section 6.2 of this report) and the limited semi-works experience have indicated low rates of attack on the chromium-plated cast iron drums which are being used.

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[1] *Whitman, A., and Blum, J. F., Summary Tech. Rpt., p. 65, NLCO-565, July 15, 1955.*

[2] *Whitman, A., Blum, J. F., and Collopy, T. J., Summary Tech. Rpt., p. 37, NLCO-577, October 17, 1955.*

6.2 LABORATORY STUDIES OF THE CORROSION RESISTANCE OF A CHROME-PLATED DRUM DRYER TO NLO RAFFINATE SOLUTIONS – N. N. Peters and F. H. Meyer

A program was initiated by Chemical Department personnel[1] of National Lead Company of Ohio to investigate the feasibility of drum-drying raffinate concentrate solutions in the Acid Recovery Area. Progress in that program led to this investigation of materials of construction for the dryer unit by the Corrosion Section of the Metallurgical Department. The purpose of this study was to determine whether or not failure of the drum dryer surface (gross pitting) would be produced by long-term exposure to the raffinate solution.

The unit to be purchased for the test in the Acid Recovery Area was to be fabricated from cast iron, with the drying surface chromium-plated to a thickness of approximately 0.006 inch. Two grades of cast iron were available for drum fabrication, one being more resistant to corrosive conditions than the other. Their analyses were as follows:

Cast Iron for Use Under Normal Noncorrosive Conditions

C (%)	S (%)	P (%)	Mn (%)	Si (%)
2.9 to 3.2	0.13 (max)	0.20 (max)	0.90 to 1.20	1.1 to 1.4

Ultimate tensile strength (2-inch-diameter test bar): 38,000 to 42,000 psi.

Brinell hardness on drum surface (unplated): 170 to 230 BHN

Cast Iron Alloy for Use Under Corrosive Conditions

C (%)	S (%)	P (%)	Ni (%)	Mo (%)
2.95 to 3.15	0.13 (max)	0.15 (max)	1.65 to 1.85	0.65 to 0.85
	Cr (%)	Mn (%)	Si (%)	
	0.25 to 0.35	0.60 to 0.70	1.15 to 1.25	

Ultimate tensile strength: 50,000 to 60,000 psi.

Brinell hardness: 250 to 290 (on test specimen)

240 to 280 (on machined surface)

Flake graphite size: A 5 or smaller.

The unit purchased for use in the Acid Recovery Area was made of the second-listed cast iron.

The raffinate solution that was to be dried contained 32.9 per cent HNO_3, 800 ppm fluoride, and 182 ppm chloride. From preliminary tests, it was suspected that minute pinholes in the chromium plating would leave the cast iron base metal exposed to the corrosive attack of the raffinate solution.

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[1] *Whitman, A. and Blum, J. F., Summary Tech. Rpt., p. 65, NLCO-565, July 15, 1955.*

Methods, Data, and Discussion

A laboratory-scale drum was received from Buflovak Equipment Division of the Blaw-Knox Company, Buffalo, New York. It was fabricated from the first listed cast iron and had a 0.002 to 0.004-inch chromum plating. Choice of this drum was made primarily because Blaw-Knox had a unit available. It was thought likely that if the cast iron used in the corrosion studies proved satisfactory, the cast iron used in the larger drum dryer would prove equally satisfactory or superior.

A mounting frame, drive mechanism, heating units, temperature controllers, etc. were assembled in the laboratory for use with this unit, which is shown in Figures 6-1 and 6-2. The drum was driven at approximately five rpm and was heated internally by gas burners, the surface temperature being maintained at 325°F by a pyrometer controller.

As Table 6-1 indicates, the raffinate solution (which analyzed 32.9 per cent HNO_3, 800 ppm fluoride, and 182 ppm chloride) initially was sprayed onto the heated drum surface and the dried materials were scraped off, using various types of blades. It was thought, after 30.5 hours of operation, that the initial coating of dried materials tended to protect the chromium-plated surface from exposure to the liquid raffinate solutions. Therefore, the method of applying raffinate solution was changed so that the rotating heated frum was partially immersed in a bath of the solution. This allowed almost continuous exposure of the chromium-plated surface to the solution. No measures were taken to remove the dried particles from the drum surface, since they went back into solution when re-immersed in the raffinate bath.

Table 6-1 summarizes data which were obtained when the immersion technique of applying the raffinate was used. It will be noted that this technique actually cleaned the drum surface of the discolored surface areas which had been noted during the first few days of operation when the spraying technique was used. After 45 hours of operation, a number of areas showing mild pitting were observed. One area was particularly noticeable with the naked eye, while other areas were discernible only with a hand lens. A second batch of raffinate solution, which was received for testing purposes on Fabruary 16, 1956, analyzed 28.2 per cent HNO_3, 450 ppm fluoride, and 138 ppm chloride. Tests were started on Fabruary 16, 1956, with this solution and were suspended February 18, 1956, as is indicated in Table 6-1.

A series of auxiliary heat-transfer-type tests were run, using the unit shown in Figure 6-3. In this apparatus, test specimens were clamped at the ends of the glass pipe "T", using Teflon gasketing. The glass pipe (fitted with test specimens) was filled with raffinate solution and heat was applied to the metal test specimens from the outside, using specially adapted heating units. The setup, served to show the effects of raffinate continuously in contact with the exposed metal surfaces at 325° to 350° F surface temperatures. Temperature of the heating units was controlled by a thermocouple in contact with the specimen surface. This setup allowed us to obtain useful supplementary data.

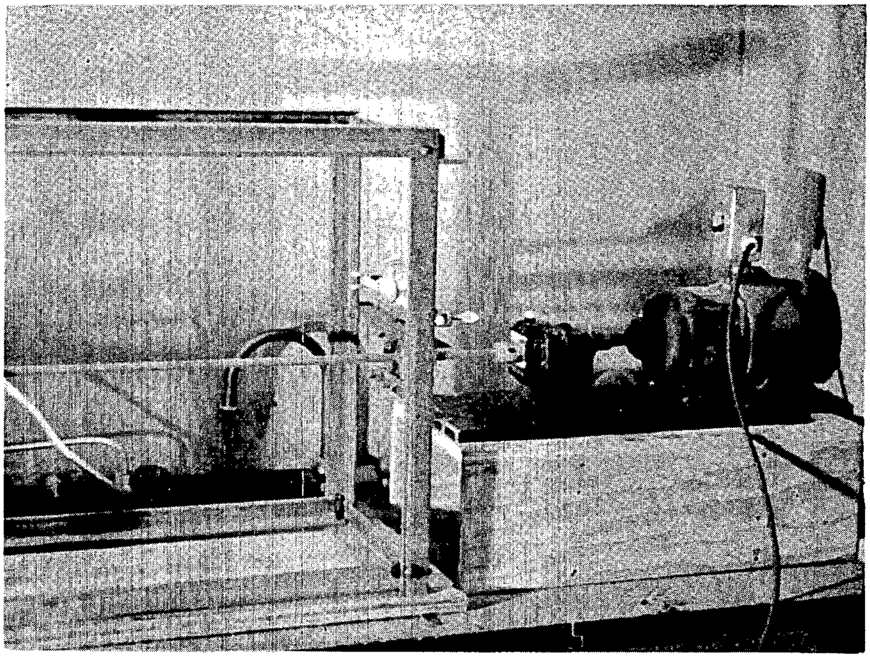

FIGURE 6-1 EXPERIMENTAL DRUM DRYER UNIT, SHOWING DRIVE MECHANISM.

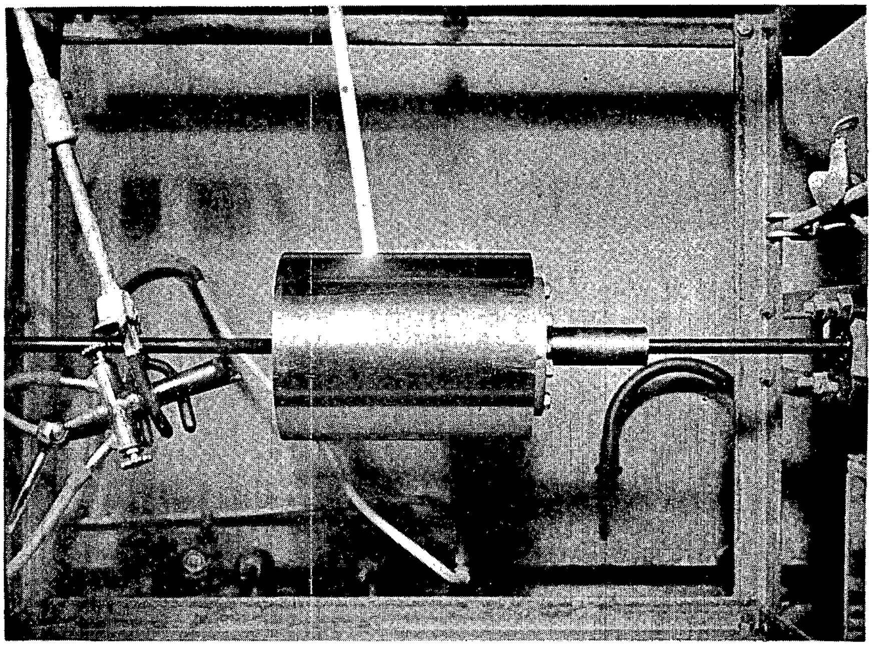

FIGURE 6-2 EXPERIMENTAL DRUM DRYER UNIT, SHOWING DRUM MOUNTING, HEATING MECHANISM, AND SURFACE BEFORE EXPOSURE.

TABLE 6-1

EXPOSURE OF HEATED LABORATORY DRUM DRYER TO RAFFINATE SOLUTION
(December 12, 1955 to February 18, 1956)

Date	Hours of Operation		Amount of Raffinate Dried (oz)		Method of Application	Remarks
	Each Day	Cumulative	Each Day	Cumulative		
12/29/55	9		72		Spray	Discoloration of chrome coating
1/3/56	6	15	48	120	Spray	Increased darkening of chrome coating
1/5/56	7	22	72	192	Spray	Significant darkening of chrome coating. Mottled dark and light surface area. Some pits showed deepening. Raffinate baked hard and was difficult to remove
1/6/56	4	26	40	232	Spray	Uniform darkening of chrome coating. Brazes on sprocket support failed
1/11/56	4.5	30.5	56	288	Spray	No change
1/11/56	2.5	33	160	448	Partial immersion of drum	Darkened surface appearance of chrome coating disappeared
1/12/56	6	39	208	656	Partial immersion	Excellent raffinate adherence to drum for drying cycle
1/13/56	6	45	192	848	Partial immersion	Mild pitting evident
1/16/56	3	48	96	944	Partial immersion	No change
1/17/56	6	54	160	1104	Partial immersion	No change
1/18/56	6	60	224	1328	Partial immersion	No change
1/19/56	6	66	192	1520	Partial immersion	No change
1/20/56	6	72	192	1712	Partial immersion	No change
1/25/56	5	77	150	1862	Partial immersion	No change
1/26/56	5	82	150	2012	Partial immersion	No change
1/27/56		82		2012		Tests suspended due to lack of evaporator by-product solution
2/16/56	5	87	256	2268	Partial immersion	New supply of raffinate evaporator by-product solution received. No change in drum surface appearance
2/17/56	4	91	224	2492	Partial immersion	No change in surface appearance noted. New raffinate supply so viscous that difficulty was experienced in extended operational time
2/18/56						Lab tests suspended

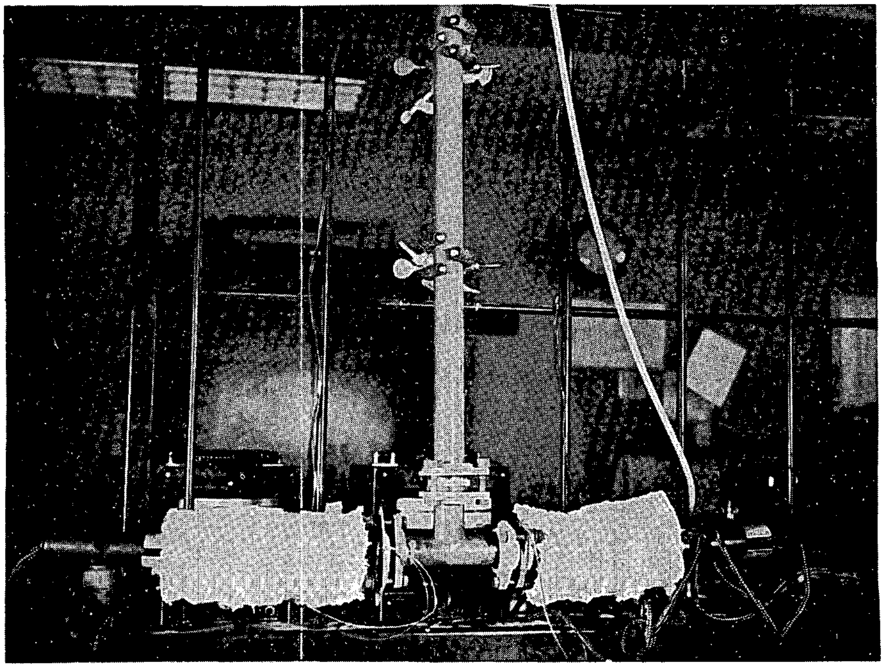

FIGURE 6-3 TWO-POSITION HEAT-TRANSFER CORROSION TEST APPARATUS.

A series of 100-hour exposure tests gave us some qualitative data on Type 430 stainless steel, Type 304 stainless steel, and Type 1020 carbon steel. Attack was mild on Type 430 stainless steel, very mild on Type 304 ELC stainless steel, and very severe on Type 1020 carbon steel. On Type 1020 carbon steel, the corrosion rates were 3020 milligrams per square decimeter per day and 555 mils per year.

The disparity of rates between the heat-transfer tests and the drum dryer operational tests indicated to us that the temperature of the drum dryer was:

1. High enough to prevent acid from staying in a liquid form on the drum surface for any period of time, and
2. High enough to prevent corrosive attack on the plated surface when dried raffinate was removed continuously.

In the case of the heat-transfer tests, however, liquid was continuously in contact with the surface of the metal, causing heavy attack.

Conclusions

1. Our tests indicate that when the chromium plate is exposed to the raffinate test solution, pitting may be expected. How serious a condition this may lead to has not been established.

2. The corrosion resistance of both the cast iron and the chromium plate on the drum surface have been considerably better than was originally anticipated.

3. On the basis of these tests, we believe that the original choice of materials of construction was suitable from a corrosion viewpoint.

7. URANIUM HEXAFLUORIDE REDUCTION PROCESS

7.1 UF_6 FLOW MEASURING DEVICE – F. M. Teetzel

The metering of UF_6 in the Uranium Hexafluoride Reduction Plant (Plant 7) has been and continues to be inaccurate and unreliable. The formation of scale (oxyfluorides) within the metering lines and on the orifice leads to inaccurate metering in the present orifice – differential pressure transmitter systems. Very close supervision is required when maintenance work is done on the systems. Other sites use this method of metering UF_6 with success, but their systems include provisions for purging their lines with fluorine or fluorine trichloride. Such a purge removes all deposits from the lines and restores a system to its original calibrated condition. This procedure is not followed at NLO, where a flow-measuring system which has become coated with oxyfluorides must be disassembled for cleaning. When the lines are reassembled, leaks sometimes occur which cause the scale to form within the lines very rapidly, making the just-completed cleanup futile.

A UF_6 measuring device which has a quickly and easily replaceable sensing element is needed. It has been recommended that an adaptation of the Hastings air flow meter be evaluated for this application. The sensing element in the Hastings meter consists of one electrically heated thermocouple and one nonheated thermocouple which can be inserted in the flow line with a tee. This sensing element is to be made of materials not subject to corrosion by the process gas, and is to be readily replaceable by a spare unit. The difference in temperature between the thermocouples can be calibrated directly as a function of the flow rate. The sensing element will be connected to a standard Hastings air flow meter which will be calibrated by checking the meter reading against material balance reports.

7.2 THERMOBALANCE DETERMINATION OF REACTION RATES FOR THE HYDROGEN REDUCTION OF UO_2F_2 – J. W. Votaw, G. G. Briggs, R. E. DeMarco, D. E. Richards, R. C. Abbott, and D. C. Bonfer

Reaction rates during the hydrogen reduction of UO_2F_2 to UO_2 were investigated at temperatures of 1200°F and 1400°F in the thermobalance.[1] The UO_2F_2, which was prepared by NLO Pilot Plant personnel by the steam hydrolysis of UF_6, was a light fluffy powder containing about 1.1 per cent volatiles (presumably moisture).

Experimental Procedures and Results

A 4.220-gram sample of the UO_2F_2 powder was placed in the platinum basket normally used for thermobalance work with powders. The bed depth was about 3/16 inch. The basket was then suspended in the thermobalance reaction chamber, which had been preheated to the desired

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

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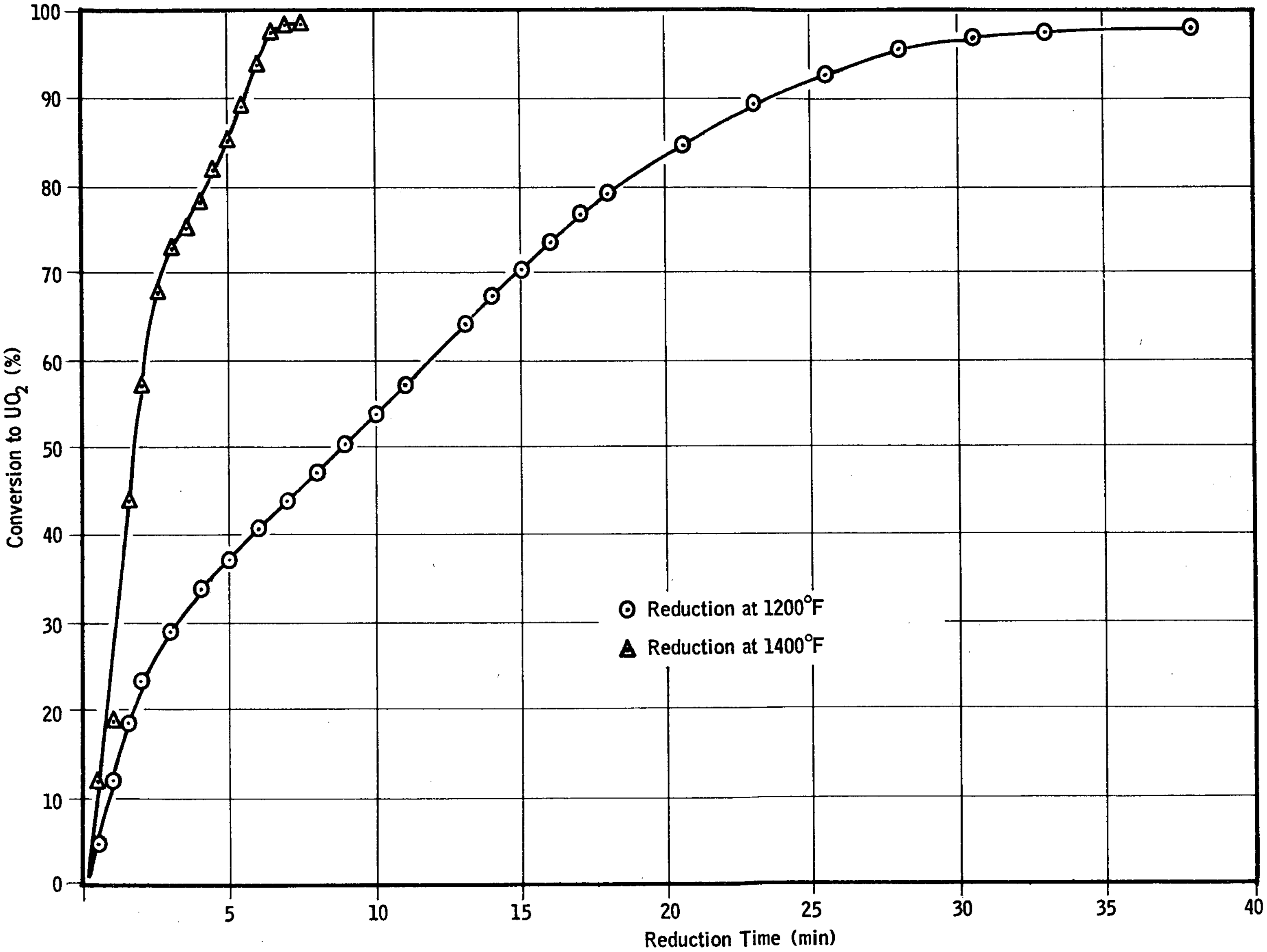

FIGURE 7-1 HYDROGEN REDUCTION OF UO_2F_2 POWDER TO UO_2

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temperature. A nitrogen atmosphere was maintained while the head was bolted onto the chamber and while preparations were made to introduce the reactant hydrogen gas. Hydrogen, at a rate far in excess of stoichiometric requirements, was then admitted. The loss in weight of the sample during reaction was recorded at 30-second or longer intervals, depending on the rate of reaction.

The reaction curves for the two runs at 1200°F and 1400°F are presented in Figure 7-1. The changes in weight of the samples indicate final conversions to UO_2 of 98 per cent. The reaction rate appears to be strongly temperature-dependent.

After the UO_2 was removed from the reaction chamber at room temperature, it was observed that the sample had undergone considerable shrinkage but that the density of the material was much lower than that of UO_2 normally produced from pot-denitrated UO_3.

The relatively rapid reduction of the UO_2F_2 in powder form is in sharp contrast with the slowness of the reaction when the UO_2F_2 has been prepared in pellet form. (Section 9.4 of this report, A Thermobalance Study of the Reactions Involved in the Conversion of Ammonium Diuranate to Green Salt.)

8. GREEN SALT PROCESS

8.1 PLANT EQUIPMENT AND PROCESS STUDIES IN THE UO_3 TO UF_4 PROCESS – W. Burkhardt, R. L. Maddox, E. W. Mautz, J. A. Mazzei and J. F. Schonberger

The majority of equipment modifications made to the experimental bank in the Green Salt Plant have been reported previously.[1] During the first three months of 1956, a Buell-design cyclone was installed in the HF off-gas system, and a Dracco paddle-type level-controller was installed in the UF_4 product seal hopper. These equipment modifications, as well as process studies on NLO sulfated UO_3 and Port Hope UO_3 are reported here.

Equipment Modifications

1. A Buell-design cyclone was installed to replace the Hoffman-design cyclone formerly used in the HF off-gas system. The Buell-design cyclone failed mechanically at the light-gauge flanges, and as modifications would have delayed process studies, the Hoffman-design unit was reinstalled. The Hoffman cyclone has served satisfactorily.

2. A Dracco torque-motor, single-agitator level-controller was installed in the UF_4 product seal hopper. This unit has performed satisfactorily after the shaft packing gland was modified. Braided Teflon installed as a continuous-length packing interfered with the operation of the level-controller either by producing high torque or by allowing HF to leak, depending upon the packing gland adjustment. Therefore, the packing employed for the Dracco unit consisted of individual rings of braided Teflon cut to a snug fit around the shaft.

   A Bin-O-Matic level-controller of similar principle was unsatisfactory due to the integrated bearing-packing assembly, which allowed leaking of HF into the motor.

3. Electric clocks have been installed in the reactor temperature control circuits of all heating zones to permit heat balance and efficiency studies.

4. Other equipment which has given satisfactory service includes the reduction reactor steam-injection system, the air-cooling system for the first hydrofluorination reactor, and the seal hopper between the reduction reactor and the first hydrofluorination reactor (HFN). The reduction reactor screw (fitted with 16 thermocouples) has permitted internal temperature measurement. Since installation, four of the original sixteen thermocouples have failed.

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[1] *Burkhardt, W., Maddox, R. L., Mautz, E. W., Mazzei, J. A., and Schonberger, J. F., Summary Tech. Rpt., Vol I, pp. 49-50, NLCO-600, December 15, 1955.*

Process Studies

Feed materials processed during this period included NLO sulfated orange oxide and Port Hope orange oxide (from Eldorado Mining and Refining, Ltd.). Two types of Port Hope material were processed: (1) as-received orange oxide and (2) orange oxide which had been dissolved in nitric acid and denitrated at National Lead. Table 8-1 summarizes the product analyses and the process variables; Table 8-2 presents other process rates held constant throughout the tests for the NLO sulfated UO_3. Tables 8-3 and 8-4 show the same kind of data for the Port Hope UO_3 tests.

Using NLO sulfated UO_3, it is noted (Table 8-1) that the product UF_4 assay was improved by increasing the reduction reactor main screw speed from 4 to 8 rpm. The use of steam in the reduction reactor improved the UF_4 assay at both 4 and 8 rpm and, in addition, permitted the AOI specification (ammonium oxalate content: 1.90%) to be met, whereas the change in screw speed alone did not lead to attainment of AOI specification.

Table 8-3 shows that the AOI specification was met by lowering the set temperatures in the first hydrofluorination reactor when redenitrated Port Hope orange oxide was used. Unfortunately, the virgin Port Hope UO_3 could not be tested at the same conditions, due to an inadequate inventory of this material. Lowering the reduction reactor set temperatures while testing virgin Port Hope UO_3 did not appreciably improve the UF_4 assay, since the AOI content decrease was accompanied by a UO_2F_2 content increase. The lowered first HFN temperatures permitted the production of specification (conversionwise) green salt. (The specification, conversionwise, means AOI content 1.9 per cent maximum, UO_2F_2 content 2.9 per cent maximum, and UF_4 content 96 per cent minimum.)

TABLE 8-1

PROCESS RATES – REDUCTION AND HYDROFLUORINATION OF NLO SULFATED UO_3

Test	Feed Rate ($lb\ UO_3/hr$)	Reduction Reactor: Main Screw Speed (rpm)	Reduction Reactor: Steam (SCFH) Rate at 1000°F and 10 psig	HF* Rate	Product Analysis: % AOI**	Product Analysis: % UO_2F_2	Product Analysis: % UF_4
A	380	4	0	2.5	2.71	2.15	95.14
B	390	8	0	2.4	1.93	1.27	96.80
C	394	4	700	2.5	1.49	1.42	97.09
D	370	8	700	2.5	1.61	0.99	97.40

* HF rate is given as "times theoretical".

** Ammonium oxalate insoluble content.

TABLE 8-2

PROCESS RATES THAT WERE UNCHANGED DURING REDUCTION AND HYDROFLUORINATION OF NLO SULFATED UO_3

1. H Rate: 1.5 × "theoretical" (dissociated ammonia used)
2. Main Screw Speed
   First HFN: 11 rpm
   Second HFN: 12 rpm
   Final HFN: 14 rpm
3. Reactor Set Point Temperatures (°F)

	Zone 1	Zone 2	Zone 3	Zone 4
Reduction	1200	1200	1200	1200
First HFN	480	600	700	900
Second HFN	850	920	970	1050
Final HFN	1020	1070	1100	1150

4. The first hydrofluorination reactor was air-cooled to the extent needed to maintain set temperatures.
5. The steam used in the reduction reactor was approximately at 1000°F and 10 psig.

TABLE 8-3

PROCESS RATES – REDUCTION AND HYDROFLUORINATION OF PORT HOPE UO_3

Test	Feed Rate (lb UO_3/hr)	Feed Type*	Reduction Reactor		HF** Rate	Reactor Set Temp.†		Product Analysis		
			Screw Speed (rpm)	Steam (SCFH)		Redn	1st HFN	% AOI	% UO_2F_2	% UF_4
E	160	VPH	4	0	3.0	Nor†	Nor‡	3.84	1.77	94.39
F	190	VPH	4	0	2.9	Low††	Nor	2.42	2.81	94.77
G	235	RPH	8	800	2.8	Nor	Nor	4.89	1.69	93.42
H	185	RPH	8	800	3.0	Nor	Low‡‡	0.80	2.12	97.08
I	200	RPH	8	800	2.8	Nor	Low	1.24	2.17	96.59
J	175	RPH	8	0	2.9	Nor	Low	0.76	1.79	97.45

* *VPH: Virgin Port Hope UO_3; RPH: Port Hope UO_3 that had been redenitrated at NLO*

** *HF rate is given as "times theoretical"*

† *Normal reduction temperatures: All four zones at 1200°F*

†† *Lowered reduction temperatures: All four zones at 1000°F*

	Zone 1	Zone 2	Zone 3	Zone 4
‡ *Normal hydrofluorination temperature*	480°F	600°F	700°F	900°F
‡‡ *Lowered hydrofluorination temperature*	400°F	500°F	600°F	800°F

TABLE 8-4

PROCESS RATES THAT WERE UNCHANGED DURING REDUCTION AND HYDROFLUORINATION OF PORT HOPE UO_3

1. H_2 Rate: 1.5 × "theoretical" (dissociated ammonia used)
2. Main Screw Speeds
    First HFN: 11 rpm
    Second HFN: 12 rpm
    Final HFN: 14 rpm
3. Reactor Set Point Temperatures (°F)

	Zone 1	Zone 2	Zone 3	Zone 4
Second HFN	850	920	970	1050
Final HFN	1020	1070	1100	1150

4. The first hydrofluorination reactor was air-cooled to the extent needed to maintain set temperatures.
5. The temperature of the steam to the reduction reactor was approximately 1000°F.

8.2 INTERNAL TEMPERATURE MEASUREMENTS IN A REDUCTION REACTOR –

F. M. Teetzel and A. E. Abbott

The thermocouples and associated apparatus used for making temperature measurements in the reduction (cocoa) reactor of Bank 2 in the Green Salt Plant were described previously.[1] Switches have been installed which facilitate the selection of the thermocouples whose outputs are to be recorded, but otherwise the equipment is essentially unchanged.

Four of the Ceramo thermocouples are now inoperative, but the reason for their failure will not be known until the screw is again removed from the reactor. The couples which have failed are located in the zone where the highest rate of reaction and, therefore, the highest temperature occurs. Since the temperatures recorded in this zone have not been so high that this, in itself, should have caused the failures, it is postulated that the sulfate feed has caused the Inconel sheathing to corrode. Subsequent failure would occur in the hottest zone as that is where the corrosion would proceed at the highest rate. For this reason, replacement Ceramo thermocouples sheathed with Type 310 stainless steel have been ordered.

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[1] *Teetzel, F. M. and Abbott, A. E., Summary Tech Rpt., Vol I, pp. 51-55, NLCO-600, January 16, 1956.*

Experiments to determine the response characteristics of the Ceramo thermocouples have been run. The 3/16-inch, grounded-junction Ceramos such as now in use required about four seconds to indicate 90°C when moved from ice water to boiling water. This is considered to be a very good response time for such a device. More work must be done to determine the heat-transfer coefficient between the powder and the Ceramo. With such data, we should be able to interpolate fairly accurately the <u>true</u> bed temperatures from the <u>indicated</u> temperatures.

9. MOVING BED REACTOR

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

An interim report covering all MBR activities during the year, 1955, has been published.[1]

Most of the modifications[2] made to the reactor system in the last quarter were evaluated during a simultaneous reduction-hydrofluorination run (Run 30) using starch-UO_3 pellets as feed.

Objectives of Run 30

1. To continue in Run 30 the evaluation of the starch-UO_3 process which was begun in Run 29.

2. To evaluate the recent modifications to the MBR system.

Description of Run 30

UO_3 pellets containing about 7 per cent starch served as the feed material for this test. The starch pellets had been prepared during June, 1955, and represented the remainder of the feed prepared for Run 29. The operating conditions for Run 30 essentially duplicated those of Run 29:

1. Feed Rate: 350 lb UF_4/hr

2. HF Rate: 110 per cent of stoichiometric

3. Reactor Residence Time: 5 hours

4. Manifold HF Cooling: as required

Run 30 never advanced beyond the startup phase, for frequent plugging or bridging was encountered in the hydrofluorination reactor (hydrofluorinator). Additional difficulty was caused by a partially blocked seal leg and a plugged off-gas line. However, the major objective of the run, the evaluation of the recent modifications to the reactor system, was accomplished.

Conclusions (Run 30)

1. Based on the results of Runs 29 and 30, it was concluded that the existing MBR system is not amenable to the processing of starch-UO_3 pellets.

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[1] *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.*

[2] *Burkhardt, W. et al., Summary Tech. Rpt., Vol. I, pp. 77-78, NLCO-600, January 16, 1956.*

2. The cross-shaped gas distributor (spider) located in the cone of the hydrofluorination reactor could not be completely evaluated because of the intermittent, non-typical operation; however, temperature profiles recorded during reactor heatup indicated a uniform heating of the pellet bed. It was also indicated that the solids flow would not be impeded by the presence of the spider near the reactor discharge port.

3. The new six-inch rotary valve, located at the cone of the hydrofluorinator, operated smoothly throughout the run. Occasional plugging of the product downcomers was experienced, since the new valve could discharge larger lumps of material than could the previous four-inch valve; however, plugged downcomers should not be encountered in routine operations, as agglomeration of normal UF_4 pellets should not occur.

4. The redesigned cyclone separator system in the hydrofluorinator off-gas line appeared to perform satisfactorily. Plugging of the off-gas line during the run was caused by a section of the off-gas line not being heated, which permitted the condensation of water and HF. The liquid HF ran back to the cyclones and caused a buildup of wet solids which eventually plugged the line. This situation was corrected and the cyclones worked satisfactorily during the second attempted startup of Run 30.

5. A full-opening plugcock, installed in the off-gas line from the hydrofluorination reactor, worked satisfactorily. The plugcock replaced a gate valve which had tended to plug during previous hydrofluorination runs.

6. The electrical heaters installed on the bottom one-third of the hydrofluorination reactor gave trouble-free operation throughout the run. It was possible to maintain a wall temperature of 1000°F in the heated zone, thus minimizing heat losses from this sector of the reactor. The effect of the resultant higher pellet bed temperatures upon the ultimate conversion to UF_4 could not be evaluated because of operating difficulties encountered during the run.

   The heaters were also beneficial to the heatup operation, reducing by two hours the time required to bring the pellet bed to temperature.

7. The pellet feed pipe has been centered in the reduction reactor. The effect of this modification upon gas channeling will be determined during the next reduction run.

   It is anticipated that a final evaluation of all recent modifications to the reactor system can be made when sufficient UO_3 is available for normal reduction and hydrofluorination runs.

Recommendations for Future Runs

A critical analysis of the data from previous reactor runs has indicated the need for more data concerning temperature gradients and solids composition gradients within the pellet bed. Furthermore, more precise operating data are required in order to permit the calculation of energy balances and heat losses from the reactor surfaces. Alterations required in order to accomplish the above objectives have been made preparatory to the resumption of reactor operation in the near future.

9.2 MBR PELLET DEVELOPMENT - PILOT PLANT INVESTIGATIONS - R. H. Sisson, P. W. Henline, E. J. Walter, and A. J. Klee

Confirming principles developed during recent laboratory studies, Pilot Plant investigations of the factors affecting UO_3-H_2 mixture characteristics have demonstrated that:

1. NLO sulfated UO_3 may be continuously mixed and extruded in the present Pilot Plant equipment by the addition of 10 per cent NH_4OH to the slurrying liquor. Yield and reactivity of the resultant pellets, however, are relatively poor.

2. NLO sulfated UO_3 may be continuously mixed and nodulized in the present Pilot Plant equipment with the die plate removed, at NH_4OH concentrations ranging from 0 to 5 per cent. The yield is not significantly reduced from that obtained by extrusion in the Pilot Plant equipment and the reactivity, as indicated by laboratory tests, compares favorably with that of laboratory pellets made from the same UO_3 powder.

3. Port Hope UO_3 may be continuously mixed and extruded at 5 per cent NH_4OH. Since this particular lot of UO_3 was used to determine the validity of the conclusions from laboratory studies, no yields were determined nor were reactivity tests made on the resultant pellets.

Operating difficulties and excessive downtime of present equipment ensuing from a completely frozen pug mill have been materially reduced by (1) Controlling the moisture content of the UO_3-water mixture so that is stays below the critical value, (2) Operating the mixer-extruder at reduced feed rates (500 lb/hr or less) and at maximum speed in order to reduce the holdup of UO_3-H_2O mixture in the unit, and (3) Using NH_4OH to prolong the set time.

Low pellet yields may have resulted from variations in mixture consistency with time. The variation has been checked by (1) The Bendix Ultra-Viscoson and (2) Moisture determinations on grab samples taken at regular intervals.

Future Work

To decrease consistency variations in the present equipment, it is planned to:

1. Install a more efficient spray system for H_2O addition to UO_3 in the pug mill. (The spray system has been designed.)
2. Evaluate a muller-mixer to be used in conjunction with the present pug mill. The unit has been obtained on a rental basis.

Low pellet yields may result from poor material-handling facilities following extrusion or nodulizing. To overcome the effect of this factor and to further reduce manpower requirements, it is planned to:

1. Move and combine the present screening station with the present milling system.
2. Screen out and mill only +½-inch material.
3. Lower the Bonnot extrusion unit to the minimum possible height above the present drying belt.

Although the determination of critical mositure content on particular lots of UO_3 has proved to be a significant test for Pilot Plant mixing, the method for determining set times (as measured in the laboratory) must be revised. This is particularly true for pellets that are extruded.

9.3 THE EFFECTS OF REDUCTION TEMPERATURE AND DEGREE OF HYDRATION ON THE REACTIVITY OF UO_2 PELLETS – G. G. Briggs, J. W. Votaw, R. E. DeMarco, D. E. Richards, R. C. Abbott, and D. C. Bonfer

Previous studies[1] performed in the Green Salt Laboratory indicate that two factors are of major importance in their effect on the hydrofluorination reactivity of UO_2 pellets produced in the MBR. These are:

1. The degree of hydration of the UO_3 powder accomplished during the manufacture of the UO_3 feed pellets.
2. The temperature existing in the reduction reactor during the conversion of the UO_3 to UO_2.

A study was undertaken to obtain more detailed information concerning these two factors.

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[1] *Votaw, J. W., Briggs, G. G., Richards, D. E., Abbott, R. C., and Drew, J. D., Summary Tech. Rpt., pp. 58-63, NLCO-577, October 17, 1955.*

Hydration

Two batches of hydrated pellets differing in water content were prepared in the laboratory from 100-gram quantities of a sulfated NLO pot-denitrated UO_3 (Lot 3E-16-706). The method involved the following steps:

1. Distilled water was added to the UO_3 powder in sufficient quantity to form a stiff paste. The quantity of water (13 or 14 ml per 100 grams UO_3) was in excess of that required to form the hydrate, $UO_3 \cdot 2H_2O$. To obtain pellets containing a high water content, 14 milliliters of water were added to 100 grams of the UO_3; pellets containing a low water content were produced by using 13 milliliters of water per 100 grams of the UO_3.

2. The paste was spread into a layer approximately ¼-inch thick on a sheet of aluminum foil.

3. The layer was sliced into ¼-inch cubes after initial setting had begun.

4. A heat lamp was focused on the pellets to hasten setting. The time of heating with the lamp was limited to 100 seconds for a final water content of 10.3 per cent (based on the weight of the hydrated pellets) and heating with the lamp for 20 minutes gave a final water content of 7.3 per cent.

5. The pellets were transferred to sample bottles which were then tightly capped to prevent escape of moisture before the hydration reaction was complete.

6. After remaining in the capped bottles for at least 15 hours, the pellets were spread out on the laboratory desk for at least 8 hours in order to allow the evaporation of that moisture which had not combined with the UO_3 to form hydrates.

The pellets formed by the above procedure were dehydrated in air at 760°F. The weight loss occurring during this step (Table 9-1) was assumed to be almost entirely due to the removal of the chemically bound water of hydration. The water contents of the two sets of experimental pellets lay within the range of water contents found for plant-produced feed pellets used in previous runs of the Moving Bed Reactor.

Reduction

Samples of each of the two sets of dehydrated pellets were reduced to essentially pure UO_2 in the laboratory reactivity train at temperatures of 1200°, 1400°, 1500°, 1600°, and 1800°F. All samples were held at temperature for 45 minutes in the hydrogen atmosphere. After the samples were cooled rapidly in hydrogen, they were removed from the train at temperatures not exceeding 150°F and were placed in capped bottles.

TABLE 9-1

HYDRATION, REDUCTION, AND HYDROFLUORINATION OF UO_3 PELLETS

Water Content* UO_3 Pellets (%)	Reduction Temperature** (°F)	Hydrofluorination Time Ratio† at Indicated Per Cent Conversion					UF_4 After a Reaction Time of 35 Minutes (%)
		70%	80%	90%	95%	97%	
10.3	1200	1.01	1.01	1.02	1.05	1.03	97.7
*10.3	1400	1.00	1.00	1.00	1.00	1.00††	97.7
10.3	1500	1.01	1.02	1.07	1.16	1.19	97.3
10.3	1600	1.15	1.18	1.32	1.59		95.3
10.3	1800	1.23	1.34	1.67	2.16		93.5
7.3	1200	1.00	1.00	1.06	1.52		95.2
7.3	1400	1.05	1.05	1.14	2.01		94.5
7.3	1500	1.03	1.07	1.32			92.8
7.3	1600	1.23	1.41	2.82			88.2
7.3	1800	1.45	2.06				82.5

* Water of hydration, based on weight of hydrated pellets and determined by weight loss after heating to 760°F.

** Time at the indicated temperature was 45 minutes for all samples.

† $\text{Ratio} = \frac{\text{Time for hydrofluorination of sample to the indicated per cent conversion}}{\text{Time for hydrofluorination of the most reactive sample to the indicated per cent conversion}}$

†† Most reactive sample was that containing 10.3% H_2O reduced at 1400°F.

Hydrofluorination

Each of the ten UO_2 samples was hydrofluorinated isothermally at 1100°F in the thermobalance. Heating the sample from room temperature at 1100°F in the reaction chamber was done under hydrogen. Anhydrous HF was then admitted, and a continuous record of weight gain versus time was obtained as the sample reacted to UF_4.

The reactivity of the ten UO_2 samples may be inferred from the data presented in Table 9-1. The rate data for the hydrofluorinations are expressed as ratios of the hydrofluorination times of the samples to that of the sample which reacted most rapidly. Values of the ratio are given at several conversion levels.

It is evident that the hydrofluorination reactivity of the UO_2 pellets was enhanced by: (1) maintaining low reduction temperatures and (2) increasing the water of hydration in the UO_3 pellets. The data also indicate that favorable conditions for the production of high-assay green salt existed at reduction temperatures up to 1500°F when the pelleted UO_3 feed contained within about one per cent of the maximum water content corresponding to the dihydrate, $UO_3 \cdot 2H_2O$. At higher reduction temperatures, the reactivity of the UO_2 diminished rapidly.

The data for those pellets which originally contained only 7.3 per cent water show that reduction at 1200°F did not insure the production of UF_4 assaying higher than 96 per cent. With these pellets, an increase in the reduction temperature was extremely detrimental to the reactivity of the UO_2.

9.4 A THERMOBALANCE STUDY OF THE REACTIONS INVOLVED IN THE CONVERSION OF AMMONIUM DIURANATE TO GREEN SALT – G. G. Briggs, J. W. Votaw, R. E. DeMarco, D. E. Richards, R. C. Abbott, and D. C. Bonfer

Since it has been known that ammonium diuranate possesses high reactivity in undergoing reduction to UO_2 and subsequent hydrofluorination to UF_4, interest has been shown in the possibility of its use as feed for the Moving Bed Reactor. A laboratory program was undertaken to study the several reactions which pertain to the conversion of the material to green salt. The studies included not only those reactions which occur during separate reduction and hydrofluorination processes, but also those which can occur if the reduction and hydrofluorination are attempted simultaneously in a single reactor.

Pellets of ammonium diuranate were prepared in the laboratory and were reacted in a series of four thermobalance runs. Each run was designed to obtain information concerning the rates of several individual reactions or of one or more reactions occurring simultaneously.

Experimental Procedure

Ammonium diuranate for the experiments was prepared in the laboratory by dissolving uranium trioxide in 6N nitric acid (5% excess). The resultant solution was diluted, and the diuranate was precipitated at 60°C by the addition of 10 per cent aqua ammonia to a final pH of 6.2. The precipitate was washed with water, alcohol, and ether, and was dried at 110°C. After the soft cake was pulverized, a tap density of 1.6 g/cc was measured for the powder.

Pellets of ammonium diuranate were prepared in the form of ¼-inch cubes by cutting up a layer of the paste formed by adding water to the diuranate in the amount of 38 milliliters of water per 100 grams of the diuranate. Drying of the pellets was accomplished by heating with a heat lamp and then heating at 110°C in an oven.

At the start of each thermobalance run, the diuranate pellets were placed in the reaction chamber at room temperature. The temperature was then allowed to rise at the maximum heating rate to a desired set point. In all cases, the diuranate was initially thermally decomposed to essentially UO_3 or essentially U_3O_8 in an atmosphere of nitrogen before the reactant gases (hydrogen and/or HF) were introduced. The order in which the reactant gases (or gas mixtures) were admitted and the temperatures at which these gases were admitted depended upon the particular objectives of each thermobalance run.

Data and Discussion – Thermobalance Runs

Figures 9-1, 9-2, 9-3, and 9-4 correlate the thermobalance weight readings and the temperature with time for each of the thermobalance runs. Indicated on these figures are the time intervals during which the various gases were admitted to the reaction chamber and the volume ratios of the flows when mixtures of hydrogen and HF were admitted. Also indicated are the weight

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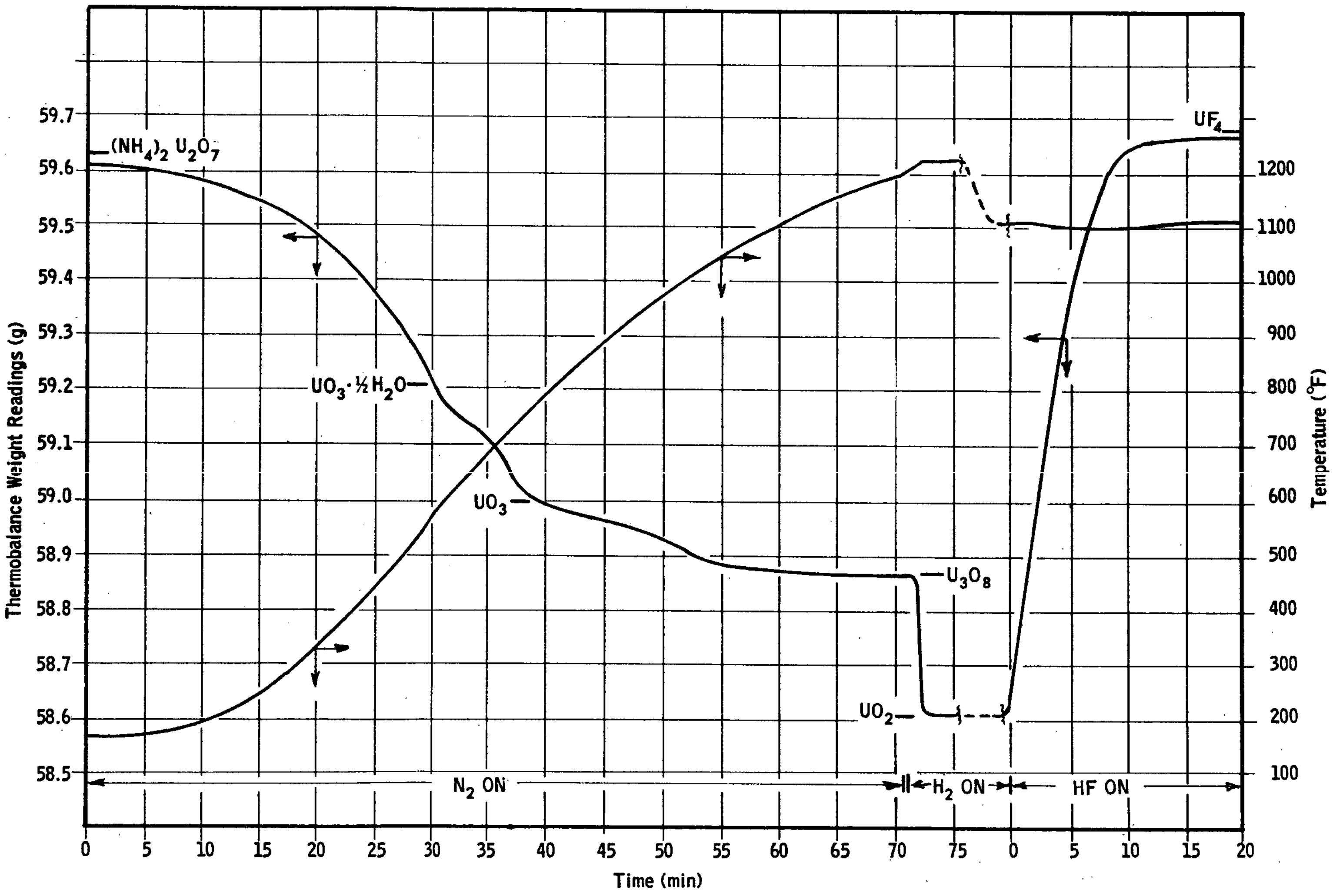

FIGURE 9-1 THERMOBALANCE RUN NO. 1. SEPARATE REDUCTION AND HYDROFLUORINATION OF AMMONIUM DIURANATE PELLETS

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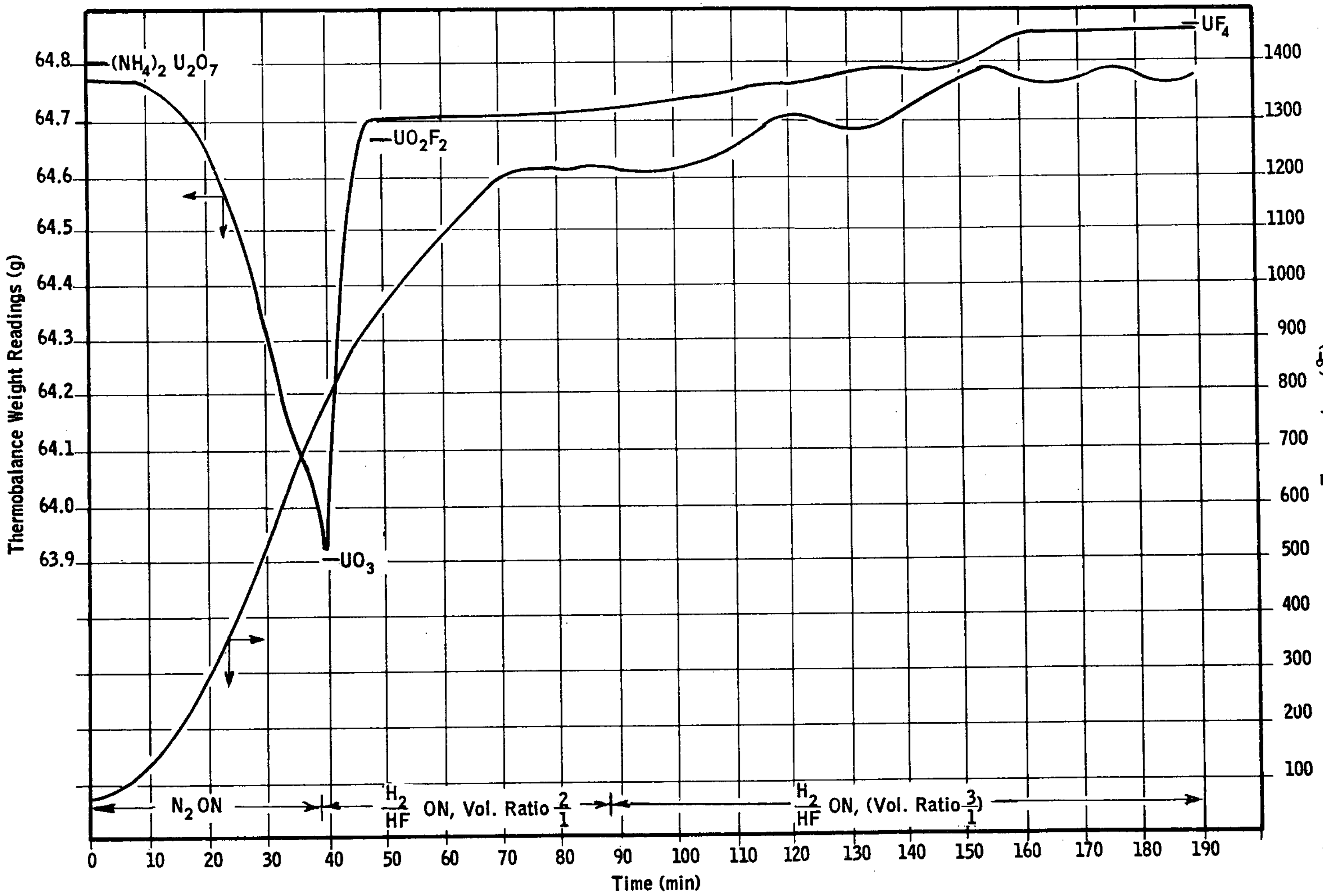

FIGURE 9-2 THERMOBALANCE RUN NO 2. SIMULTANEOUS REDUCTION AND HYDROFLUORINATION OF AMMONIUM DIURANATE PELLETS STARTING AT 750°F

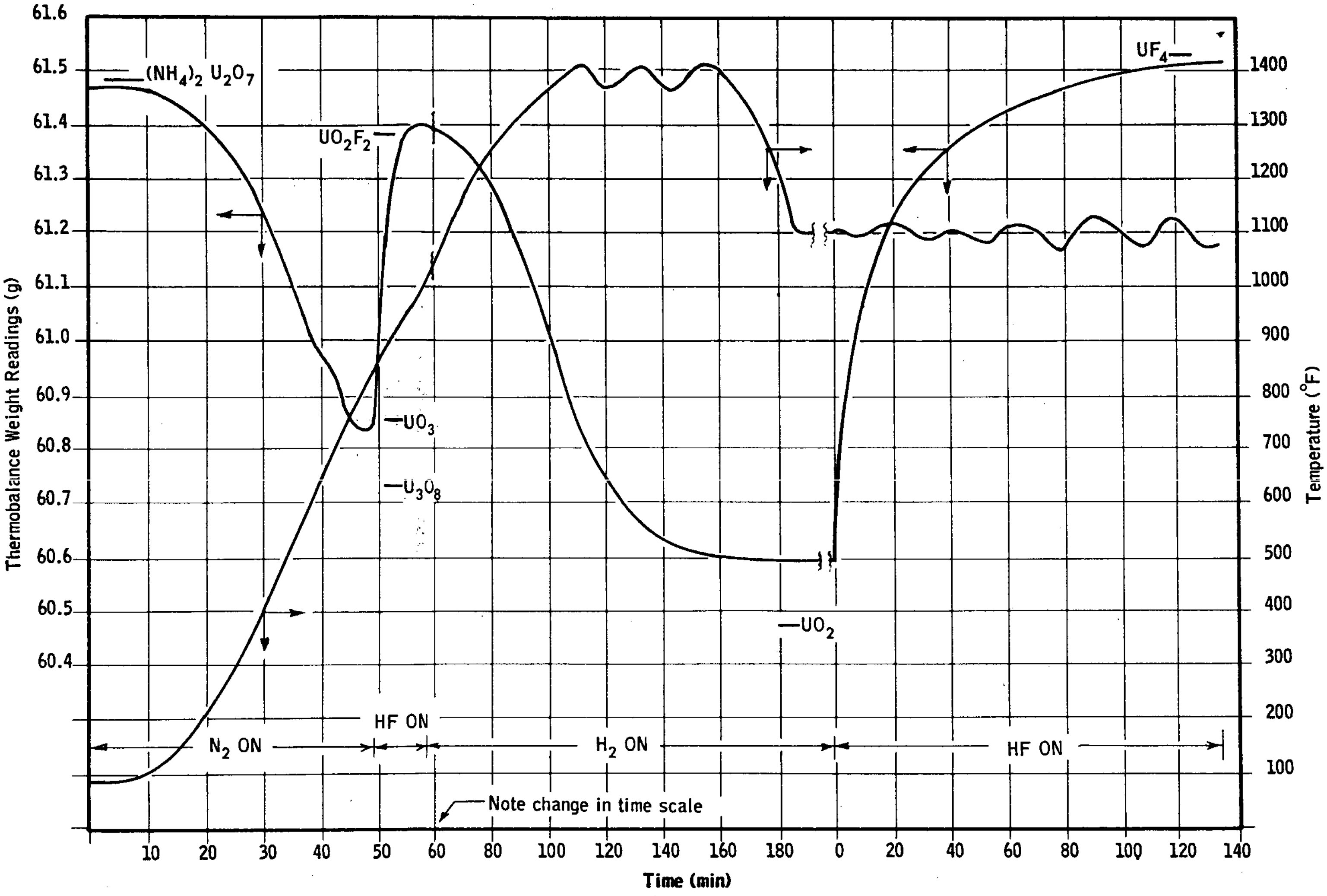

FIGURE 9-3 THERMOBALANCE RUN NO. 3. HYDROFLUORINATION TO UO_2F_2, REDUCTION OF UO_2F_2, AND FINAL HYDROFLUORINATION TO UF_4

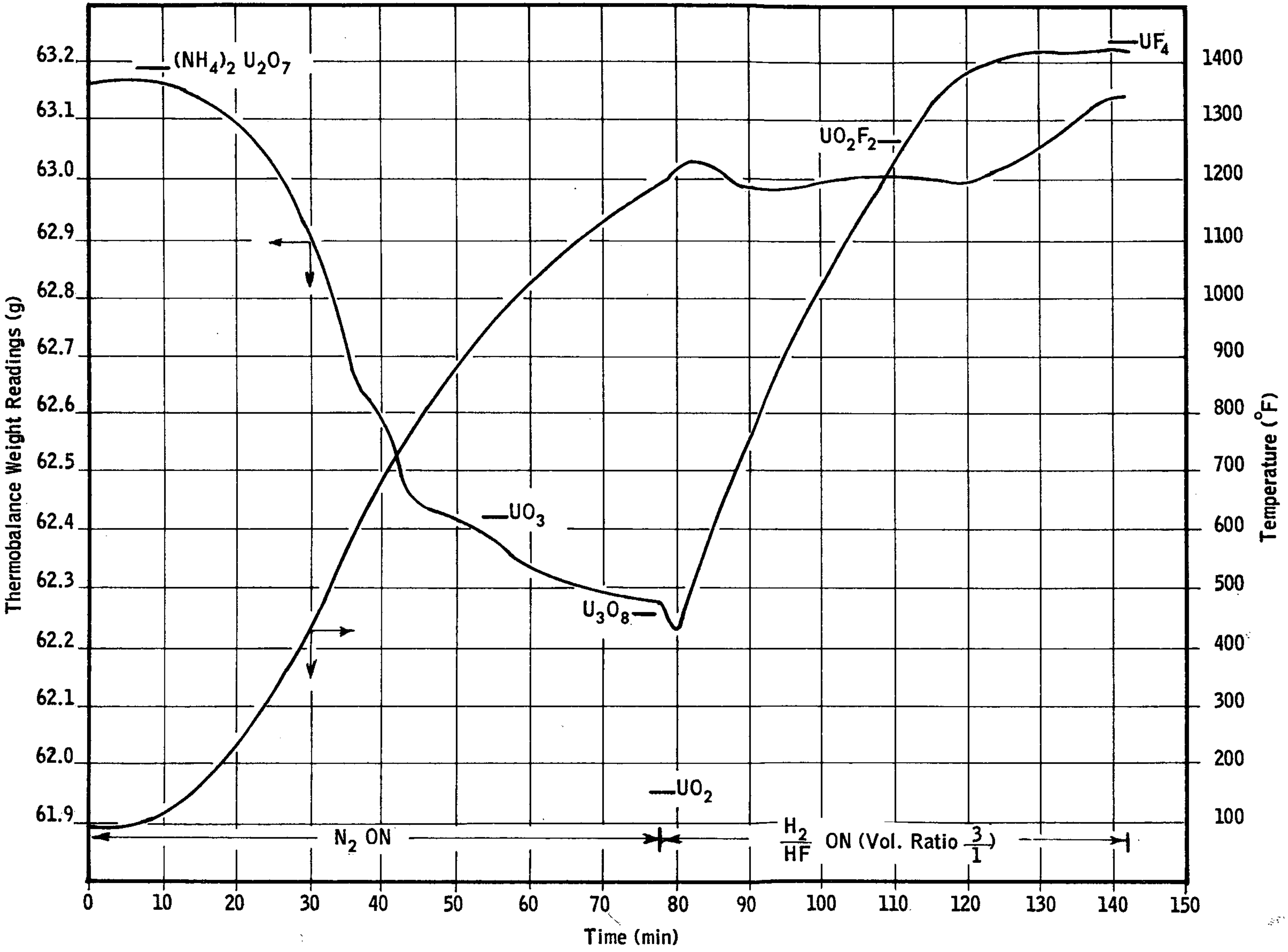

FIGURE 9-4 THERMOBALANCE RUN NO 4. SIMULTANEOUS REDUCTION AND HYDROFLUORINATION OF AMMONIUM DIURANATE PELLETS STARTING AT 1200°F

readings corresponding to the pure compounds, $(NH_4)_2U_2O_7$, UO_3, UO_2, U_3O_8, UO_2F_2, and UF_4. The bases for calculating these weight readings were the chemical analyses of the final green salt product and the known starting weights of the diuranate samples.

Figure 9-1 illustrates the thermal breakdown of the diuranate to U_3O_8. UO_3 was formed at about 800°F. At approximately 900°F, conversion of the UO_3 to U_3O_8 proceeded fairly rapidly. When hydrogen was introduced, the U_3O_8 was reduced to UO_2 very rapidly at 1200°F. The reaction was more than three times as fast as that observed when pellets of hydrated pot-denitrated UO_3 are reduced at 1200°F. The hydrofluorination of the UO_2 at 1100°F, in an atmosphere of essentially anhydrous HF, was also extremely rapid and was completed in less than half the time found for hydrofluorination of the most reactive samples of UO_2 prepared from pellets of hydrated pot-denitrated UO_3.

Figure 9-2 illustrates the first attempt to reduce and hydrofluorinate simultaneously. The mixture of hydrogen and HF contacted the pellets at a temperature of about 780°F after the diuranate had been thermally decomposed to essentially UO_3. The resulting reaction produced primarily the intermediate compound, UO_2F_2. The subsequent simultaneous reduction of the UO_2F_2 and hydrofluorination to UF_4 required prolonged heating at temperatures approaching 1400°F.

The primary purpose of the third thermobalance run (Fig. 9-3) was to isolate for study the reaction between pelleted UO_2F_2 and hydrogen, since the previous run had indicated that this reaction was rate-controlling when simultaneous reduction and hydrofluorination were attempted. The reaction curve shows that the reduction of UO_2F_2 to UO_2 is, indeed, slow. The fact that the weight reading corresponding to pure UO_2 was not reached during the reduction was probably due to the partial thermal decomposition of the sample to U_3O_8 just before and during the highly exothermic hydrofluorination reaction. Subsequent hydrofluorination of the U_3O_8 would have resulted in the partial formation of UF_4, which subsequently would not be affected during the reduction of the UO_2F_2. The final hydrofluorination (Fig. 9-3) which produced UF_4 was extremely slow. Apparently, the reactivity of the pellets was destroyed by the prolonged heating at 1400°F. The final green salt pellets were found to have sintered and formed dense hard centers.

The thermobalance run depicted in Figure 9-4 was the second attempt to reduce and hydrofluorinate simultaneously. In this case, the introduction of the two reactant gases was delayed until the temperature had reached 1200°F and until the sample had been thermally decomposed to U_3O_8. It can be seen that the reactions proceeded smoothly to yield UF_4 at 1200°F. The fact that no discontinuity appeared between the weight readings for pure UO_2F_2 and UF_4 indicated that little, if any, UO_2F_2 had been formed as an intermediate. A comparison of the results of this run with those of Run No. 2 (Fig. 9-2) shows that higher temperature favored the direct reduction reaction that produced UO_2, rather than the hydrofluorination reaction that produced the intermediate compound, UO_2F_2. This is to be expected, since the activation energies of the reactions between UO_3 or U_3O_8 and hydrogen are much greater than the activation energies of the reactions between UO_3 or U_3O_8 and hydrogen fluoride.

The over-all reaction rate during the simultaneous reduction and hydrofluorination (Run No. 4) was very good, considering the fact that the reactant gases diluted each other. For example, if it is assumed that the hydrofluorination of the UO_2 was rate-controlling, the rate at which UF_4 was produced in Run No. 4 should have been about one-fourth of the rate found for the hydrofluorination step of Run No. 1, since the partial pressure of the HF in Run No. 4 was only one-fourth that of Run No. 1.

Miscellaneous Experimental Results

The chemical analyses of the four samples of pellets after final hydrofluorination indicated conversions to UF_4 between 96.4 per cent and 99.5 per cent.

Pellets of UO_3, UO_2, U_3O_8, UO_2F_2, and UF_4 prepared from diuranate pellets were weaker than pellets of the same compounds prepared from hydrated pot-denitrated UO_3. The UO_2 pellets were lowest in strength; the UF_4 pellets were the strongest.

Tap densities measured for the green salt powders prepared by grinding the pellets from thermobalance Runs No. 1 and 4 were 2.8 g/cc and 2.7 g/cc, respectively.

In additional experiments, pellets of the diuranate were heated to 760°F, at which temperature they were decomposed to red-orange UO_3. When these pellets were dropped into water at room temperature, they underwent hydration and changed in color to pale yellow. At the same time, copious streams of bubbles arose from the pellets, indicating that the pellets had previously adsorbed large quantities of gas. The effect was indicative of the large internal surface within the pellet structure and helped explain the great reactivity of the diuranate. After the pellets were redehydrated, their strength and hardness appeared to be somewhat improved over those of the original diuranate pellets. A thermobalance run was made with these pellets in the same manner as that employed in Run No. 1 (Fig. 9-1). The times for completion of the reduction and hydrofluorination were almost identical with those observed in Run No. 1. After the hydrofluorination was completed at 1100°F, the temperature was allowed to rise to 1300°F and remain at this setting for 12 minutes before the reaction chamber was cooled. The tap density of the resulting green salt powder was 3.3 g/cc, which compares very favorably with the tap density of green salt produced from pot-denitrated UO_3 in the Green Salt Plant screw reactors.

When UO_3 powder, prepared by heating the diuranate, was made into a paste with water, the release of the adsorbed gas caused the mass to swell. Pellets prepared from the paste were extremely porous and poor in strength.

Summary

1. Pellets of ammonium diuranate, as well as pellets of intermediate compounds derived from the diuranate, are much lower in strength than pellets prepared by hydrating pot-denitrated UO_3 and their corresponding intermediate compounds.

2. The thermal decomposition of ammonium diuranate occurs with the evolution of ammonia and water vapor at 800°F; UO_3 if formed. At 900°F and above, conversion to U_3O_8 proceeds readily.

3. Pellets of the diuranate undergo rapid reduction and hydrofluorination when the reactions are carried out separately. The reaction rates are much greater than those observed for pellets prepared from pot-denitrated UO_3.

4. Simultaneous reduction and hydrofluorination of the diuranate feed pellets is feasible, particularly if the temperature of the reacting system is maintained at a temperature high enough to promote direct reduction to UO_2.

5. If simultaneous reduction and hydrofluorination is attempted at too low a temperature, the intermediate compound, UO_2F_2, is formed. The subsequent reduction of this material in pellet form requires prolonged heating at temperatures approaching 1400°F.

6. Ammonium diuranate can be heated to about 800°F to form UO_3. The UO_3 can then be hydrated, but the reaction is accompanied by the copious release of adsorbed gas. The gas can escape if the UO_3 is in pellet form, but remains entrapped in pastes of the powder with water.

10. REDUCTION TO METAL PROCESS (URANIUM)

10.1 CONTINUOUS REDUCTION OF URANIUM TETRAFLUORIDE – O. R. Magoteaux, V. E. Minutolo and G. E. Wuller, Jr.

The present bomb process for preparing large quantities of uranium derby metal has these disadvantages:

1. It is costly.
2. It is a batch operation.
3. It has many process variables that are influenced by operating techniques.
4. It requires costly equipment.

Costs are greatly affected by the requirement for a high purity refractory liner, which is used in the bomb to prevent contamination of the uranium and fusion of the uranium with a steel vessel (furnace pot). Production rates are limited by the batch methods. Yields are influenced by the preheat period, charging techniques, and other variables.

A process for the continuous, open-type reduction of uranium tetrafluoride (green salt) offers the advantages of high production rates and low direct material and operating costs, with metal quality that may be comparable to that obtained by batch methods. Production rates considerably higher than obtainable by use of the bomb process are possible. This process consists of two main steps: (1) Reduction of the green salt and (2) Separation of the slag from the metal.

Pilot Plant development of such a process is being pursued and is primarily aimed at increasing the production capacity of the derby-preparation step. Simultaneously, a method of continuously separating and casting uranium from the slag-metal mixture is being developed. One of the major problems of this type of process, finding a suitable refractory, is now being studied at Battelle Memorial Institute.[1] Other problems are size, shape, and weight of the charge, preheating the reactor chamber, ignition of the charge for startup, rate of charging, and control of the products. Although slag-metal separation can be accomplished batchwise by allowing the uranium to settle to the bottom of a container placed below the reduction vessel, it is essential to develop a method for continuously separating the slag from the metal.

Reductant

The reductant was to be chosen on the basis of cost and the amount of heat needed to maintain the reduction reaction. In a cost analysis of a continuous reduction process, magnesium, calcium,

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[1] *Dayton, R. W. and Tipton, C. R., Jr., Progress Relating to Civilian Applications During December, 1955, pp. 27-28, BMI-1062, January 1, 1956.*

and sodium were evaluated as reductants for the green salt. This analysis showed a possible considerable reduction in the cost per pound of uranium if magnesium were used and an even greater savings if sodium were used. The present high cost of high-purity calcium makes its use uneconomical on a production scale, although it its cost were reduced it could be used economically. Mixtures of reductants such as calcium-magnesium, calcium-sodium, and magnesium-sodium might further reduce costs as compared to the present bomb process, and will be evaluated.

Heat-balance studies were made in order to determine whether heat must be added to provide slag-metal separation when magnesium, sodium, or calcium is used as the reductant. It was calculated that external heat will be required in order to separate slag and metal if magnesium or sodium is used, but not if calcium is used as the reductant. Because external heating facilities were not yet available, the experimental reductions reported here were made with calcium metal used as the reductant.

Equipment

Basic equipment needed for experimental tests has been designed, fabricated, and installed. A ventilated enclosure and platform area (Fig. 10-1) is used to conduct the tests. A steel chute (tube) permits the charging of blends of reductant and green salt into an open-type reaction chamber. Windows in the enclosure permit observation during the reduction reaction. Ventilation is accomplished by 6-inch and 8-inch-diameter tubes exhausted by a 3000-cfm motor-driven fan.

The presently used unit consists of two identical graphite vessels called a reaction container and a separation container, one above the other. The top container serves as a reduction chamber and the bottom container as a separation chamber for the slag-metal. A ½ inch to 5/8-inch-diameter pour hole permits the products to flow from the reduction chamber to the separation chamber. Fiberfrax insulation is packed between the graphite vessels and sillimanite retaining rings. This arrangement insulates the entire unit and prevents extreme heat losses, except through the charge opening. A zirconia cover plate is offset on the upper vessel (Fig. 10-1).

Process Studies

Ignition of the reaction is accomplished by placing burning magnesium on top of an initial small charge of UF_4-Ca (30 lb). This initial charge is placed on a magnesium metal sheet in the bottom of the reaction container. The present method of charging additional calcium-green salt blend is to add small quantities of it in sealed paper sacks. Each charge weighs approximately five pounds. This method both permits a series of small continuous reactions (which are less violent than would be obtained with a large charge) and allows better feed control

The use of 4 to 10 per cent excess calcium in reductions has been evaluated. No definite correlation could be established between reduction yields and the per cent excess calcium.

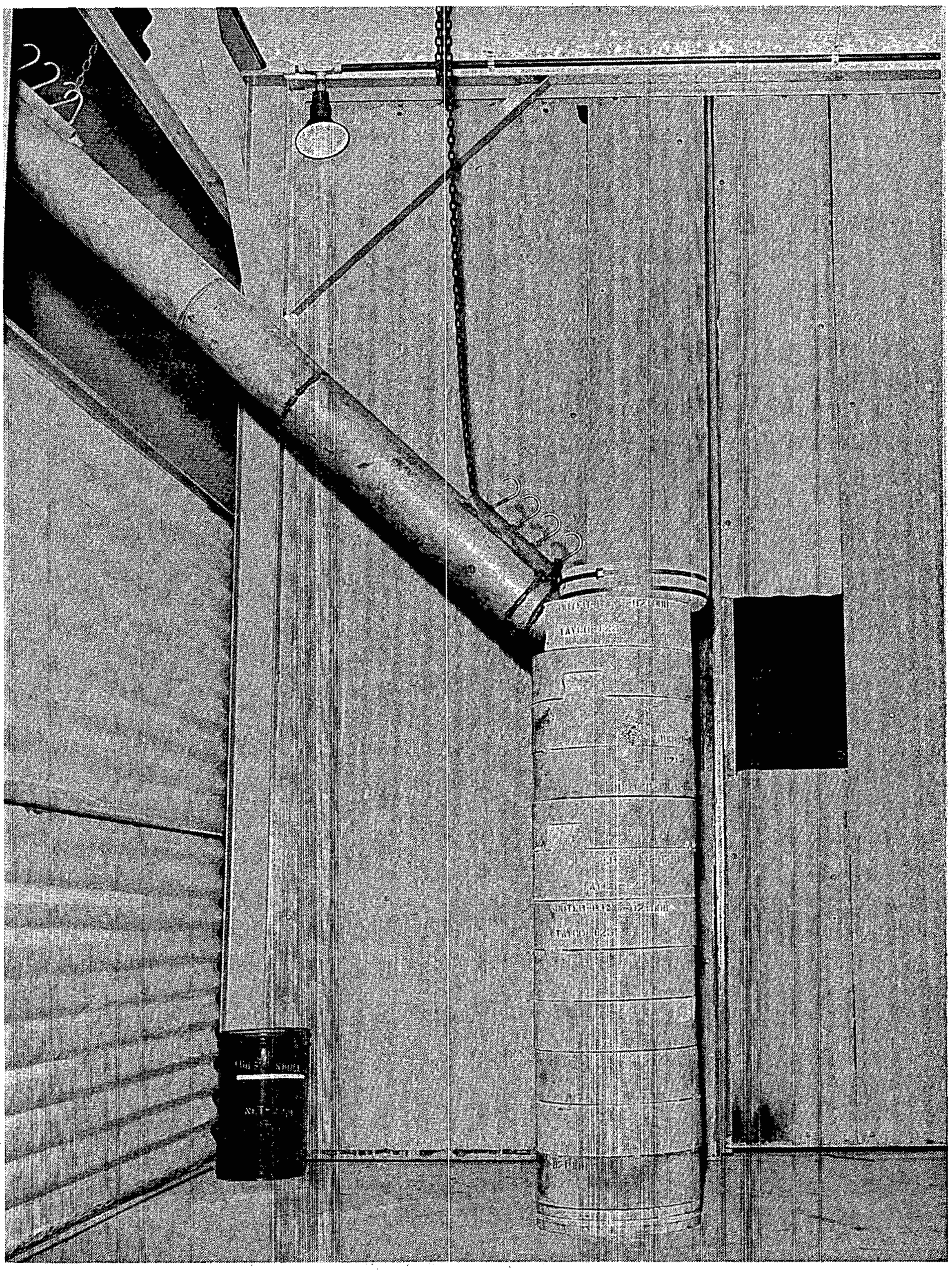

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FIGURE 10-1 REACTOR ASSEMBLY AND CHARGING CHUTE INSIDE VENTILATED ENCLOSURE

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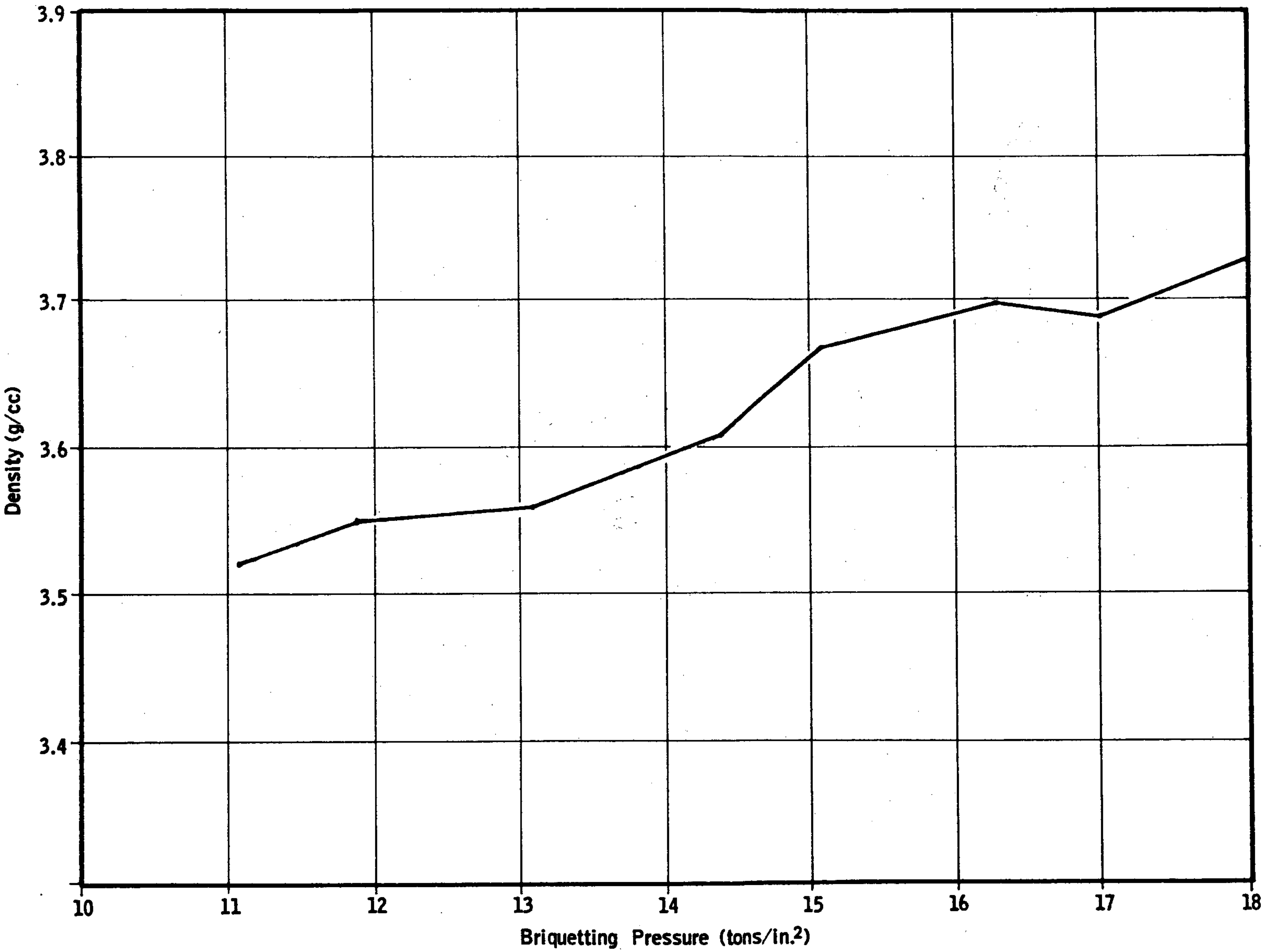

FIGURE 10-2 DENSITY vs BRIQUETTING PRESSURE

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Slag-metal separation appeared to be influenced most by the charging rate. The faster feeding rate improved slag-metal separation. It was also found that with a pour hole of 5/8-inch diameter and a charging rate of 25 to 50 pounds of green salt (18.9 to 37.9 pounds of uranium) per minute, a pool of molten slag and metal was maintained in the reaction container. A reaction has been sustained for 15 minutes thus far, and it is thought that a reaction could be sustained indefinitely with adequate quantities of feed.

Green Salt-Magnesium Briquettes

A mixture of normal green salt and magnesium has been briquetted for evaluation as a charge material. Approximately 400 briquettes, 3¼ inches in diameter by about 5 inches in height (weighing about 5 pounds each), were pressed, using blends of powdered normal uranium tetrafluoride and magnesium. The briquettes were formed using a manually controlled Elmes Hydraulic press, which is rated at 350 tons on the vertical ram and has a tonnage regulator and a double-action mold assembly. The clearance of 0.002 inch between the mold cylinder and the plunger did not prevent a building of magnesium on the mold wall. A thin layer of magnesium stearate was dusted onto all mold components before each run for lubrication purposes. After about 25 runs, it became necessary to hone the inside wall of the mold cylinder for efficient operation. The briquette was ejected through the bottom of the mold with a dummy block. An operational procedure was established which produced one briquette about every two minutes.

Total compacting pressure and percentage excess reductant were varied for further evaluation. No correlation between density of the briquette and percentage excess magnesium could be established (Fig. 10-2). These briquettes will be evaluated when external heating facilities are provided for the reactor. Similar work for an evaluation study using briquetted charges in batch-type reductions has been reported.

Future Work

Future work will include the design, fabrication, and installation of equipment to sustain an operation for long periods of time. A stopper rod mechanism is being investigated as a possible means of controlling the flow of slag-metal from the reaction container. A stopper rod may permit the formation of slag, which will act as a protective cover over the molten pool of uranium. Other pour hole sizes will be investigated. Studies will be undertaken on (1) reaction container and separation container design, (2) an improved type of charge, (3) optimum charging rates, (4) a better ignition technique, and (5) product pouring.

11. METAL CASTING PROCESS (URANIUM)

11.1 REMELTING OF PICKLED AND UNPICKLED DERBIES – E. W. Torok, H. M. Eikenberry, and A. Church, Jr.

MCW has been producing derbies in slag-lined furnace pots and has determined[1] that to obtain ingots of good metal quality, these derbies must be pickled before they are used in the remelt charge. Since NLO will be producing derbies in slag-lined furnace pots, 25-ton test lots of pickled and unpickled derbies were obtained from MCW and remelted in the Metals Plant at NLO to determine whether or not derbies produced in slag liners at NLO should be pickled.

Materials and Procedure

The procedures used to remelt 25 tons each of unpickled and pickled derbies produced at MCW and 25 tons of derbies produced in dolomite liners at NLO (control derbies) were as follows:

1. Two basic types of charges were used: One type consisted of two derbies, plus 250 pounds of briquettes and enough solid scrap (rolling mill scrap, rod ends, rejected slugs, and scrap ingot crops) for a 1230-pound charge. The other type consisted of three derbies, plus 250 pounds of briquettes and enough solid scrap for a 1230-pound charge.

2. The charges were loaded into the remelt furnaces at random but were charged in the following sequence:

Sequence	Type of Charge
1	2 unpickled derbies produced in slag liner by MCW
2	2 pickled derbies produced in slag liner by MCW
3	2 control derbies. Unpickled derbies produced in dolomite liners by NLO.
4	3 unpickled derbies produced in slag liner by MCW.
5	3 pickled derbies produced in slag liner by MCW
6	3 control derbies. Unpickled derbies produced in dolomite liners by NLO.

3. The derbies were remelted in only one bank of furnaces.

4. Standard Plant Practices (described below) were carefully followed:

   a. A vacuum pressure ranging from 100 to 15 microns was obtained after the heat had melted.

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[1] *Vander Weyden, A. J., Metal Quality Meeting at St. Louis, March 30, 1954, to G. F. Quinn April 22, 1954.*

b. The power level was held at 120 kw until an optical pyrometer reading of 2550°F was obtained. The power was then cut back to 50 kw and held 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 density and chemical analysis.

e. The ingots were rolled to SRO size, except for approximately 18 ingots that were rolled to HGE rod size.

This study was expanded to include an evaluation of NLO and MCW green salt, as the boxes in which the derbies had been shipped were labeled as follows:

1. MCW nonpickled
2. MCW pickled
3. NLO nonpickled
4. NLO pickled

It was confirmed by MCW that the markings on the boxes identified the source of the green salt from which the derbies were made. This resulted in the evaluation of 10 different charge categories as follows but did not affect the charging sequence.

2 unpickled derbies produced in slag liner by MCW using MCW green salt.

2 unpickled derbies produced in slag liner by MCW using NLO green salt.

2 pickled derbies produced in slag liner by MCW using MCW green salt.

2 pickled derbies produced in slag liner by MCW using NLO green salt.

2 unpickled derbies produced in dolomite liners by NLO using NLO green salt. (Control derbies).

3 unpickled derbies produced in slag liners by MCW using MCW green salt.

3 unpickled derbies produced in slag liners by MCW using NLO green salt.

3 pickled derbies produced in slag liners by MCW using MCW green salt.

3 pickled derbies produced in slag liners by MCW using NLO green salt.

3 unpickled derbies produced in dolomite liners by NLO using NLO green salt. (Control derbies).

These 10 different charge categories were evaluated for differences in density, carbon content, and nitrogen content in the ingot samples. In addition, differences in the slug reject rate for visual metal quality defects were evaluated. All ingots were considered in the carbon, nitrogen, and density evaluation. Only those ingots rolled to SRO size were considered in the slug reject rate evaluation.

Results and Conclusions

From an analysis of slug reject rates, it appears that:

1. Pickling of MCW derbies made from MCW green salt, regardless of the number of derbies per charge, reduces the slug rejection rate considerably.

2. Pickling of MCW derbies made from NLO green salt, regardless of the number of derbies per charge, does not seem to affect the slug reject rate.

Statistical calculations on these data indicate that:

1. There is no significant difference in the slug reject rates for ingots made from (1) pickled derbies produced in slag liner by MCW using MCW green salt, (2) unpickled derbies in slag liner by MCW using NLO green salt, and (3) unpickled derbies produced in dolomite liner by NLO using NLO green salt. This is true, regardless of the number of derbies charged.

2. There is no significant tendency for the number of derbies in the charge to affect the slug reject rate for ingots made from (1) pickled derbies produced in slag liner by MCW using MCW green salt, (2) unpickled derbies produced in slag liner by MCW using NLO green salt, and (3) unpickled derbies produced in dolomite liner by NLO using NLO green salt.

The analyses of ingot samples indicate that the density and carbon content are not noticeably affected by pickling of derbies, regardless of the type of green salt used and the number of derbies charged.

The effect of pickling on the nitrogen content of ingot samples is summarized in Figure 11-1, where frequency distributions of individual nitrogen values are presented. From this summary it is apparent that:

1. The use of pickled derbies in the charge results in a reduction in the nitrogen content, regardless of the green salt used in producing the derby.

2. Nitrogen content tends to increase with the number of derbies charged.

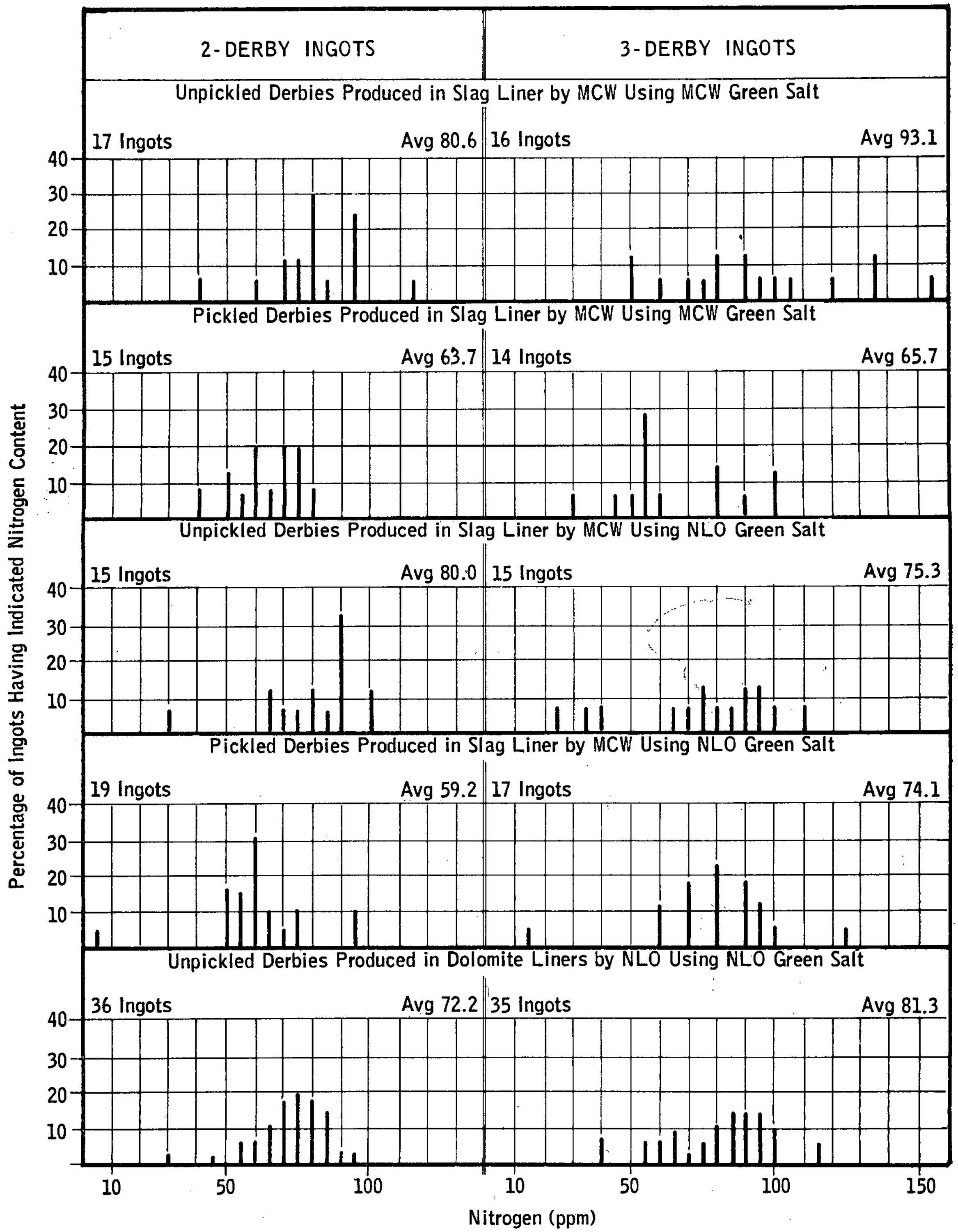

FIGURE 11-1 NITROGEN CONTENT OF INGOT SAMPLES

The conclusions of this study are, of course, limited by the conditions under which the test was run. It would be particularly unwise to assume that the above conclusions can be generalized. It should be pointed out that the green salt used in the production of these derbies came from a comparatively few lots produced at very nearly the same time under the operating conditions in effect at that time. The same applies to the derbies and ingots used. This test does point out, however, that differences of the order of magnitude indicated can exist in slug reject rates and nitrogen content. Whether these differences persist through time and remain relatively constant has not been answered by this test.

11.2 MELTING AND CASTING OF NIOBIUM-URANIUM ALLOY — W. E. Palmer and S. L. Reese

Much of the nuclear reactor work involves the use of alloys of uranium. Niobium alloys with greater than seven weight per cent niobium have considerable corrosion resistance and may be used in reactor fuel or blanket fabrication. The work reported here covers the experimental production of nominal 10 weight per cent (w/o) niobium-uranium alloy.

Data and Discussion

On the basis of 21 melts made in a bottom-pour induction type furnace, it was determined that homogeneous ingots could be made by remelting previously melted stock. Shrinkage in cold-mold castings, however, produced ingots with voids throughout.

On the basis of 41 melts made in induction furnaces having a top-pour mechanism and adequate mold-heating facilities, it was determined that sound ingots which have a 9.2 to 10.6 w/o niobium range (top and bottom analyses) and which are suitable for extrusion can be cast. The method of sampling is critical, since variations in the order of one per cent niobium have been found in different areas of the same horizontal plane.

Conclusions

The work done to date indicates that homogeneous, sound ingots can be cast. Work to reduce the number of melts required to produce a sound, homogeneous alloy will continue.

Materials

Niobium was charged either as cold-pressed bar, as powder, or as sintered pellets.

Virgin melts made using niobium pellets gave poor niobium dissolution. A typical analysis of such an ingot that had a calculated niobium content of 10.5 w/o was: top, 14.8 w/o niobium; bottom, 6.25 w/o niobium.

When niobium powder was used, the average spread between top and bottom was much smaller: 11.2 w/o at the top and 8.8 w/o at the bottom. Cropping of the top and bottom is employed to bring the spread within specifications.

The cold-pressed niobium bar did not dissolve.

There was a high niobium loss in any skull material that formed in the crucibles of bottom-pouring furnaces, since niobium metal is lighter than uranium and floats to the top of the furnace with the impurities. Such skull material was usually high in oxides and other impurities, which made it undesirable for remelt stock. It was found desirable, prior to charging the furnace, to pickle in nitric acid any uranium metal that was coated with oxides, oil, or other impurities. This reduced the skull formation in the crucible and eliminated much of the niobium loss as skull.

Crucible

A BeO-BeSO$_4$ crucible coating, properly applied to the graphite crucible and allowed suitable time to cure, is satisfactory for these metals at 3100°F and provides acceptable crucible life and low carbon contamination of the metal.

Some action in the melt is desirable to aid solution of the niobium, but rapid agitation erodes the crucible coating. Therefore, the power level should be regulated to allow moderate agitation, and sufficient melt time must be allowed for the niobium to go into solution.

Furnace Type

Melting and casting was done in both top-pouring and bottom-pouring vacuum induction furnaces. It has been demonstrated that the top-pouring induction furnaces aid greatly in producing homogeneous ingots. The stirring action produced when the metal is poured into the mold aids in obtaining homogeneity; the niobium-rich melt at the top of the melt is poured into the mold first and mixes with the remainder of the melt as this less dense fraction moves upward in the mold. In top-pouring, some dross is poured into the mold, which is not desirable.

Mold

The mold must be heated to obtain a sound ingot. A mold coating of magnesium zirconate, well applied and used below 2600°F, has been satisfactory. If the mold is heated above 2600°F, the mold coating decomposes and graphite seizure occurs. If a 10 w/o alloy is poured at 3100°F into a mold having a temperature of 2100°F or less, ingots with voids result. The optimum mold conditions found are as follows: At time of pour, the temperature near the top of the mold should be 2300°F and the temperature near the bottom of the mold should be 400° to 800°F (Table 11-1).

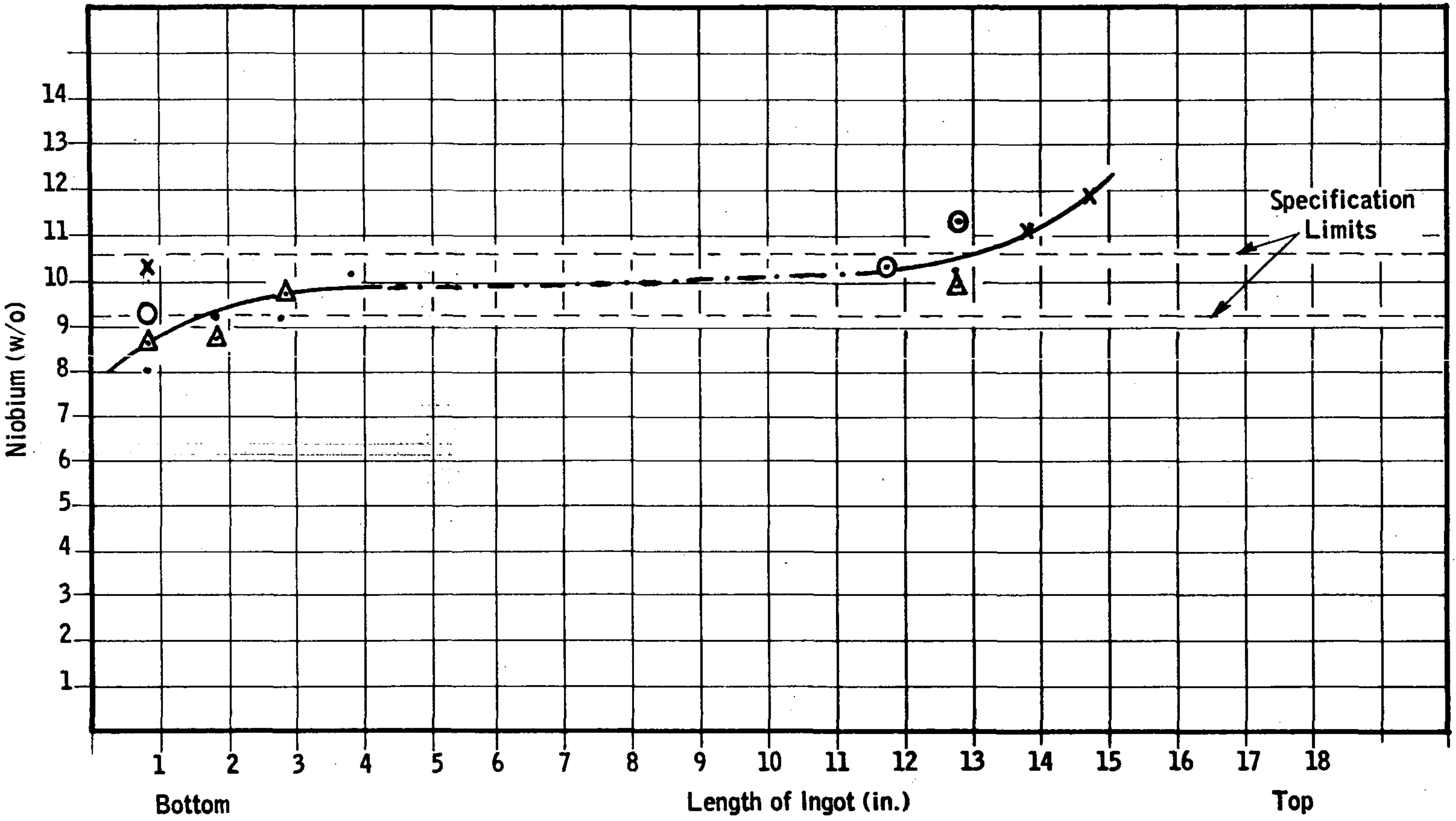

FIGURE 11-2 NIOBIUM DISTRIBUTION IN FOUR REPRESENTATIVE 6-3/8-INCH-DIAMETER INGOTS (THEORETICAL ALLOY: 10.5 WT % Nb)

TABLE 11-1

OPTIMUM MELT CONDITIONS AT TIME OF POUR (U-Nb HEATS)

Heat Time (min)	Melt Temp at Pour (Optical Reading)		Mold Temp at Pour (Thermocouple Reading)	
	In Crucible (°F)	Pour Stream (°F)	Top (°F)	Bottom (°F)
180	3092	3119	2300	400

Fifty kilowatts are applied to the mold for one munites after pour; this is then decreased by five kilowatts every three minutes until the power level is zero. Destructive tests and ultrasonic tests, as well as data obtained during further fabrication, indicate that ingots cooled in this manner are sound. More rapid cooling of sound ingots is desirable to decrease the occurrence of the niobium-rich phase.

Even if the conditions given in Table 11-1 are achieved, a definite gradient in niobium between the top and bottom of typical ingots is evident (Fig. 11-2). The top and bottom crops must be double-melted in order to obtain homogeneity. Occasional ingots are completely out of specification and must be remelted.

12. METAL FABRICATION PROCESS (URANIUM)

12.1 PRELIMINARY STUDIES ON THE PRODUCTION OF URANIUM WASHERS – A. E. Guay, R. E. Yount, J. Fritzke, and J. Farr

A customer has requested that we investigate the feasibility of producing uranium in the shape of washers. The ultimate use of such a shape would be as a component of an assembled reactor fuel element.

The preliminary work described here has been performed to investigate the production of washers having the following dimensions:

Washer Type	Thickness (in.)	OD (in.)	ID (in.)	Hole Concentricity (in.)
2	0.062 ±0.002	1.370 ±0.002	$0.485^{+0.005}_{-0.002}$	0.003
3	0.125 ±0.002	1.370 ±0.002	$0.485^{+0.005}_{-0.002}$	0.003
4	0.188 ±0.002	1.370 ±0.002	$0.485^{+0.005}_{-0.002}$	0.003

The following general limitations also have been imposed:

1. The warp must not exceed 0.005 inch after the pieces have been annealed at 600°C.
2. Surface discontinuities must not be deeper than 0.002 inch nor longer than 0.2 inch, and the pieces must be burr-free.
3. The grain size of the finished pieces measured at 20X must not exceed 0.35 millimeter, and the grain structure must be beta transformed.

Additional requirements, because the washers are to be components of fuel elements, were that they be free of stress raisers, have a minimum residual stress, and have a minimum preferred orientation.

Choice of Manufacturing Process

Shortly after the inquiry for such a product was received, an appraisal was made of the relative economy of manufacturing the washers by punching them from a rolled strip and by machining them from a solid or hollow round piece. For the pieces now under consideration, it was shown that punching from a strip would be the most economical approach.

Meeting the thickness specifications with a punch press operation requires that a closely sized plate be rolled, in fact, the thickness tolerances demand a cold-rolled strip. Also, the dimensional tolerances require a precision punching operation.

Because punching from a precision cold-rolled plate was chosen as the first manufacturing process used to produce the washers, associated difficulties were realized. Among the difficulties are those of the rolling process and the beta heat treating of cold-rolled materials to achieve the required grain size. The preliminary experiences in the rolling, heat treating, and punching operations are reported here.

Description of the Rolling Operation

The rolling operation consists of the following steps:

1. Preheating the ingot.
2. Hot slabbing the preheated ingot to a 1½-inch-thick slab in a reversing mill.
3. Removal of the surface and edge imperfections from the slab (conditioning).
4. Preheating the conditioned slab.
5. Hot roughing the preheated slab to a 0.350-inch-thick strip in a reversing mill.
6. Cooling the 0.350-inch-thick strip (only when a thickness reduction to 0.148 inch is to follow).
7. Finishing the 0.350-inch-thick strip to a thickness 15 per cent greater than the specified thickness in a continuous mill.
8. Shearing the finished strip into 8-foot lengths.
9. Pickling the strip.
10. Conditioning the edges of the hot rolled strip.
11. Cold rolling the finished strip to the specified thickness in a 4-high mill.

To date, only two thicknesses of strip have been rolled: 0.195 inch for the 0.188-inch-thick washer and 0.132 inch for the 0.125-inch-thick washer. The strip has been rolled to 0.195-inch and 0.132-inch thicknesses to allow for the losses in thickness by scaling during heat treating and subsequent skin-pass sizing prior to punching. The following paragraphs describe the rolling operation in detail

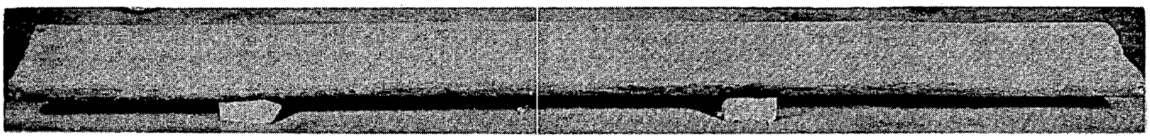

FIGURE 12-1 SLAB THAT WAS HOT ROLLED FROM A RECTANGULAR INGOT (OVER-ALL SLAB DIMENSIONS ARE APPROXIMATELY 100 INCHES BY 10-5/8 INCHES BY 1½ INCHES.)

Casting

A 4 by 11-inch rectangular ingot with rounded corners is cast by the conventional production process used for 7-inch-diameter round ingots. The rectangular ingot weighs 1000 to 1050 pounds.

Hot Slabbing

The ingot is preheated for one hour at 1190°F in a Li_2CO_3:K_2CO_3 (46:54 w/o) salt bath. The ingots are slabbed on a 20 inch, 2-high reversing mill. Using the schedule shown below, a slab approximately 100 inches long, 1½ inches thick, and 10½ to 10¾ inches wide is made.

Pass No.	Type of Pass	Pass	Parting (in.)
1	Flat	Bull Head	3-1/2
2	Flat	Bull Head	3-1/8
3	Edger	No. 3 Edger	7-1/4 (11)
4	Flat	Bull Head	2-7/8
5	Flat	Bull Head	2-5/8
6	Flat	Bull Head	2-3/8
7	Edger	No. 4 Edger	8 (11)
8	Flat	Bull Head	2-1/8
9	Flat	Bull Head	1-3/4
10	Flat	Bull Head	1-1/2

This schedule was designed for use with existing rolls (schedule used for rolling 7-inch-diameter round ingots into oval billets). Maximum straightness is a major factor of consideration; slabs are held straight between the sideguards until they are cool. Finishing temperatures, taken after the last pass with a radiamatic head, average 1100°F.

A photograph of a typical slab is shown in Figure 12-1. Figure 12-2 shows the grain structure of a typical slab.

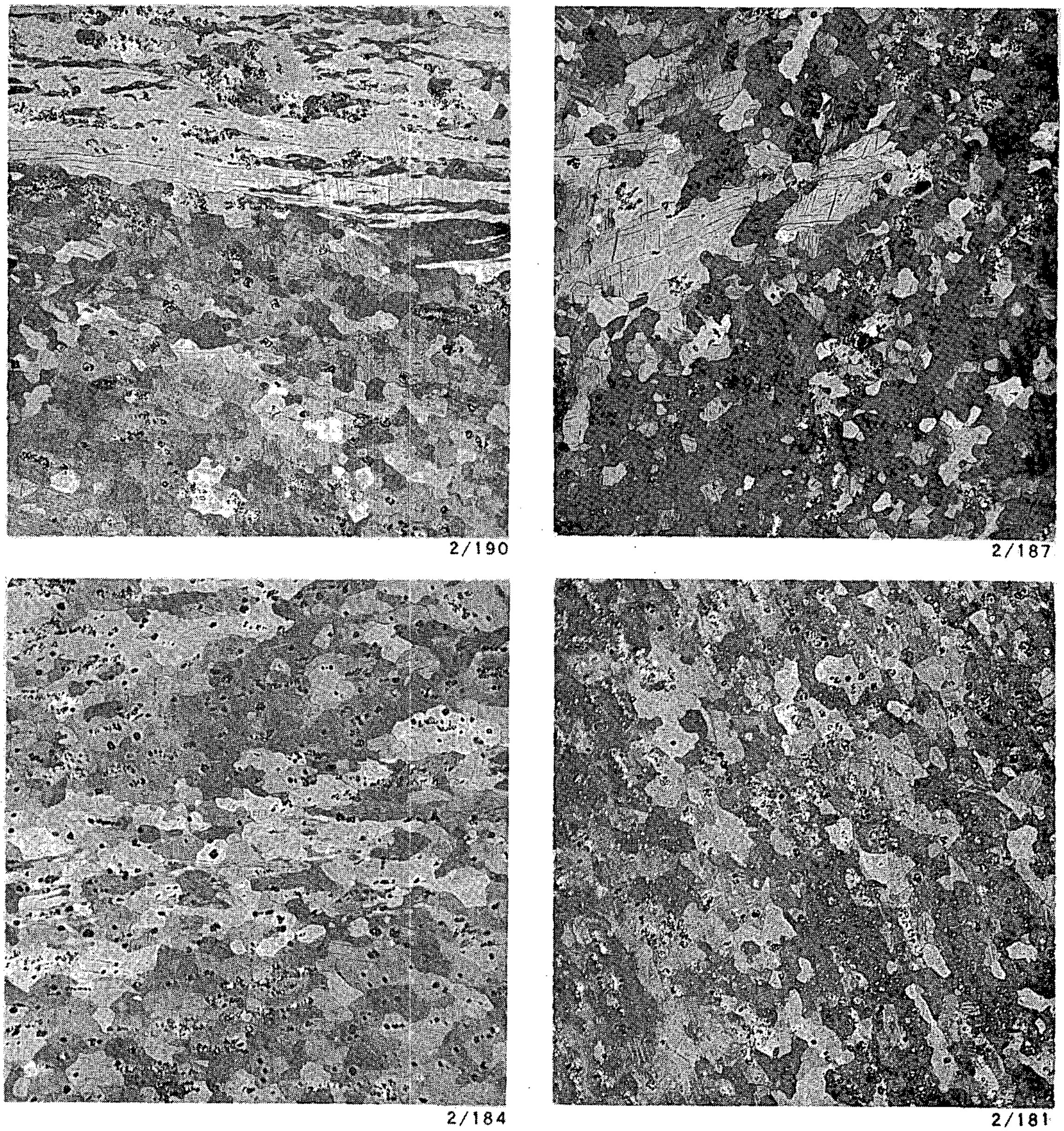

FIGURE 12-2 GRAIN STRUCTURE OF SLAB F-8142. (100X, POLARIZED)
TOP LEFT: BACK END OF SLAB AT CENTER; LONGITUDINAL SECTION
TOP RIGHT: BACK END OF SLAB AT EDGE; LONGITUDINAL SECTION
BOTTOM LEFT: LEAD END OF SLAB AT CENTER; LONGITUDINAL SECTION
BOTTOM RIGHT: LEAD END OF SLAB AT EDGE; LONGITUDINAL SECTION

Hot Roughing

Before the slabs are roughed, they are conditioned on their edges and faces by planing and/or milling. To remove the surface and edge imperfections, the section is usually reduced to a width of 10¼ inches and a thickness of 1-3/16 to 1¼ inches.

The conditioned slab is preheated in a $Li_2CO_3:K_2CO_3$ (46:54 w/o) salt bath for 30 minutes at 1190°F. The slab is roughed to a 0.350-inch-thick strip in a 22-inch, 3-high reversing mill in five passes of approximately equal reduction.

Hot Finishing

If 0.148-inch-thick strip is to be finished, the 0.350-inch-strip is allowed to cool slightly before finishing; no cooling period is required if the finished gage is to be 0.224 inch, as there is little chance of overheating during the lighter reductions which are taken in the 3 passes.

The 0.350-inch strip is finished to final gage in 3 stands of a 5-stand continuous mill. Each stand is a 4-high mill with 14-inch-diameter work rolls backed with 30-inch-diameter rolls. Approximately equal reductions are made in each stand. The finished width of the strip is approximately 10¼ inches and uniform cooling and maximum flatness is achieved by idling the strip back and forth on the run-out rolls until it is cool. Figure 12-3 shows a typical grain structure of a hot-finished strip.

Shearing, Pickling, and Machine Conditioning

Before cold rolling, the hot finished strip is sheared into approximately 8 foot lengths and is pickled to remove salt and oxide.

It was confirmed in earlier cold rolling studies that uranium is extremely notch-sensitive. Unless all discontinuities and notches are removed from the edges, the metal upon reduction fails at these notches, and cracks propagate through the strip, causing scrapping of portions or all of the metal. It was found that for total cold reductions up to 15 per cent:

1. Machine conditioned edges almost never develop defects that result in cracks.
2. Knife-sheared edges are superior to the average hot-rolled edge.
3. Hot-rolled edges are third in preference and, if they are of high quality and the plate in general has a minimum gage variation, will generally behave satisfactorily.
4. Slit edges are inferior to the average hot-rolled edges.

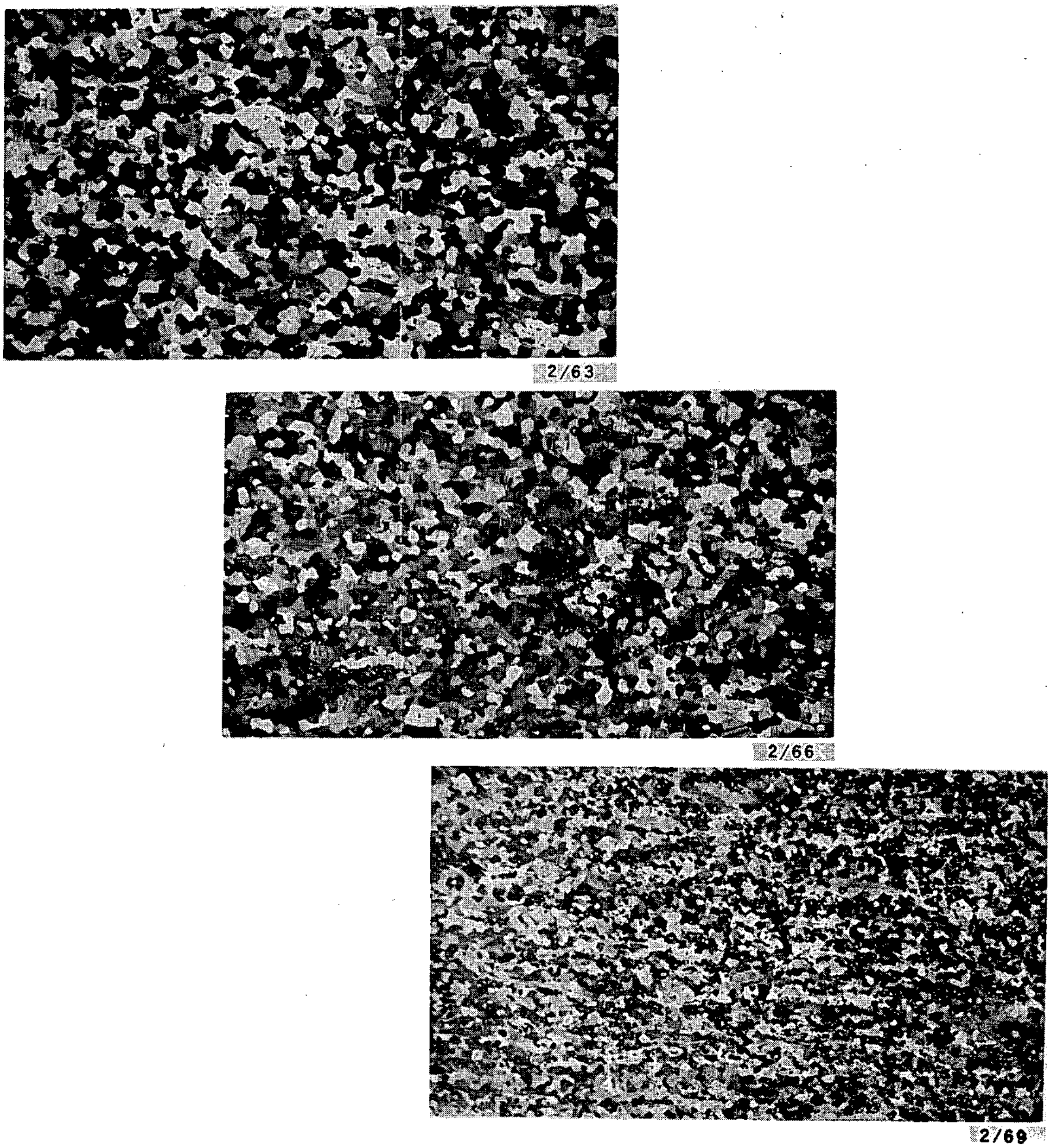

FIGURE 12-3 GRAIN STRUCTURE OF HOT-ROLLED STRIP F-8142 (100X, POLARIZED)
TOP: FRONT END OF THE STRIP CLOSE TO ITS EDGE; LONGITUDINAL SECTION
MIDDLE: MIDDLE OF THE STRIP CLOSE TO ITS EDGE; LONGITUDINAL SECTION
BOTTOM: BACK END OF THE STRIP CLOSE TO ITS EDGE; LONGITUDINAL SECTION

Because of these data, it was decided to condition all hot-rolled edges by machining prior to cold rolling (until good hot-rolled edges are routinely assured and a minimum of gage variation is achieved).

The maximum gage variation that can be allowed in the plate is that which is imposed on the thickness of the washer. Generally, 85 per cent of the hot-rolled gage variation has been and will be at ±0.003 inch, with the remaining 15 per cent of wider variation. To reduce the gage variation to ±0.002 inch, all hot-rolled strip has been finished 15 per cent oversize and then cold reduced. To date, this has been satisfactory in maintaining ±0.002-inch tolerance.

Cold Rolling

Metal is cold rolled in a 4-high mill having 15-inch-diameter work rolls (24 inches long) and back-up rolls 30 inches in diameter. The 0.224-inch plate is cold sized in two passes; the first pass gives a thickness of 0.208 to 0.209 inch, and the second pass gives the final gage. Similarly, the 0.148-inch plate is reduced in two passes to final gage; here, the intermediate thickness is nominally 0.140 inch. Because of the variation in gage of the hot-rolled strip, the gage after the first cold pass has some variation, although of a lesser magnitude than at the start.

Though it is probably possible to reduce the strip in one pass, no such attempts have been made because of the cracking encountered in earlier work. Whereas this cracking was associated with edge defects and gage variation (particularly a heavy section along the center line due to crown in the rolls), reductions since then have not exceeded 8 per cent per pass.

Results of Rolling Operation

Surface finish, straightness, and flatness of the strip have been excellent. Gage variation has been acceptable in most cases and should improve as more experience is gained. Grain structure that is typical of the cold-rolled strip is shown in Figure 12-4.

Heat-Treating – Background Information

When it was first realized that a product would be fabricated from a plate that had been subjected to prior cold work, a literature search was made. It was determined that there is little technology available on methods of fabricating a product so that it would have a minimum residual stress, a minimum of preferred orientation, and the specified grain size. Too, it was apparent that the thin section would be difficult to handle and keep flat. Other problems were associated with extrapolation of the data obtained from heat-treating the rods that are an intermediate everyday product of the plant.

Because there was little data available for guiding this work by known procedures, it was decided to base this investigation on the following information and requirements:

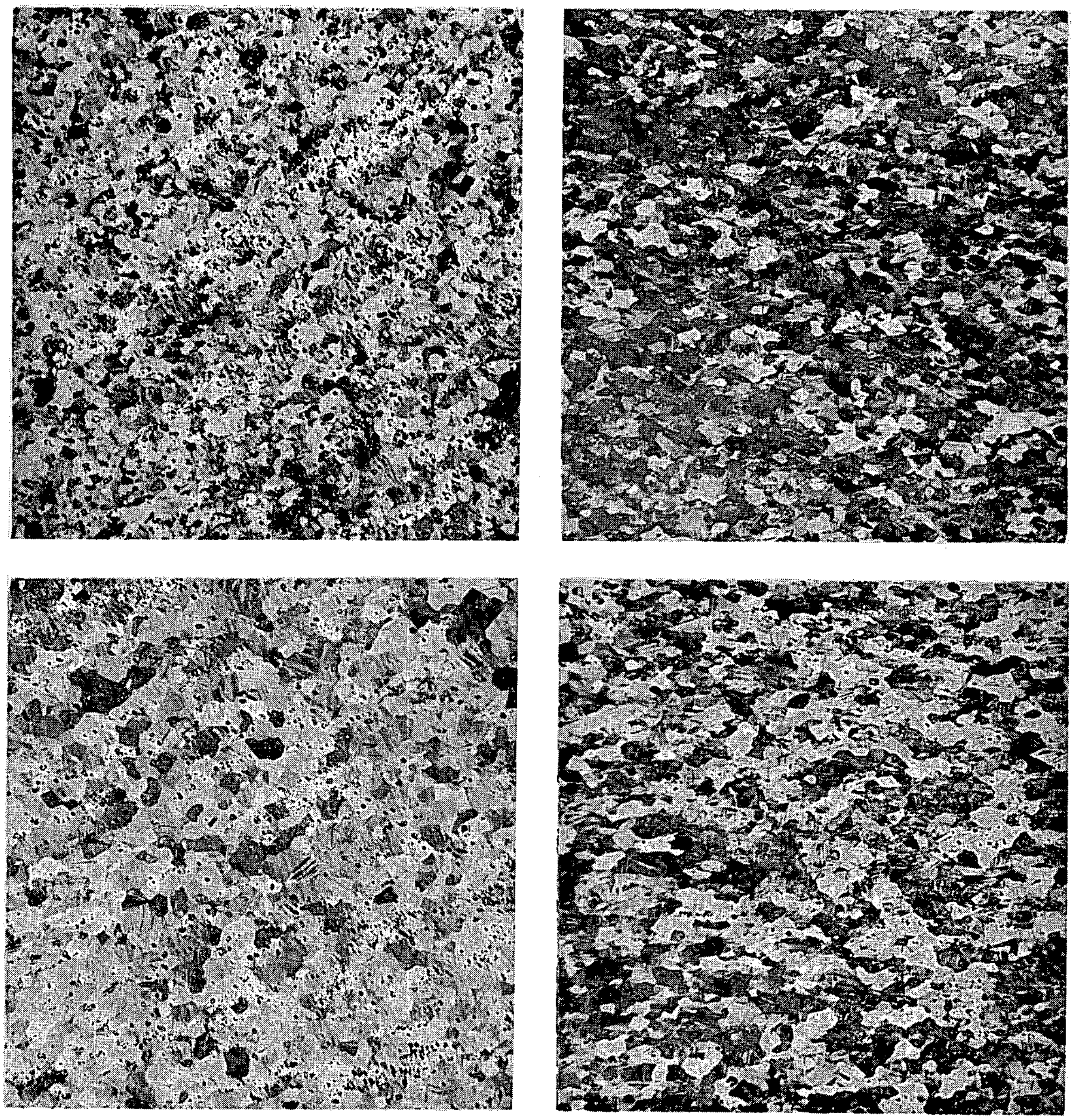

FIGURE 12-4 GRAIN STRUCTURE OF COLD-ROLLED STRIP (11% REDUCTION) F-8142 (100X, POLARIZED)
TOP LEFT: STRIP SURFACE NEAR ITS EDGE
TOP RIGHT: LONGITUDINAL SECTION AT THE EDGE
BOTTOM LEFT: STRIP SURFACE NEAR ITS CENTER
BOTTOM RIGHT: LONGITUDINAL SECTION AT THE CENTER

1. Current production practice is to treat hot-rolled rod at 730° C.

2. At a temperature of 730° C, metallographic examination shows that transformation in a 1.43-inch-diameter rod is complete after four minutes.

3. Current production practice requires that a safety factor of not less than three be applied to the residence time of a rod, i.e., residence time equals three times the time required for transformation.

4. When heat-treating is done in a molten carbonate salt bath, the hydrogen content of the metal is related to the composition of the bath in which it is treated. For a more complete description of this relationship, attention is directed to Section 15.5 of this report and to other reports.[1,2]

5. Recent studies by workers at another site have shown some fundamental relationships concerning the heat treating of hot-rolled plate material of nominal 0.180-inch thickness. Their work, aimed at producing polygonized structures when beta treated and quenched structures are annealed, has shown that the prime requisite for polygonization is the residual stress imparted by cooling through the gamma:beta or beta:alpha transformation. In particular, they have studied the cooling rate in air of their plate section and prescribed the delay times which, if exceeded, will result in air-cooled structures rather than quenched structures. As is well known, air-cooled structures cannot be refined by annealing, whereas quenched structures can be refined by annealing.

The data available from the preceding five points, coupled with the data on the grain size refining of beta-heat-treated rod metal having a delay time of not less than 19 seconds, are being studied to develop procedures for refining transformed and quenched structures.

Once a structure is produced and determined to be acceptable by metallographic techniques, the ultimate criterion of acceptability of the heat-treating technique will be determined by dilatometric and X-ray techniques to show whether the plate has a minimum anisotropy. However, it is realized in advance that the state of stress may be the all-important variable of a successful punching operation.

Heat Treating – Results to Date

The heat treatment found to give the least edge cracking is as follows:

1. Beta treatment at 730° C for 4 minutes.

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[1] *Guay, A. E., Summary Tech. Rpt., pp. 126-132, NLCO-577, October 17, 1955.*

[2] *Griffith, R. L., Summary Tech. Rpt., Vol. II, pp. 71-79, NLCO-601, January 16, 1956.*

2. Water quench

   a. The delay from salt bath to water quench should be less than 10 seconds.

   b. The water quench temperature should be held between 55°F and 95°F.

3. Alpha treatment at 640°C for 20 minutes.

4. Air cool.

Although it is not possible to give a complete report of detailed experiments now under way, certain important facts are now available:

1. Metallographic examination shows that sections 0.132 to 0.194 inch thick are completely transformed after a 1-minute residence time at 730°C.

2. For cold-worked sections 0.132 and 0.195 inch thick, the grain size after beta transformation at 730°C for four minutes (followed by 10-second air delay and a quench) is smaller than the grain size shown in rod metal (13-minute residence at 730°C, followed by a 17-second air delay and a water quench).

3. Although the data are somewhat conflicting for 0.195-inch-thick plates, air delays longer than 16 to 19 seconds result in air-cooled structures (i.e., structures whose grain size will not be refined by annealing at 640°C for 20 minutes). At the present time, the grain structures of annealed samples are thought to be reasonably independent of the temperature of the quench water in the range of 45° to 125°F.

4. Again based on a limited amount of data, it appears that the refining mechanism is somewhat dependent on the period of residence of a sample in the beta phase. When beta-quenched samples having increasing residences in the beta phase were annealed, the number of grains that were refined increased with increasing residence time; when longer residence times were used, the proportion of grains that refined upon annealing decreased in some cases. This may be an important relation in determining whether a plate is completely transformed.

To illustrate the grain structures that have been achieved, Figures 12-5 through 12-7 have been included.

Preparation of Stock for Punching

Stock prepared by three procedures has been studied in order to correlate the condition of the plate with the condition of the as-punched washer.

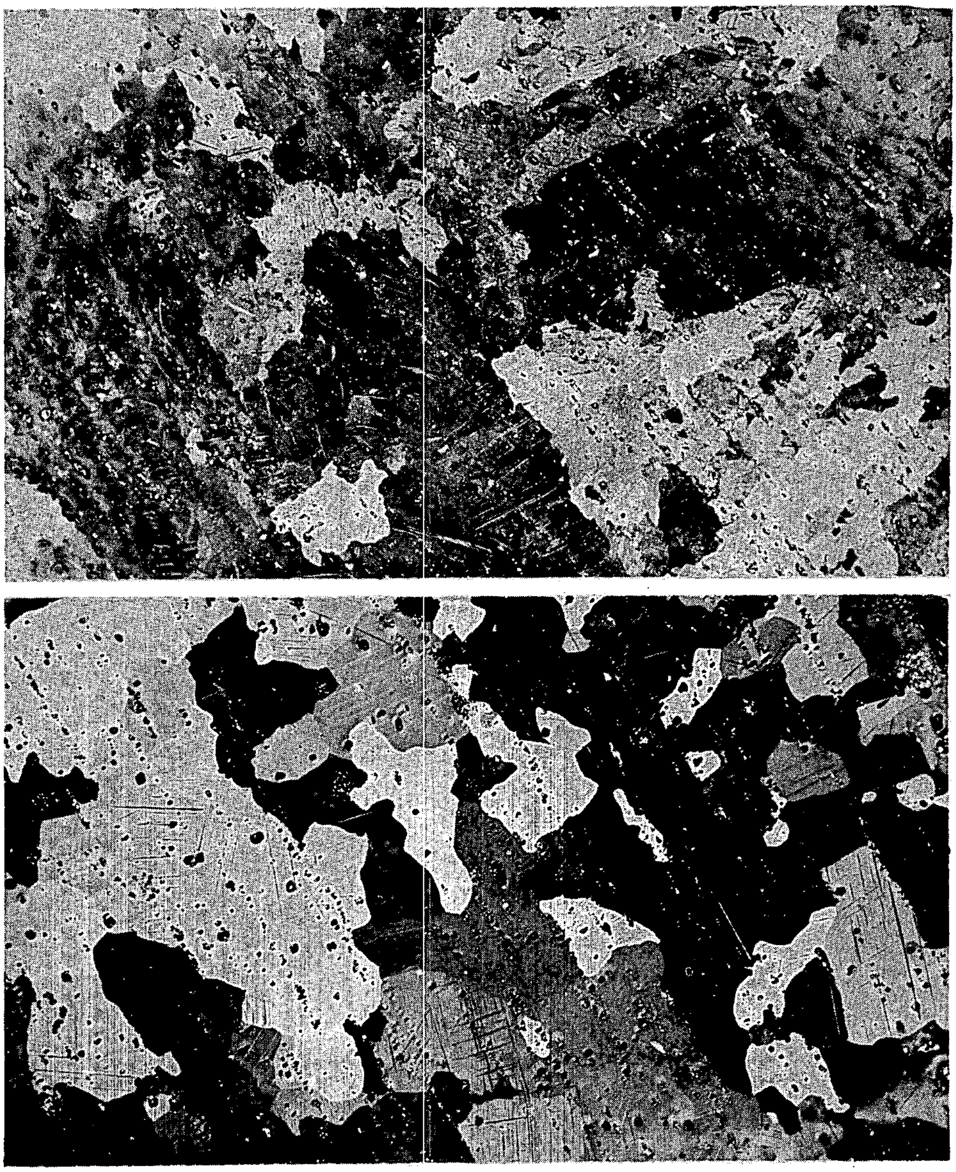

FIGURE 12-5 SAMPLES FROM A STRIP 0.195 INCH THICK THAT HAD BEEN COLD ROLLED FROM A HOT-ROLLED SAMPLE 0.224 INCH THICK. THE ANNEALED STRUCTURE SHOWS GRAIN REFINEMENT. (100X, POLARIZED)
TOP: GRAIN STRUCTURE AFTER BETA TREATMENT AT 730°C FOR 4 MINUTES, A 10-SECOND DELAY IN AIR, AND A WATER QUENCH AT 35°F
BOTTOM: GRAIN STRUCTURE OF A STRIP TREATED AS WAS THE SAMPLE SHOWN ABOVE, FOLLOWED BY ANNEALING AT 640°C FOR 20 MINUTES AND AIR COOLING

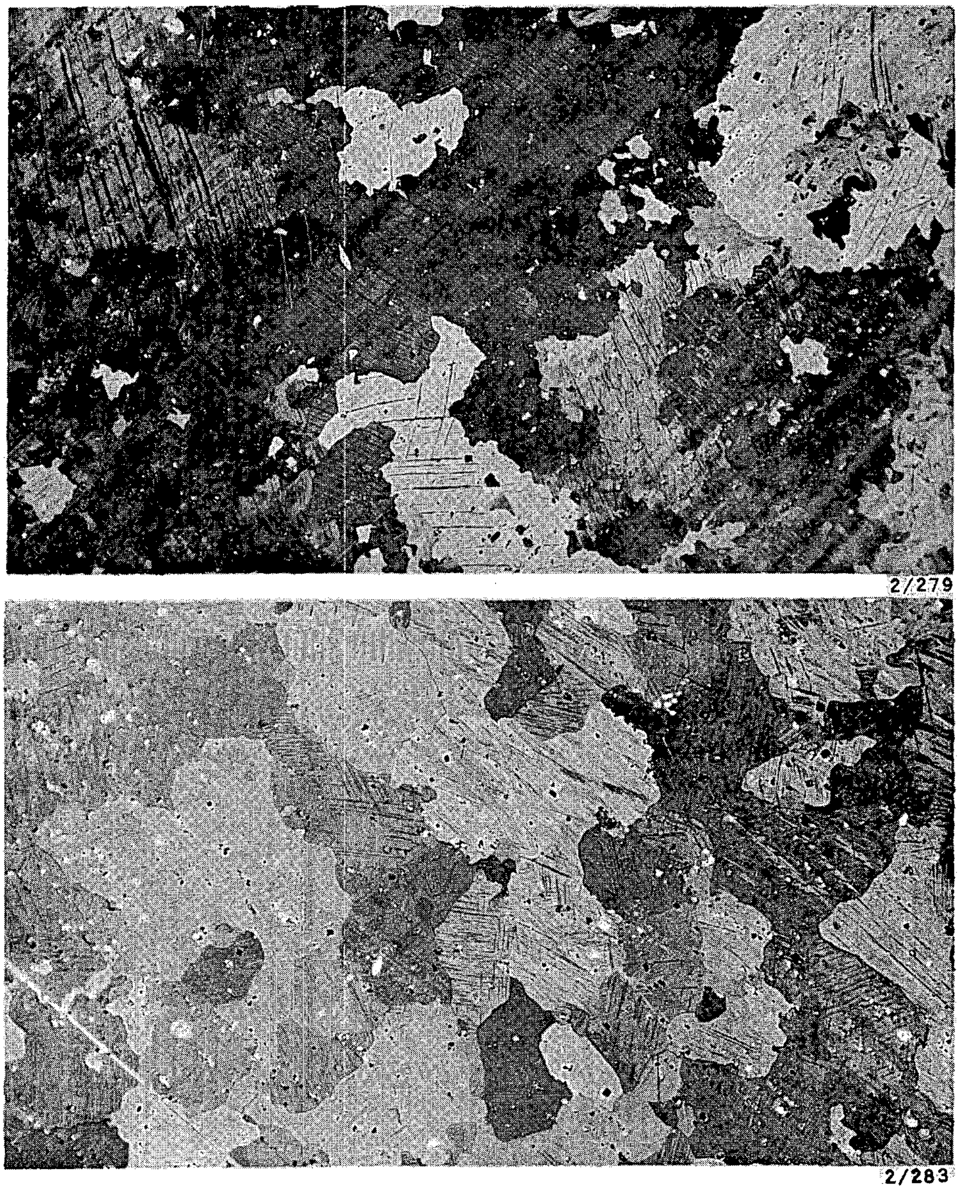

FIGURE 12-6 SAMPLES FROM A STRIP 0.132 INCH THICK THAT HAD BEEN COLD ROLLED FROM A HOT-ROLLED SAMPLE 0.164 INCH THICK. AGAIN THE ANNEALED STRUCTURE HAD BEEN REFINED. (100X, POLARIZED)
TOP: GRAIN STRUCTURE AFTER BETA TREATMENT AT 730°C FOR 5 MINUTES, AN 8-SECOND DELAY IN AIR, AND A WATER QUENCH AT 75°F
BOTTOM: GRAIN STRUCTURE OF A STRIP TREATED AS WAS THE SAMPLE SHOWN ABOVE, FOLLOWED BY ANNEALING AT 640°C FOR 20 MINUTES AND AIR COOLING.

FIGURE 12-7 SAMPLES FROM A STRIP 0.195 INCH THICK THAT HAD BEEN COLD ROLLED FROM A HOT-ROLLED SAMPLE 0.224 INCH THICK. HERE, THE ANNEALED STRUCTURE HAS NOT BEEN REFINED. (THE BETA-TRANSFORMED STRUCTURE MUST BE CONSIDERED TO HAVE BEEN AIR-COOLED; THE BETA-TRANSFORMED STRUCTURE IN THE PREVIOUS TWO FIGURES WERE WATER-QUENCHED.) (100X, POLARIZED)

TOP: GRAIN STRUCTURE AFTER BETA TREATMENT AT 730°C FOR 4 MINUTES, A 21-SECOND DELAY IN AIR, AND A WATER QUENCH AT 35°F

BOTTOM: GRAIN STRUCTURE OF A STRIP TREATED AS WAS THE SAMPLE SHOWN ABOVE, FOLLOWED BY ANNEALING AT 640°C FOR 20 MINUTES AND AIR COOLING.

It was believed that a surface stress imparted by cold working would tend to lessen edge cracking. Several pieces of both 0.188 and 0.125-inch stock were given cold reductions of from 1.5 to 9.0 per cent in increments of 1.5 per cent. A comparison of the resulting washers showed that edge cracking was always more severe in stock that had received cold work. Rockwell "C" hardness of cold-worked plate ranged from 33 to 37.

The use of a beta-treated, water-quenched, alpha-treated, water-quenched stock resulted in very severe edge cracking at all die clearances.

When the water quench that followed the alpha heat treatment was eliminated, edge cracking was reduced to a minimum; the Rockwell "C" hardness of the heat-treated plate was approximately 31. This heat treatment is recommended for production stock.

Piercing and Blanking Operations – Equipment, Method, and Results

A progressive die has been used on a 52-ton mechanical press to form about 1000 washers to date. This type of die imparts a great deal of warp in conjunction with the initial piercing operation. This warp remains in the washer after blanking and produces between 0.013 and 0.018 inch dishing in the 0.188-inch stock and 0.008 to 0.012 inch in the 0.125-inch-thick stock.

A compound washer die with simultaneous piercing and blanking operations has produced washers with a warp of less than 0.0005 inch. It appears that this type of washer die is suitable for the punching of all thicknesses of uranium to form flat concentric washers.

The most trouble relating to both the compound and the progressive die sets has been encountered on the OD punch. The ID punch of both dies has remained practically flawless.

Only two die steels have been used with success thus far: Carpenter 610 and Vasco Supreme. These are both oil hardening steels that are shock-resistant. The Carpenter 610 galls more heavily than does the Vasco die steel and as a result has not lasted as long. The galling present on a Vasco punch is easily flicked off, which demonstrates that only light galling is involved. One Carpenter 610 punch was carbonitrided for 72 hours, giving a case depth of about 0.015 inch. This punch broke, and the failure was of the brittle shear type. Vertical lapping of this punch was tried unsuccessfully in an attempt to eliminate any horizontal ridges which may tend to pick up uranium metal upon stripping. Carbide punches and dies will be tried in the near future.

The first die clearances used had a 10 per cent diametral clearance, or diametral difference between punch and die, which is a good approximation of that used for ferrous materials. (All clearances mentioned in this report will be the diametral differences between punch and die.) All 0.188-inch-thick washers produced with the 10 per cent clearance had cracked edges around 100 per cent of the perimeter. When the clearances were decreased to 0.009 inch on both the ID and OD punches and dies, there was distinctly less perimetral breakage on the 0.188-inch-thick washer, and most 0.125-inch-thick washers had no breakage visible at 10X magnification. After the washers were pickled in concentrated nitric acid for a few minutes, however, large cracks opened up in the region where cracks had previously appeared.

A 0.006-inch and 0.012-inch diametral clearance were used on the compound die; with the 0.006-inch clearance on the compound die, there was somewhat more edge cracking on the 0.188-inch stock than on the 0.125-inch stock. Reduction of die clearances below 0.004 inch will tend to increase punch breakage and galling, although the edge finishes will get better and the sides straighter.

Lubrication of punch and dies has so far proved unsuccessful. Three types of lubricant have been tried. These are:

1. Varying proportions of lard oil and kerosene.
2. Oster No. 1.
3. A graphite slurry.

All lubricants were applied before the punching operation started. Recently, a new method of application has been proposed. This involves spraying the lubricants onto the punch after blanking and before stripping because the blanking operation seems to strip the lubricant from the punch.

Effect of Die Clearance on Edge Finish and Cracking

Washers have been successfully punched from nominal 0.125-inch heat-treated uranium stock. All warp and nearly all edge cracking have been eliminated from this stock by using a compound washer die.

About 20 per cent edge cracking remains in the best-punched 0.188-inch-thick stock to date. When the same compound washer die was used for this thicker stock, there was no detectable warp.

For both thicknesses rough edges typical of a uranium fracture are still present on 95 per cent of all ID and OD surfaces. The clearances that have been found to be best are between 0.006 and 0.009 inch. Clearances less than this are still to be investigated, but it is feared that excessive galling and punch breakage will result from their use.

Washer Surface Condition

Barrel tumbling has been tried as a method of removing burrs resulting from the punching operation. Two Minnesota Mining and Manufacturing products called Super Honite and Speed Cut were used in a barrel to tumble washers. The best surface on a 0.188-inch-thick washer was obtained after about 5 hours, but severe rounding of the washer corners was also detected. Continued tumbling up to 24 hours produced no perceptible increase in surface quality. Tumbling of 0.125-inch washers for only 90 minutes produced a good surface. Further development studies are planned, in which other tumbling abrasives and tumbling times will be used.

It is planned to use a shaving die to remove about 0.010 inch from all edge surfaces in order to provide a better edge finish on a washer.

Future Work

Tests are under way and others are being planned to determine the effect of the following variables on the rolling process:

1. The effect of the slab conditioning practice on the surface quality of hot-rolled strip.
2. The effect of the edge condition of hot-rolled strip on the cold rolling behavior of the strip.
3. The effect of the percentage reduction per pass and the total reduction on the following:
    a. The edge condition.
    b. Gage variation and flatness.
4. The effect of the total amount of reduction on the conditions required to completely anneal a cold-worked sample.

The work to be done to evaluate heat-treating of plate must encompass the following:

1. Determination of the effects of the variables of the heat-treating process, i.e., for a treating temperature of 730°C, the effects of the following:
    a. The residence time.
    b. The delay time.
    c. The quench temperature.
2. The perfection of dilatometry and X-ray techniques for determining the preferred orientation and the amount of orientation in heat-treated strip.

3. Determination of the relationship of prior rolling history to the preferred orientation and residual stress of the heat-treated strip.

4. Determination of how the stress and the amount and type of preferred orientation in beta-quenched strip is related to that in beta-quenched and annealed strip.

13. RECOVERY OF URANIUM FROM SCRAP MATERIALS

13.1 PROCESSING OF AMMONIUM DIURANATE BACKLOG – A. B. Kreuzmann, E. O. Rutenkroger, and B. C. Doumas

During the period between November 1, 1955, and January 1, 1956, the NLO Metal Recovery Plant was engaged in a campaign in which the backlog of ammonium diuranate accumulated prior to the installation of the new diuranate furnace was being processed by calcination in all of the large furnacing units available in the plant. In an effort to increase the effective diuranate processing capacity of the Recovery Plant, a series of laboratory experiments[1] were conducted to examine the possibility of processing a portion of the backlog diuranate cake by a wet chemical process. The results of this laboratory work showed that a uranium concentrate containing 49 per cent uranium, 0.3 per cent fluoride, and 22 per cent phosphate could be obtained by (1) leaching the ammonium diuranate cake with hydrochloric acid (pH 0.5), (2) precipitating the leach liquor without prior filtration at pH 1.5 by the addition of phosphoric acid and ammonium hydroxide, and (3) drying the resulting filter cake. A flowsheet of this process is shown in Figure 13-1.

Because of the successful results obtained in the laboratory, this process was adopted by the Recovery Plant. During the period, January 10, 1956, to February 1, 1956, a total of 288,906 pounds of wet diuranate cake having an average assay of 20 per cent uranium and 5.79 per cent fluoride (dry basis) was processed by the phosphate precipitation technique in the manner indicated in Figure 13-2

Digestion of ammonium diuranate cake was conducted by adding approximately 10,000 pounds of wet material to a digest tank containing 1200 gallons of water and 300 gallons of hydrochloric acid (30%). Upon completion of the diuranate cake addition, the slurry was adjusted to pH 0.2 or less with additional hydrochloric acid. Dilution water was added to produce a final slurry volume of approximately 4000 gallons. After the slurry had been allowed to agitate for one hour or longer at ambient temperature, phosphoric acid was added in an amount sufficient to produce a phosphate/uranium weight ratio of at least 3/5. Upon completion of the phosphoric acid addition, the slurry was adjusted to pH 1.0 to 2.0, using 20 per cent ammonium hydroxide to precipitate the uranium. The liquors were then filtered on a rotary vacuum filter which was precoated with Dicalite.

The filtrates resulting from filtration of the precipitated slurries were neutralized with ammonium hydroxide and were filtered prior to disposal.

The phosphate cake obtained from this operation was calcined in a rotary kiln at a rate of 300 to 600 pounds per hour. During the operation, the temperature at the feed end of the kiln was 800° to 1000°F, at the middle it was about 1200°F, and at the discharge end it was 1300° to 1400°F. The total residence time in the kiln was approximately 11 hours. The calcined product obtained during the operation had an average assay of 37 per cent uranium, 0.15 per cent fluoride, 0.013 per cent chloride, and 21.4 per cent phosphate.

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[1] *Kreuzmann, A. B., Kutenkroger, E. O., and Johnson, E. R., Summary Tech. Rpt., Vol. I, p. 132, NLCO-600, January 16, 1956.*

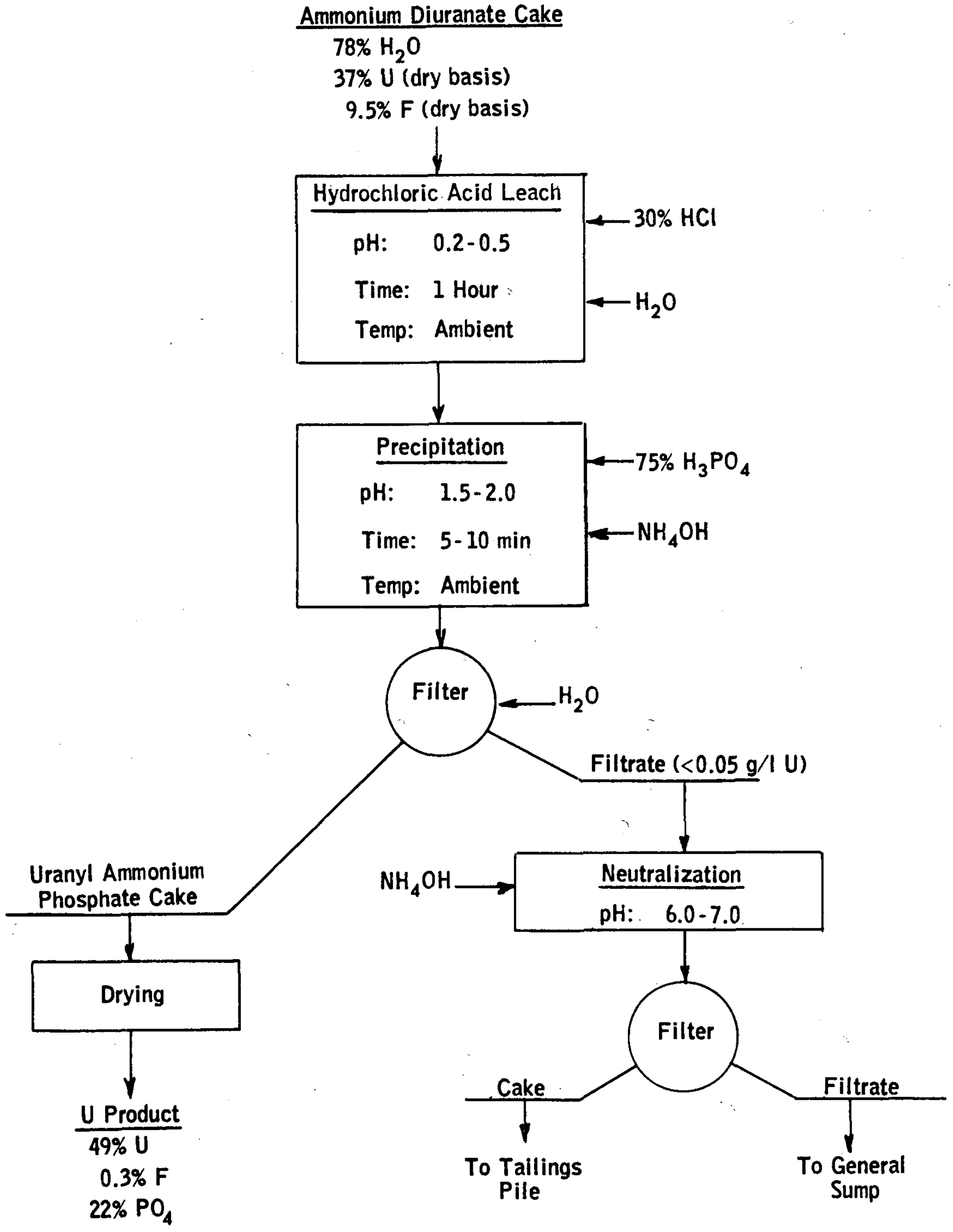

FIGURE 13-1 PROCESSING OF THE AMMONIUM DIURANATE CAKE BACKLOG BY A HYDROCHLORIC ACID LEACH - PHOSPHATE PRECIPITATION PROCESS

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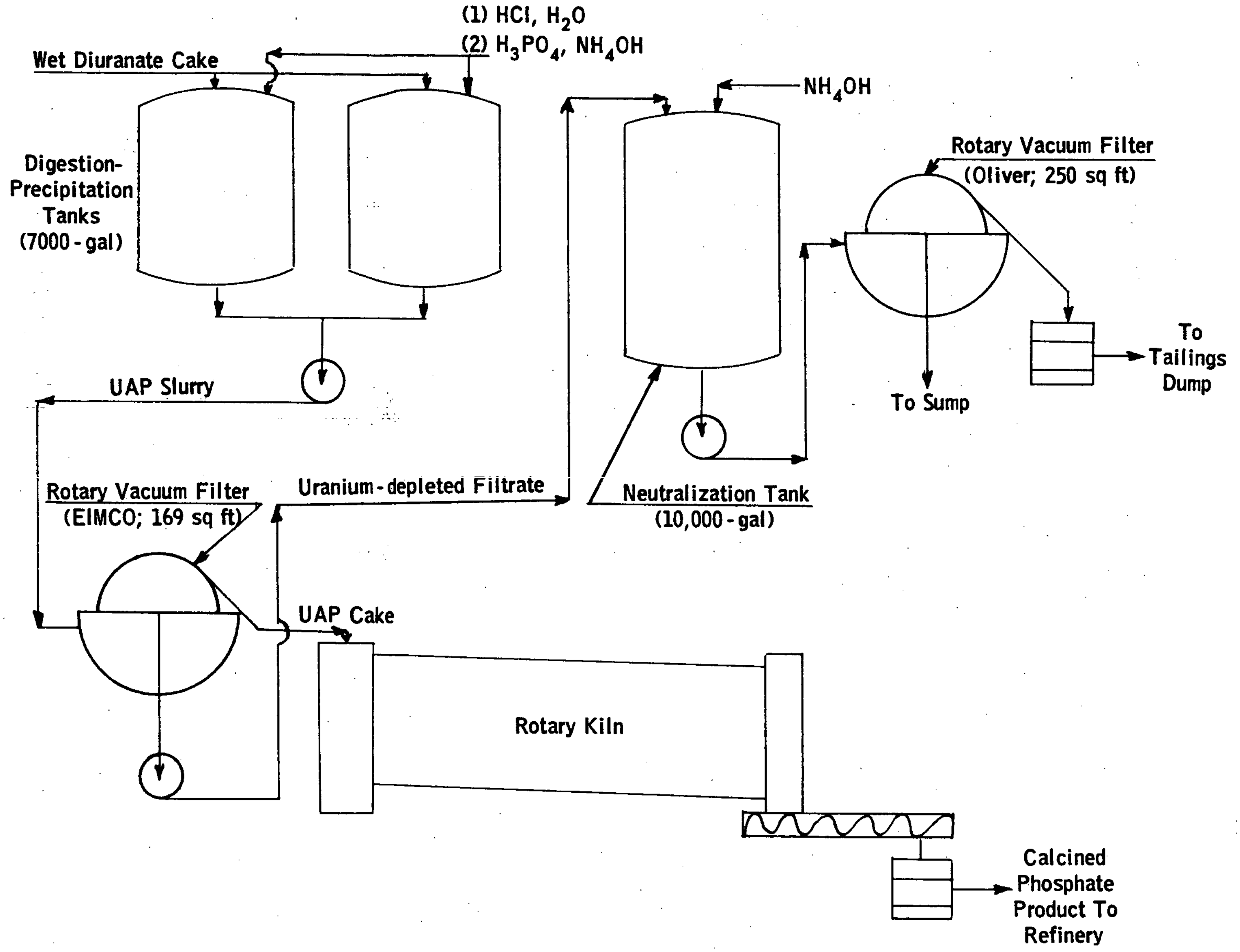

FIGURE 13-2 PROCESSING OF BACKLOG DIURANATE CAKE – EQUIPMENT FLOWSHEET

CONFIDENTIAL

This operation has successfully demonstrated, on a large scale, the ability of the phosphate precipitation process to recover uranium from high-fluoride scrap materials in the form of a high-grade uranium concentrate of low fluoride content.

13.2 RECOVERY OF URANIUM FROM MgF_2 SLAG – A. B. Kreuzmann, E. O. Rutenkroger, R. L. Doyle, and B. C. Doumas

Since the introduction of the use of MgF_2 slag as a refractory for lining reduction bombs, considerable development effort has been expended in investigating methods of recovering uranium from the reject slag resulting from the preparation of liner material. From the results of early work, it was apparent that the hydrochloric acid leach-ammonium hydroxide precipitation process (currently used at NLO for processing C-Oxide) was not capable of recovering uranium from the slag in the form of a concentrate having a low fluoride content. It was found that the small amounts of fluoride which dissolved during leaching coprecipitated with uranium during the precipitation of the latter at pH 6.2.

An investigation was conducted in the NLO laboratory to study the possibility of recovering uranium from these acid leach liquors by precipitation at a pH below that at which the fluoride was known to precipitate (pH 2.0).[1] A successful process was developed in which uranium was precipitated from the leach solution at pH 1.5 as uranyl ammonium phosphate (UAP). This process (Fig 13-3) consisted of the following steps:

1. Roasting the slag to convert metallic uranium and magnesium to their respective oxides, thereby facilitating grinding and preventing the generation of hydrogen during leaching;
2. Pulverizing the roasted slag;
3. Leaching the roasted and pulverized slag with hydrochloric acid in the presence of an oxidant in order to solubilize the uranium present, followed by filtration of the leach slurry;
4. Precipitation of the uranium from the leach solution as UAP, using orthophosphoric acid and ammonium hydroxide, followed by filtration of the precipitated liquor;
5. Caustic treatment of the UAP cake by slurrying with sodium hydroxide to convert the uranium to sodium diuranate, solubilize the phosphate, and liberate the ammonia, followed by filtration of the resulting slurry; and
6. Drying the resulting soda salt product for use as a feed material for the Refinery.

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[1] *E. R. Johnson, et al, Uranium Recovery from Composite UF_4 Reduction Bomb Waste, FMPC-511, January 28, 1954.*

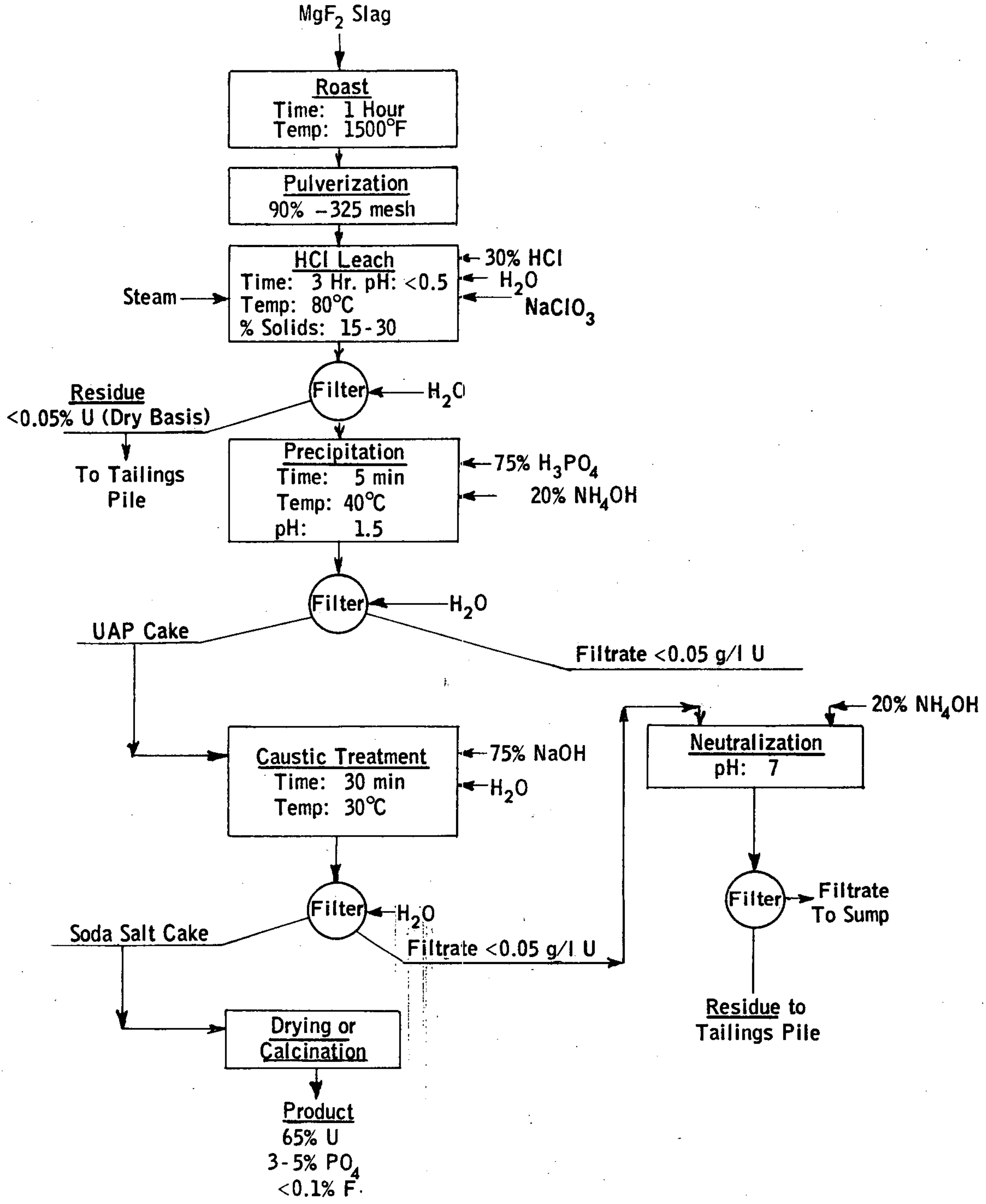

FIGURE 13-3 RECOVERY OF URANIUM FROM MgF_2 SLAG BY A HYDROCHLORIC ACID LEACH – PHOSPHATE PRECIPITATION PROCESS

The results of these tests showed that a soda salt product which assayed 65 per cent uranium, less than 0.1 per cent fluoride, and 3 to 5 per cent phosphate could be obtained by such a process.

It was decided that the favorable results obtained by this process in laboratory experiments merited further testing on a plant scale in the NLO Recovery Plant. Approximately 54 tons of reject MgF_2 slag (RMF), assaying 7 to 9 per cent uranium, was obtained from the MCW slag liner plant for this test.

The plant-scale processing of the RMF material was conducted batchwise, using the equipment currently used for processing C-Oxide. The RMF material was crushed to minus 4 mesh in a Gyracone crusher, roasted for two hours at 1500°F in a Herreschoff furnace, and ground to 85 per cent minus 325 mesh in a Williams ring-roll mill. The roasted and pulverized material was leached with hydrochloric acid for three hours at 185° to 200°F, and the resulting slurry was filtered on a rotary vacuum filter. The residue obtained from the filtration operation averaged less than 0.05 per cent uranium. The uranium present in the filtered leach liquors was precipitated (pH 1.5) by the addition of phosphoric acid and ammonium hydroxide and the resulting precipitated slurry was filtered on a rotary vacuum filter. A PO_4/U weight ratio of 1/1 was used during precipitation. The resulting UAP cake was slurried with a five per cent sodium hydroxide solution, using a NaOH/U weight ratio of 1/1, and the resulting mixture was filtered on a rotary vacuum filter. The soda salt product obtained from this operation was dried at 1200°F in a Herreschoff furnace. The dried material averaged 54.2 per cent uranium, <0.1 per cent fluoride, 0.039 per cent chloride, and 3.2 per cent phosphate.

The results of both the laboratory and the plant tests showed that the phosphate precipitation technique was successful in recovering uranium from MgF_2 slag in the form of a uranium concentrate having a low fluoride content. A complete report of the processing of MgF_2 slag by this process is in preparation.

13.3 FLUORIDE VOLATILIZATION DURING EVAPORATION AND CALCINATION OF REFINERY RAFFINATES – E. O. Rutenkroger

Previous studies[1,2] of the effect of fluoride-complexing agents on the volatilization of fluorides during evaporation and calcination of Refinery raffinates have been extended to include an investigation of a number of other metal ions as possible fluoride-complexing agents.

A series of experiments was conducted in which ten per cent nitric acid solutions containing approximately 0.5 g/l fluoride (added as NaF) were spiked with various metal ions to produce approximately ten times the stoichiometric requirement necessary for the formation of the MF_6^{-3} ion. Each sample was placed in a round-bottom flask, which was heated with a gas flame. The vapors from this flask were condensed in a Liebig condenser and collected in a receiver which was vented to a gas-scrubbing bottle containing 18 per cent KOH.

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[1] *Johnson, E. R. and Rutenkroger, E. O., Fluoride Volatilization During Boildown and Calcination of Raffinate Materials, FMPC-379, January 25, 1954.*

[2] *Johnson, E. R., and Rutenkroger, E. O., Fluoride Volatilization During Nitric Acid Recovery from Solvent Extraction Raffinates – Laboratory Investigation, NLCO-576, May 1, 1955.*

Samples were evaporated until the flask temperature started to increase rapidly (280°F). At this point, the receiver and scrub solution were changed and the heating was continued (800°F) until there was no further evidence of NO_2 evolution. The distillates and scrubber liquors were analyzed for fluoride, and the percentage of the fluoride volatilizing in the evaporation and calcination steps was calculated.

A list of the metal ions used and their effect on fluoride volatilization is given in Table 13-1. The effect of aluminum additive, as determined in previous studies, is also shown.

The results of these studies showed that, of the additional metal ions studied, thorium, tin, zirconium, and titanium were effective in reducing fluoride volatilization from 10 per cent HNO_3 solutions during plant-simulated evaporation and calcination experiments. However, none of these ions was as effective in reducing fluoride volatilization as was aluminum. Previous studies showed that aluminum was effective in reducing fluoride volatilization to less than five per cent of the total fluoride, as compared to 17 per cent for thorium (which was the most effective of the additional metal ions studied).

TABLE 13-1

THE EFFECT OF ADDITIVES ON FLUORIDE* VOLATILIZATION DURING EVAPORATION AND CALCINATION OF NITRIC ACID SOLUTIONS

Additive	Wt** of Additive (g/l)	Per Cent of Fluoride Volatilized During	
		Evaporation	Calcination
$Al(NO_3)_3 \cdot 9H_2O$	25.0†	3.1†	0.4†
$Th(NO_3)_4 \cdot 4H_2O$	24.3	16.6	0.7
Sn	5.2	67.0	0.9
$Ti_2(SO_4)_3$	8.4	69.0	3.2
ZrO_2	5.4	73.1	0.0
MgO	3.7	95.8	0.0
$Cr_2(SO_4)_3 \cdot K_2SO_4 \cdot 24H_2O$	44.2	97.5	3.2
ZnO	3.6	99.0	0.0
CuO	3.5	99.1	0.9
$Co(NO_3)_2 \cdot 6H_2O$	12.9	100	0.0
Ni	2.6	100	0.0
$Pb(NO_3)_2$	14.7	100	0.0

* 1000 ml of 10 per cent HNO_3 containing 0.470 g/l F (added as NaF) was used for each trial.

** The weight of each additive used was approximately 10 times the stoichiometric requirement for the formation of MF_6^{-3}.

† From previous experimental data[1].

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[1] *ibid.*

13.4 KINETIC STUDY OF THE MECHANISM OF THE REACTION BETWEEN URANIUM AND NITRIC ACID – B. C. Doumas

Periodically, at NLO and other sites, explosions have occurred when uranium metal was being treated with nitric acid. Similar incidents have occurred during nitric acid treatment of some alloys of uranium. Verbal diagnoses of these occurrences have been conflicting and definite remedies and preventive measures have been difficult to prescribe. In view of these conditions, a survey of existing literature was conducted in an attempt to obtain satisfactory explanations of these explosive reactions.

Explosion problems encountered during the dissolution of uranium-zirconium alloys with nitric acid have been thoroughly investigated and have apparently been solved. A dissolving solution of 11<u>M</u> nitric acid, 0.75<u>M</u> aluminum nitrate, and 0.3<u>M</u> hydrofluoric acid has proved satisfactory for the safe dissolution of alloys of this kind.

As a result of the literature survey, it has been established that explosions which have occurred during the dissolution, pickling, or deoxidation of uranium with nitric acid may be attributed to one or both of the following mechanisms:

1. Hydrogen Evolution

$$U + 4HNO_3 \longrightarrow 2NO + UO_2(NO_3)_2 + 2H_2O\ (g)$$

$$U + 2H_2O \longrightarrow UO_2 + 2H_2$$

$$2H_2 + O_2 \longrightarrow 2H_2O\ \text{(Explosive Reaction)}$$

   This mechanism is based on the assumption that the nitric acid present is completely consumed (at least locally) and that therefore the remaining hot uranium metal can react with the available water or water vapor to form hydrogen. The hydrogen subsequently reacts explosively with oxygen.

2. Reaction of Nitrogen Oxides with Uranium

$$U + 4HNO_3 \longrightarrow 2NO + UO_2(NO_3)_2 + 2H_2O\ (g)$$

$$3U + 8NO \longrightarrow U_3O_8 + 4N_2\ \text{(Explosive Reaction)}$$

$$3U + 8NO_2 \longrightarrow U_3O_8 + 8NO\ \text{(Explosive Reaction)}$$

   This mechanism is based on the fact that uranium can react violently with nitric acid vapors or nitrogen oxides.

The hydrogen evolution mechanism is not supported by any experimental data. Available off-gas analyses of dissolution operations indicate that the reaction of uranium with nitrogen oxides is more likely to proceed, as large amounts of these gases are generated during the reaction. The supporting data for either postulated mechanism are meager.

A laboratory study of the uranium-nitric acid reaction has been initiated to determine the mechanism of the reaction. Attempts are being made to establish a kinetic rate equation for the operation by studying the effects of nitric acid concentration and temperature, as well as the uranium surface area, on the reaction rate.

13.5 OXIDATION OF GRINDER SLUDGE - S. Cseplo

A project was initiated to evaluate the possibility of oxidizing uranium grinder sludge in a closed reactor. The reactor is to be evacuated, heated to about 1000°F, and purged with an inert gas to carry off the water and soluble oil. Then oxygen is to be introduced at a slow, controlled rate.

Small-scale laboratory tests indicated that at 150° to 170°F the water distilled quite readily under simultaneous evacuation and an inert gas purge, but that the soluble oil residue did not vaporize until a temperature of 600° to 700°F was reached. Further heating to 1000°F caused "cracking" of the remaining oil, leaving a blackish "varnish" on the uranium sludge. Introduction of oxygen to the heated sludge, after the inert gas purge was stopped, caused a small explosion, as there was a rapid oxidation of the uranium and "varnish" present. Probably, the sludge still contained residual oil in the mass of the sludge, indicating that a longer heating cycle at 1000°F was needed in order to volatilize all of the oil. A laboratory determination of the flash point, boiling point and ignition temperature of the oil showed values of 329°F, 590°F, and 626°F, respectively. Presumably, the soluble oil is either lard oil or a similar type of oil.

A new remote-control reactor was designed which will place operating personnel at a safe distance while a larger charge (approximately 15 pounds of sludge) is processed in the reactor. The furnace consists of a 6-inch-diameter graphite cylinder, 24 inches long, wrapped with three Calrod heating elements, and insulated with a two-inch coating of furnace cement. The three Calrod elements will be controlled electrically from a control station so that various temperatures can be obtained in the reactor. The reactor pot, which will rest inside the furnace, will be equipped with electrically operated solenoid valves on the helium purge line, the oxygen line, and the off-gas line. The entire unit will be enclosed in an insulated box to minimize heat losses. A steam jet will supply the necessary vacuum for the reactor.

14. THORIUM DEVELOPMENT

14.1 FABRICATION OF THORIUM ELECTRODES – H. H. Baker

Additional work to determine some of the parameters of consumable thorium electrode fabrication has been completed. Minimum pressures consistent with resistivity and breaking strength have been determined.

The pressing of thorium sponge in a 5/8-inch by 5/8-inch by 6-inch die, reported earlier,[1] was accompanied by die seizure. Needed was a collapsible die to permit rapid extraction of the pressed bar.

The Elmes 1000-ton press at the Bureau of Mines Station, Albany, Oregon, was used for pressing derby sponge to an electrode size suitable for melting. This press has a side ram that gives the die a "collapsible" feature. A series of 2-inch by 2-inch by 10-inch compacts were pressed from derby pieces having a maximum dimension of ¾ inch. A pressure of 200 tons was used as the minimum, as below that pressure, pressure readings are not reliable. Pressures varied from 10 to 46 tons per square inch. Resistivity was measured on a Kelvin Double Bridge with a 4-inch gage length. Breaking strength was determined in a testing machine, by the use of a standard flexure fixture with anvils spaced seven inches apart. Properties of the bars are shown in Table 14-1.

TABLE 14-1

EFFECT OF PRESSURE ON THE PROPERTIES OF PRESSED THORIUM ELECTRODES

Total Pressure (tons)	Pressure (tsi)	Theoretical Density (%)	Resistance 4-in. Gage Length	Resistivity (ohm-cm)	Breaking Load (lb)
200	10	74.1	0.0103	0.030	864
400	20	85.2	0.0042	0.011	1808
600	30	89.2	0.0070	0.017	1915
800	40	92.6	0.0029	0.0067	2232
920	46	94.0	0.0051	0.012	2600

The results of this work indicate that 30 tsi is the optimum pressure for yielding a strong bar without severe die seizure. Resistivity does not appear critical at pressures higher than 20 tsi.

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[1] *Baker, H. H., and Magoteaux, O. R., Summary Tech. Rpt., Vol. II, pp. 25-26, NLCO-601, January 16, 1956.*

Two ingots were produced by the electrode-pressing route to determine ingot quality. Eleven whole dezinced derbies were broken in a Baldwin 100-ton press. The derbies collapsed readily, as had been experienced earlier in a forging press at room temperature. It was then necessary to feed those crushed derby pieces that were in the 1 to 3-inch range through an alligator shears to reduce the size to less than one inch. This material was pressed as 2-inch by 2-inch by 10-inch bars at 30 tsi. The pressed bars were uniform and possessed ends of sufficient density and strength for butt welding. The bars were butt welded and melted to form two 7-inch-diameter, 24-inch-long ingots.

15. NEW PROCESSES AND SPECIAL PROBLEMS

15.1 ULTRASONIC DIFFERENTIATION BETWEEN GROSS VOIDS AND MICROPOROSITY WITHIN THORIUM SLUGS – H. W. Hesselbrock and J. P. Scheuer

It is required that thorium slugs for use in reactors be sound and free from internal voids. It has been shown that gross voids of the type shown in Figure 15-1 can be located by the use of a Reflectoscope.[1] Voids of this type result in a decreased back-reflection and a sizeable defect reflection which can be noted on the Reflectoscope.

It was observed that in some cases a slightly decreased back-reflection occurred with no accompanying defect reflection. The significance of these readings has been investigated. A photomicrograph of the cross section of a typical slug giving this type of reading appears in Figure 15-2. The microporosity observed in this photomicrograph was typical of the entire slug. It may be compared with the photomicrograph of a cross section typical of an acceptable thorium slug (Fig. 15-3).

It has been found that gross voids in thorium slugs can be located by observing the presence of a deflect reflection of the Reflectoscope screen. The presence of microporosity is indicated by a decreased back-reflection in the absence of a defect reflection.

15.2 ULTRASONIC VOID DETECTION IN 10 PER CENT NIOBIUM, 90 PER CENT URANIUM INGOTS – V. Morton

The purpose of this project is to locate voids in uranium-niobium ingots in order that we might prevent the further processing of out-of-specification material.

Ingots cast at National Lead Company of Ohio are machined, inspected, and sent to Bridgeport Brass Company. There, the machined ingot is extruded and subjected to further processing.

It was brought to our attention that some ingots contained voids that were not apparent upon inspection but were found to be present during extrusion. If internal voids could be detected prior to shipment of the ingots to the Bridgeport Brass Company, the processing of unacceptable material would be eliminated.

In the early stages of the production of ingots, considerable difficulty was encountered. A proportion of the ingots contained porous sections, and internal voids on the order of ¼ to 1½ inches were detected upon sectioning. Some irregularities appeared to close over or smooth out during the extrusion process. Voids appearing on the surface during and after processing are cause for rejection. Various personnel have expressed the opinion that voids on the order of 5/16 inch and smaller can be "rolled out".

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[1] *Scheuer, J. P., and Guay, A. E., Ultrasonic Inspection of Thorium Metal, NLCO-573, August 1, 1955.*

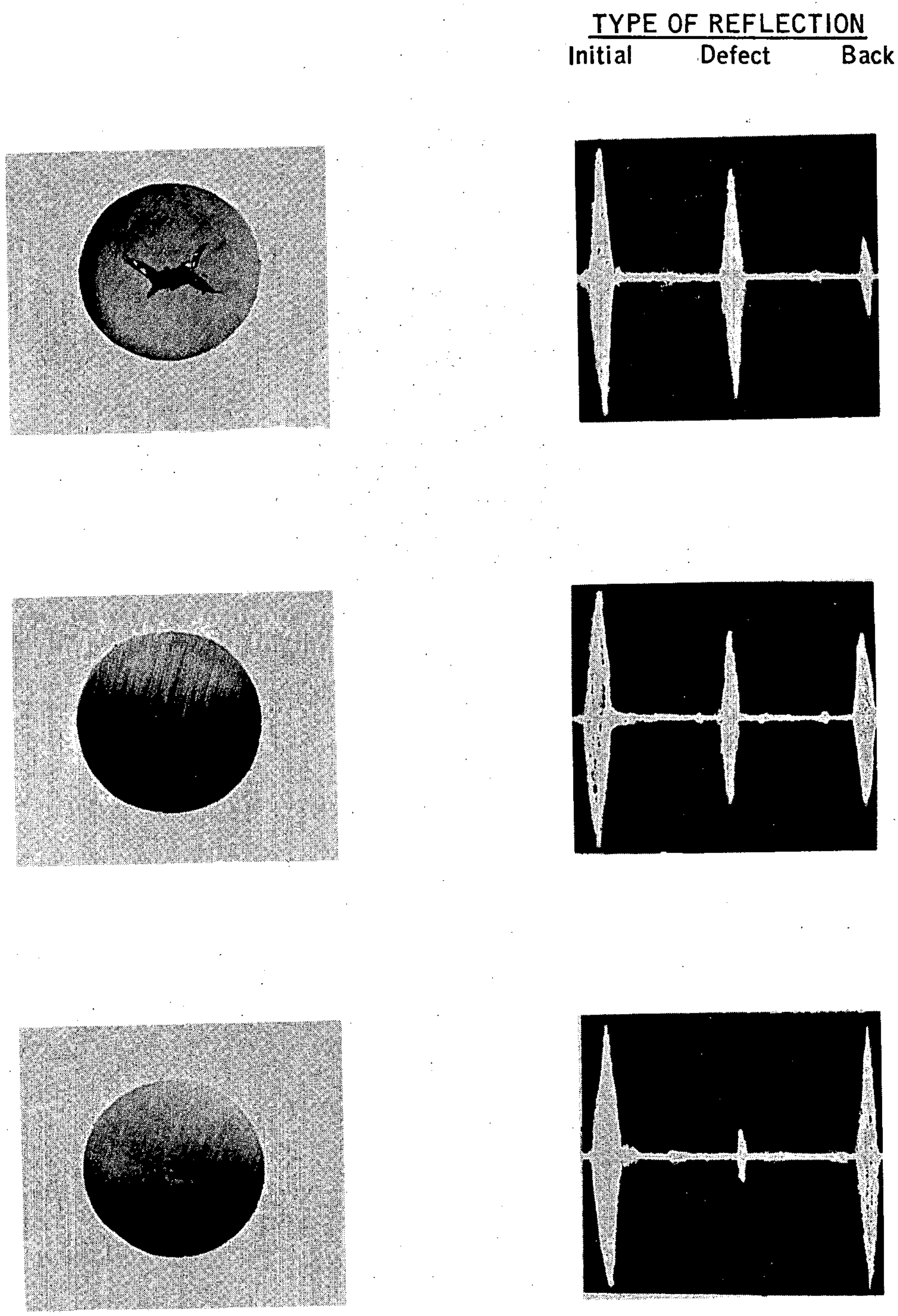

FIGURE 15-1 TYPICAL GROSS VOIDS IN THORIUM SLUGS (1X); OSCILLOGRAMS.

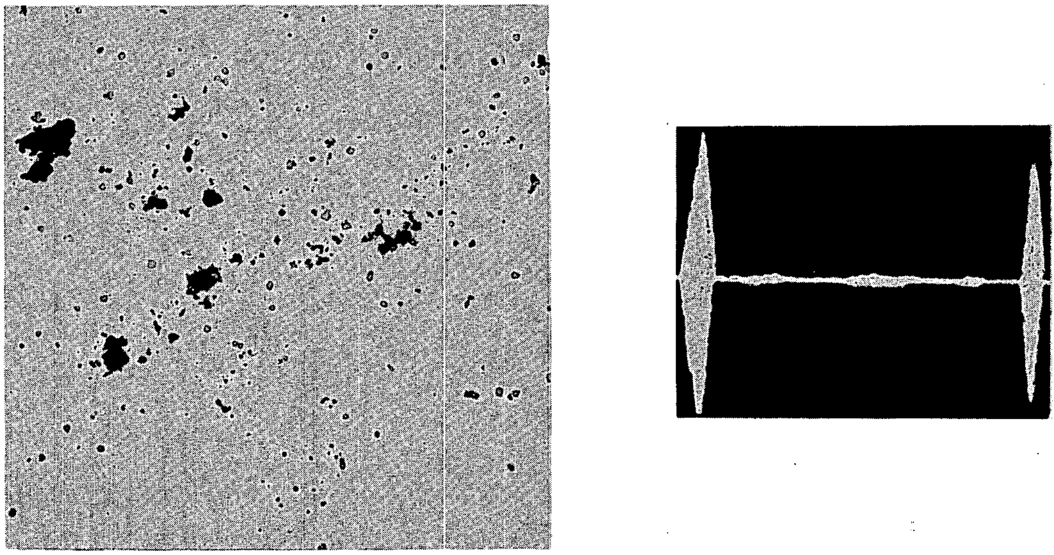

FIGURE 15-2 CROSS SECTION OF THORIUM SLUG (100X) CONTAINING MICROPOROSITY; OSCILLOGRAM.

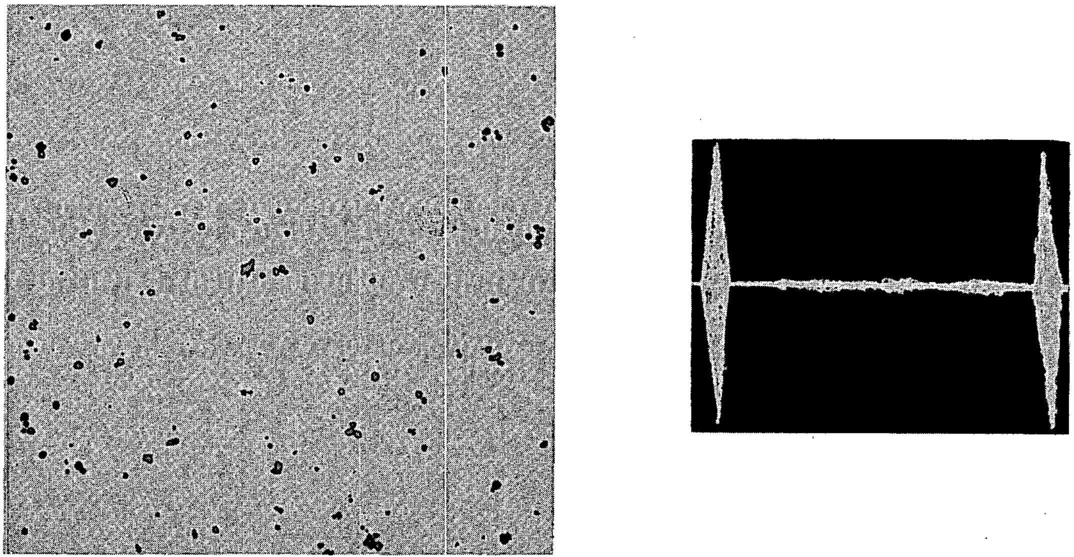

FIGURE 15-3 CROSS SECTION OF THORIUM SLUG (100X) SHOWING NO MICROPOROSITY; OSCILLOGRAM.

We were requested to examine the possibility of nondestructive testing which would allow discrimination between ingots of good quality and those that should be rejected. After considering all of the instruments available, we decided upon the "Mark V Flaw Detector". This instrument was developed by Kelvin-Hughes, Ltd. and operates on the reflection or echo principle, as described by Carlin.[1] The Flaw Detector was selected for its depth of penetration, its high resolution, and its sensitivity over a wide frequency range.

In the developmental phase of this project, the ingots were inspected before they were machined. However, some of the ingots did not have a sufficiently smooth surface to permit proper coupling between the transducers and the ingot surface. Therefore, the ingots that were shipped had been inspected after machining.

In order to calibrate this instrument, one ingot that did not meet chemical specifications was sectioned to determine whether or not voids existed. A large void, approximately 1½ inches in diameter, was found in the plane of section. The instrument was calibrated on this section, which fortunately had a relatively smooth surface. Another out-of-specification ingot was examined and the instrument indicated a void of approximately 1¼ inches. The ingot was then sectioned and the void that was found measured 1 inch by 5/8 inch across the two axes. This is shown in Figure 15-4.

Each ingot shipped to Bridgeport Brass for extrusion has been ultrasonically inspected at NLO and the data recorded. These data indicate a steady improvement in the casting practice but because this improvement must be further verified, no rejections have been made on the basis of this test.

An inspection method also has been set up at Bridgeport Brass where the Sperry U. R. Reflectoscope has been used for examination of the extruded pieces in an effort to obtain data that can be correlated with our findings. There was an effort to compare the data obtained with the two instruments, but few results have been obtained as yet and no definite conclusions can be reached at this time.

Summary

Voids in niobium-uranium ingots, ¼ inch and larger, have been located by the use of a Kelvin-Hughes Mark V Flaw Detector.

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[1] *Carlin, B., "Ultrasonics", McGraw-Hill, New York, 1949.*

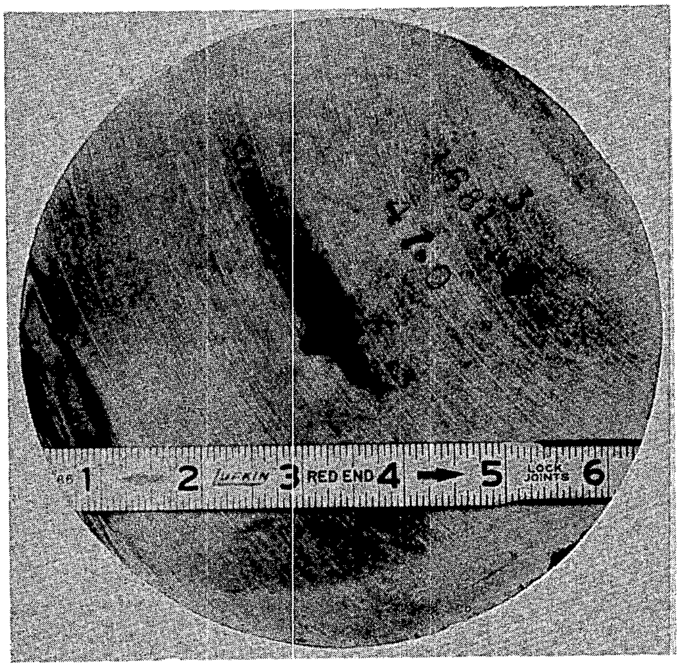

FIGURE 15-4 CROSS SECTION OF A MACHINED URANIUM - NIOBIUM INGOT. A 1¼-INCH VOID WAS INDICATED BY THE FLAW DETECTOR. A 1-INCH BY 5/8-INCH VOID WAS FOUND 7 INCHES FROM THE TOP OF THE INGOT.

15.3 DEVELOPMENT OF THE PROCESS FOR CENTRIFUGALLY CASTING HOLLOW FUEL ELEMENTS – E. B. Blasch, J. C. Straub, and A. E. Guay

During the past quarter, attention has been focused upon the development of a casting technique for hollow sections and special shapes, as there is considerable interest in hollow fuel elements (slugs) at the present time. Most of the work on hollow slug casting was of a scoping nature.

A larger aluminum mold having 18 cavities and a diameter of 32 inches (Fig. 15-5) has been used for this series of tests, (the previous mold had a 24-inch diameter). Hollow and solid castings 1-1/8 inches in diameter and 8½ inches long were made. When fuel elements of this size were cast solid, the castings were apparently sound with no macroporosity; the first attempts to cast around a graphite core showed a fairly good surface condition but porosity within the slug. Investigation of this porosity shows that it probably resulted from turbulence during filling the mold and from excessive chilling. Heating of the mold was considered desirable.

As a possible method of mold heating, a change in design was incorporated; the induction coil power was used to preheat the mold. A graphite thief was attached to the mold cope ring in such a way that it acted as a funnel during the pour. During the heating cycle, this thief transferred

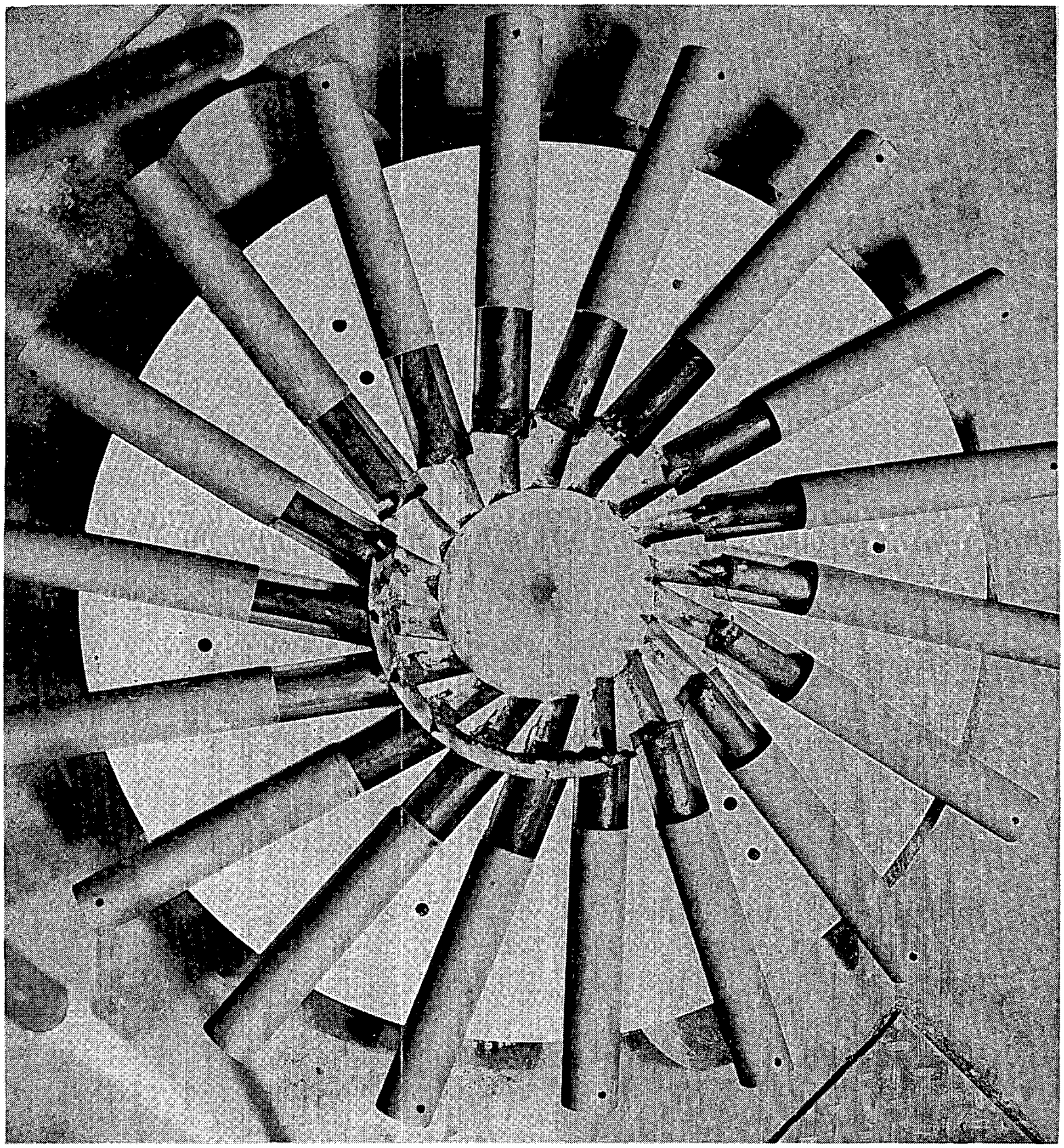

FIGURE 15-5 ALUMINUM MOLD CONTAINING HOLLOW CASTINGS. SLEEVES HAVE BEEN PULLED OUT TO EXPOSE SLUGS.

heat from the coil to the mold by conduction. Since the thief projected into the induction coil field, changing the height of the thief and changing the heat cycle made available a range of mold temperatures ranging from 100°F to 650°F. The upper limit was dependent on the mold material being used, in this case, aluminum. A thermocouple placed in contact with the top of the mold near its OD recorded the mold temperature.

Recent hollow castings (Fig. 15-6) show greater soundness, with density equalling that of the wrought piece.

Summary

Structures produced by centrifugal casting (Fig. 15-6) were typical of as-cast metal. For unalloyed sections, the grain size ranged from 1 to 5 millimeters. Exploratory tests in heat treatment showed that by beta treatment followed by high alpha anneal, grain refinement to the range of 0.1 millimeter can be obtained. Orientation measurements and physical tests are still to be made.

Heat Treating of As-Cast Slugs

In the interest of comparing the structures that result from heat-treating centrifugally cast slugs with the structures obtained by heat-treating alpha rolled rods, preliminary work has been started.

To date, studies have been confined to solid Slugs No. 12 and 13 from Heat No. 413. Preliminary examination of these slugs in the as-cast condition showed grain structures that appear to be similar to rod metal that has been beta treated and allowed to air-cool from the treating temperature. Figures 15-7 and 15-8 show photomacrographs of central longitudinal sections of each slug; the sample pieces were removed from the part of the casting furthest from the center of the mold. Possible evidence of a bottom chill is shown quite prominently in Figure 15-8, where a finer grained structure is shown at the bottom of the casting (right side of the photograph).

That these castings are reasonably stress-free (i.e., slowly and uniformly cooled) is evidenced by Figures 15-9 and 15-10. Samples from both slugs were alpha annealed at 640°C for 20 minutes; the sample piece from Slug 12 was water-quenched after the anneal and the sample from Slug 13 was air-cooled after annealing.

In order to refine the grain structure of the cast samples, it was decided to give them a standard beta heat treatment and to follow this with a quench that was severe enough to retain stresses that would cause a refinement after an anneal (thought to be polygonization mechanism) in the grain size. Figures 15-11 and 15-12 show the water-quenched structures (still large grained) obtained after beta treating at 730°C for four minutes and Figures 15-13 and 15-14 show the structure after the anneal (640°C for 20 minutes and air cooled). Although the ultimate grain size of the two samples was different, there is reason to believe that a very promising grain refinement technique has been demonstrated but further work remains in obtaining consistent, uniform structures.

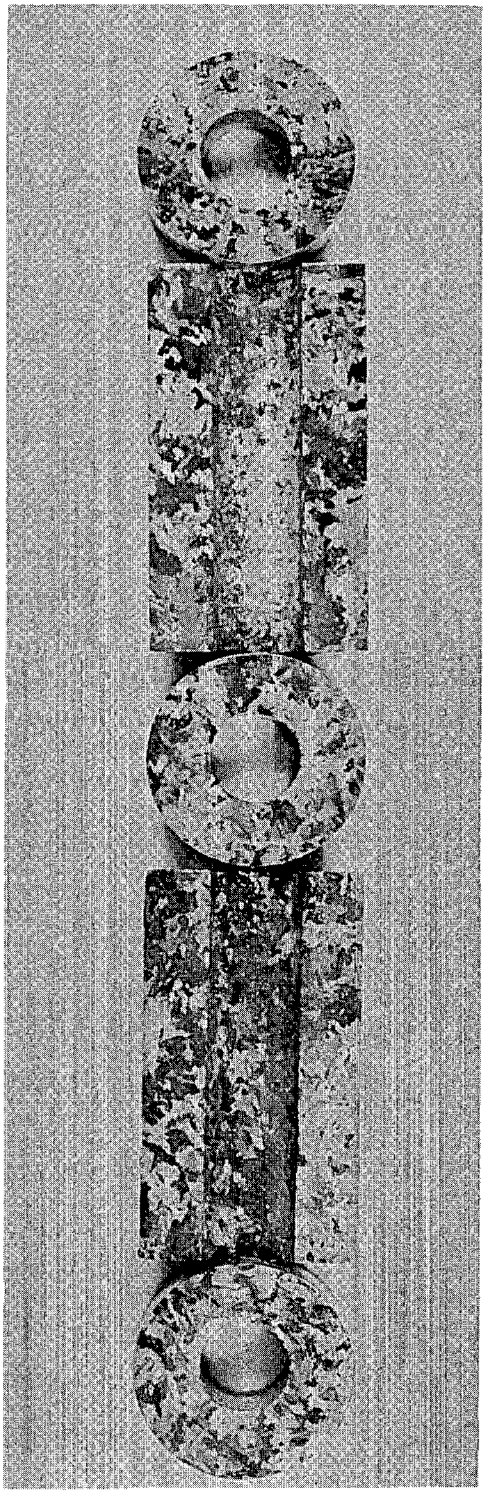

FIGURE 15-6 COMPOSITE OF LONGITUDINAL AND TRANSVERSE SECTIONS OF A HOLLOW CAST SLUG. CONC HCl ETCH; CONC HNO_3 RINSE (1X)

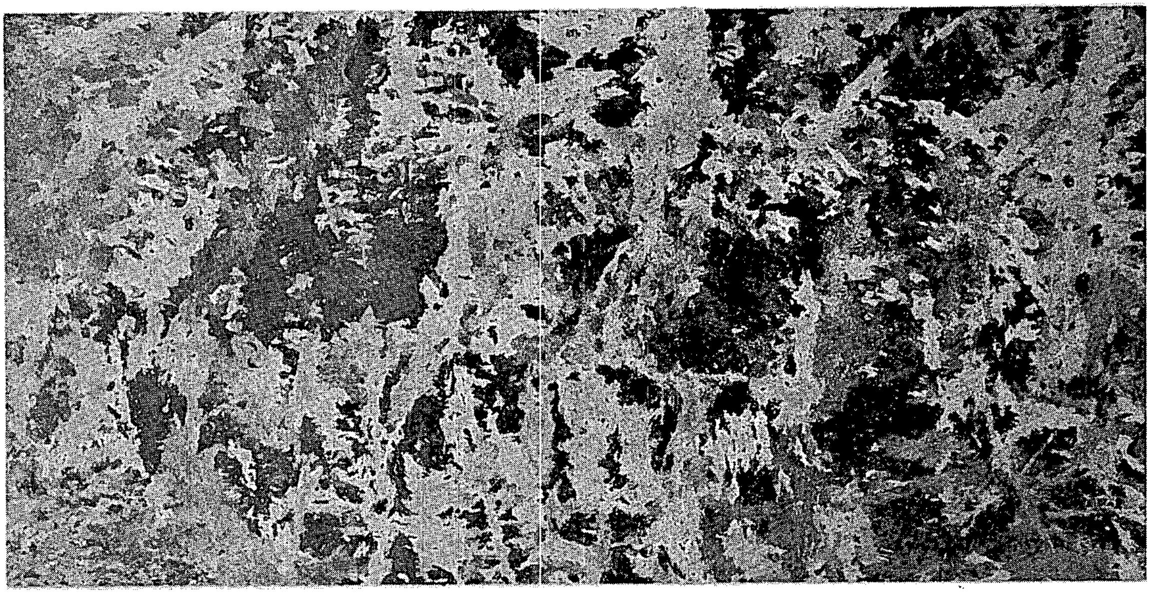

FIGURE 15-7 AS-CAST STRUCTURE – SLUG NO. 12. BRIGHT FIELD: CONC HCl ETCH, CONC HNO_3 RINSE (3X)

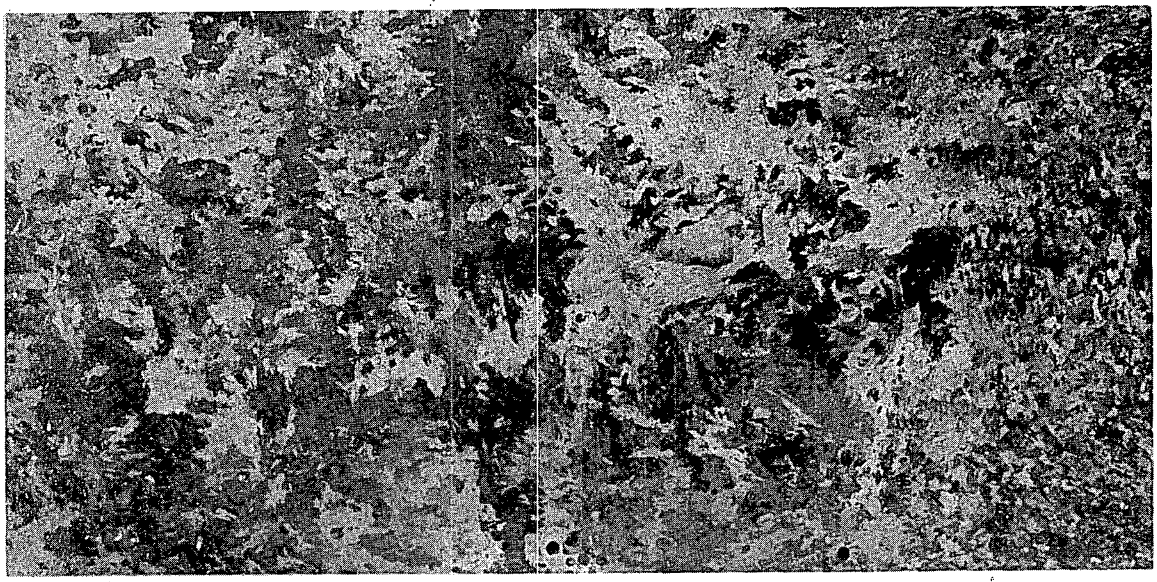

FIGURE 15-8 AS-CAST STRUCTURE, SLUG NO. 13. BRIGHT FIELD: CONC HCl ETCH, CONC HNO_3 RINSE (3X)

FIGURE 15-9 CAST STRUCTURE AFTER ALPHA ANNEALING AT 640°C SLUG NO. 12. BRIGHT FIELD: CONC HCl ETCH, CONC HNO_3 RINSE (3X)

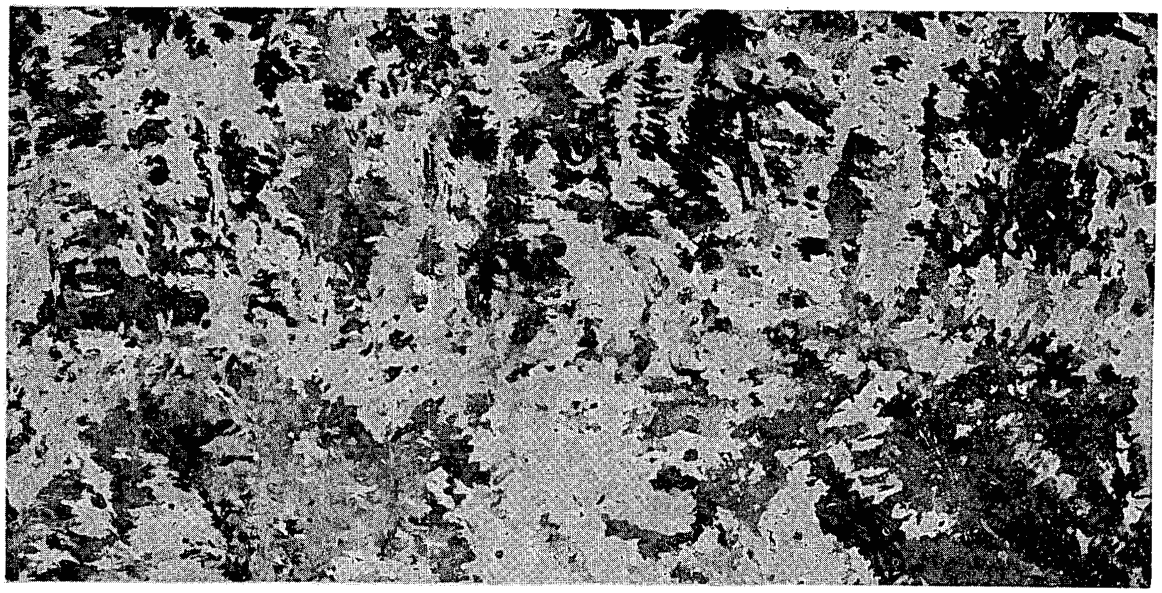

FIGURE 15-10 CAST STRUCTURE AFTER ALPHA ANNEALING AT 640°C SLUG NO. 13. BRIGHT FIELD: CONC HCl ETCH, CONC HNO_3 RINSE (3X)

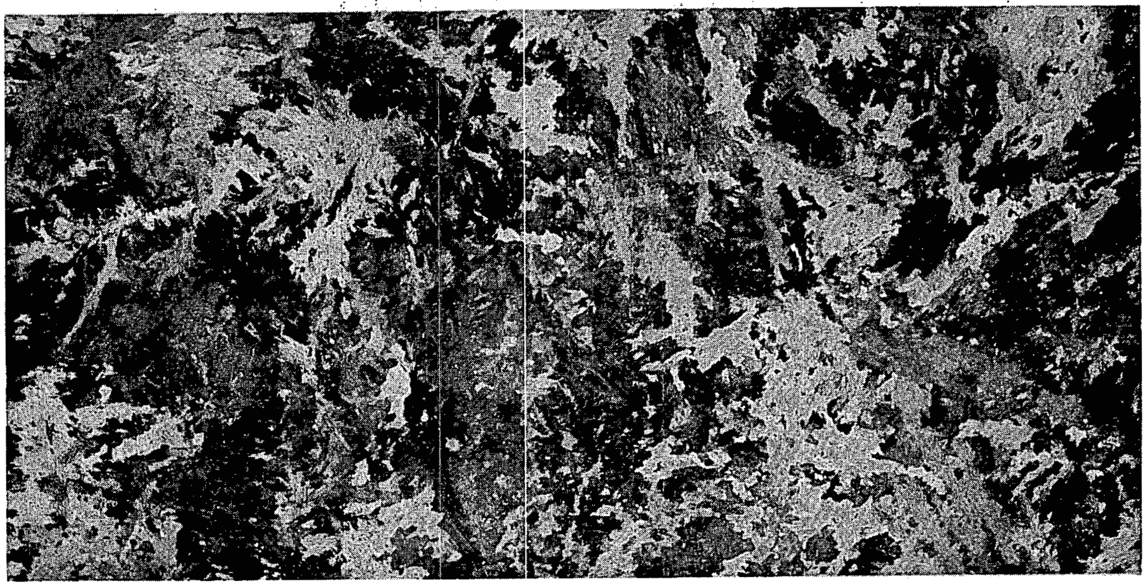

FIGURE 15-11 AS BETA TREATED AT 730°C – SLUG NO. 12. BRIGHT FIELD; CONC HCl ETCH, CONC HNO_3 RINSE (3X)

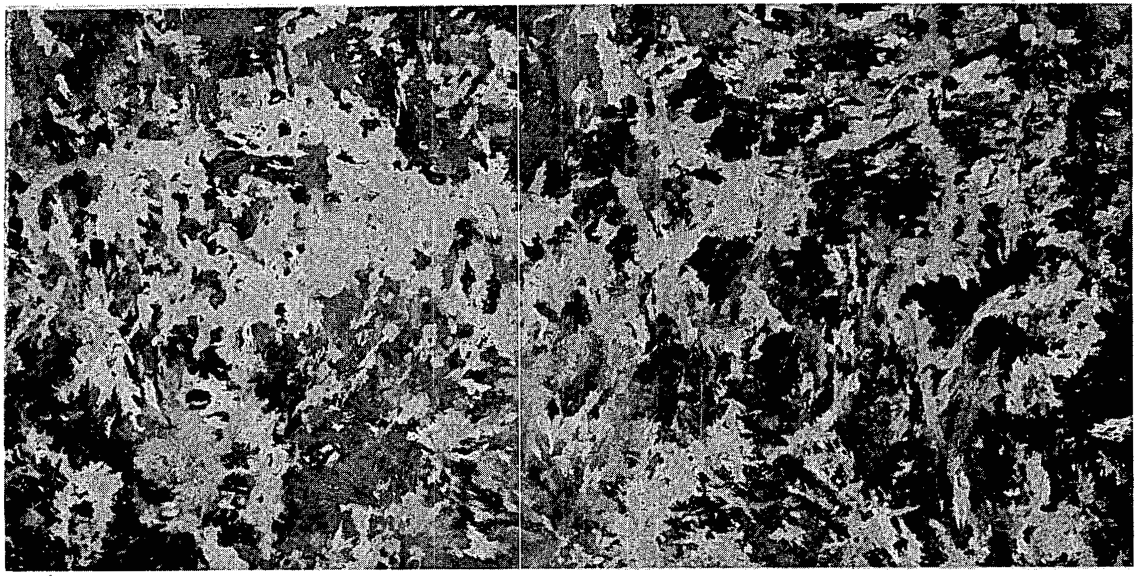

FIGURE 15-12 AS BETA TREATED AT 730°C – SLUG NO. 13. BRIGHT FIELD; CONC HCl ETCH, CONC HNO_3 RINSE (3X)

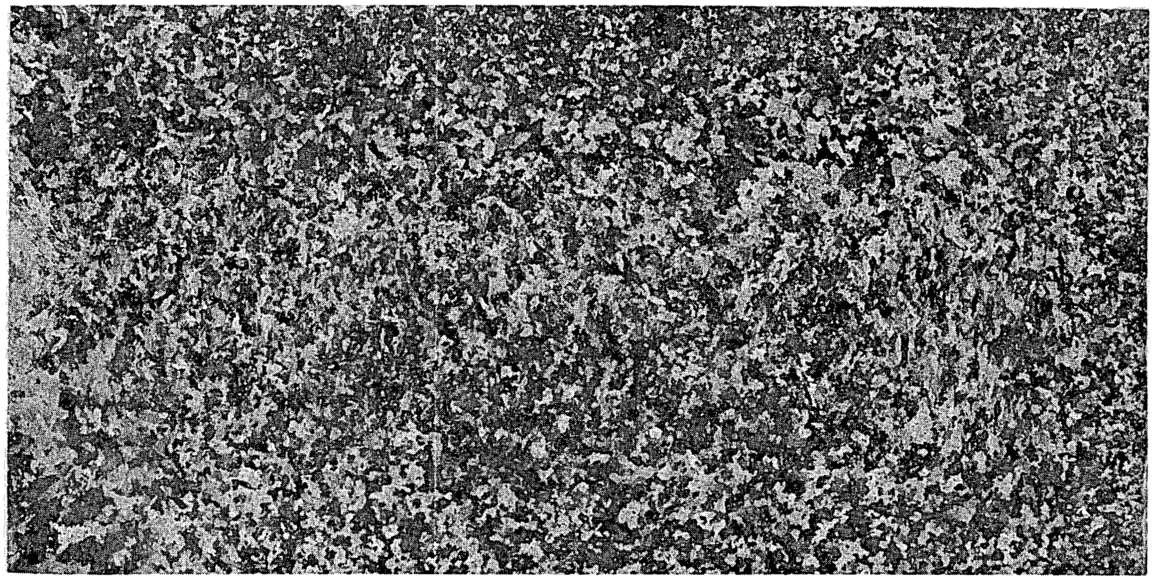

FIGURE 15-13 AS BETA TREATED AT 730°C AND ALPHA ANNEALED AT 640°C – SLUG NO. 12. BRIGHT FIELD; CONC HCl ETCH; CONC HNO_3 RINSE (3X)

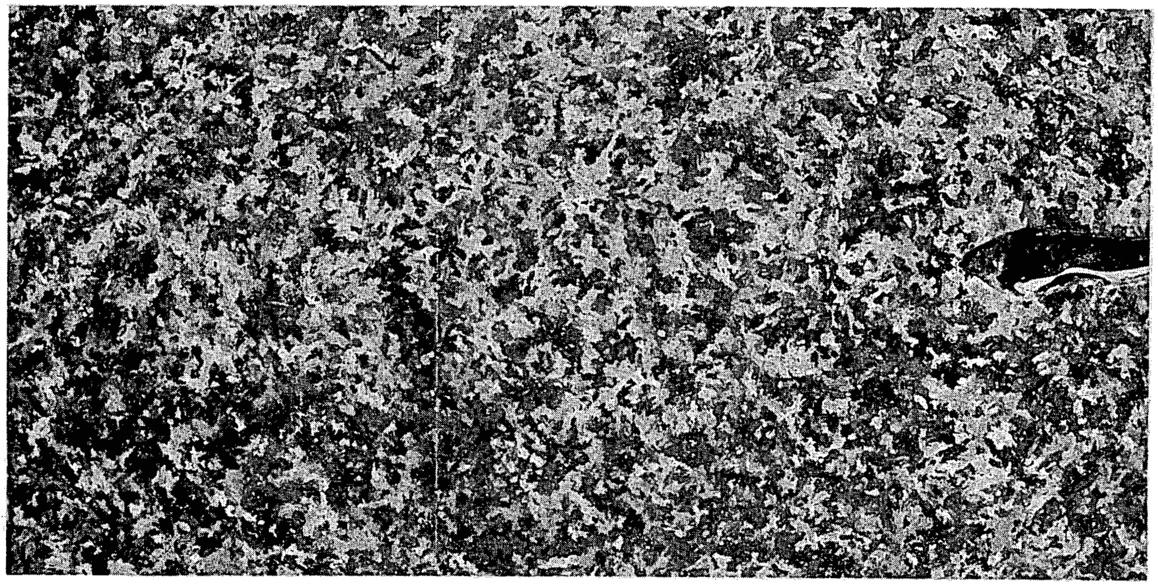

FIGURE 15-14 AS BETA TREATED AT 730°C AND ALPHA ANNEALED AT 640°C – SLUG NO. 13. BRIGHT FIELD; CONC HCl ETCH, CONC HNO_3 RINSE (3X)

Future Work

During the next quarter, more work will be done to improve the "as cast" product and to evaluate heat treatment effects further. Also during this quarter, a small production lot of solid pieces of the size previously described[1] will be cast for in-pile testing by NAA.

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

Continued interest has been expressed in the use of uranium shot (Fig. 15-15) in "matrix" compositions with immiscible metals. Other uses for uranium shot have been suggested.

Work has continued on the preparation or uranium shot to improve the rotating disk method, which has given the most promising results.[2] The materials of construction and the design of rotating disks were studied. A desirable shot-tank configuration was determined, and a large shot-tank was designed and ordered. The effects of disk speeds and pour temperatures upon shot size and yield were studied. For various uses, sizes of shot between −100 mesh and 1/16 inch were required.

Summary and Conclusions

Graphite disks gave excellent thermal shock resistance to the falling molten stream of uranium; however, since graphite has a relatively high heat capacity and is a good heat conductor, uranium solidified on the surface. Porous carbon, which has low heat conductivity, proved to be too low in mechanical strength. Zirconia refractories (provided with some mechanical support) gave the best results.

The pour temperature was very critical in the confined space of the present furnace. At too high a pour temperature, the shot struck the furnace wall before solidifying; at a subcritical temperature, considerable quantities of metal froze on the rotating disk.

At speeds below 800 rpm, the particles of the molten metal leaving the rotating disk were too large to freeze in the short trajectory space available. When the speeds were increased to over 1000 rpm, the amount of minus −40 sieve (420-micron) shot was increased. It is evident that the average shot sizes can be controlled by the disk speed and pour temperature.

Procedure

The general procedure was to pour the molten uranium from a 3/16-inch hole through a helium atmosphere; after a vertical fall of 17 inches it was dispersed as it impinged on the spinning disk.

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[1] *Blasch, E. B., Wuller, G. E., Minutolo, V. G., and Straub, J. C., Summary Tech. Rpt., Vol. II, NLCO-601, p. 38, January 16, 1956.*

[2] *Reese, S. L. and Kraus, H. A., Summary Tech. Rpt., Vol. II, pp. 45-51, NLCO-601, January 16, 1956.*

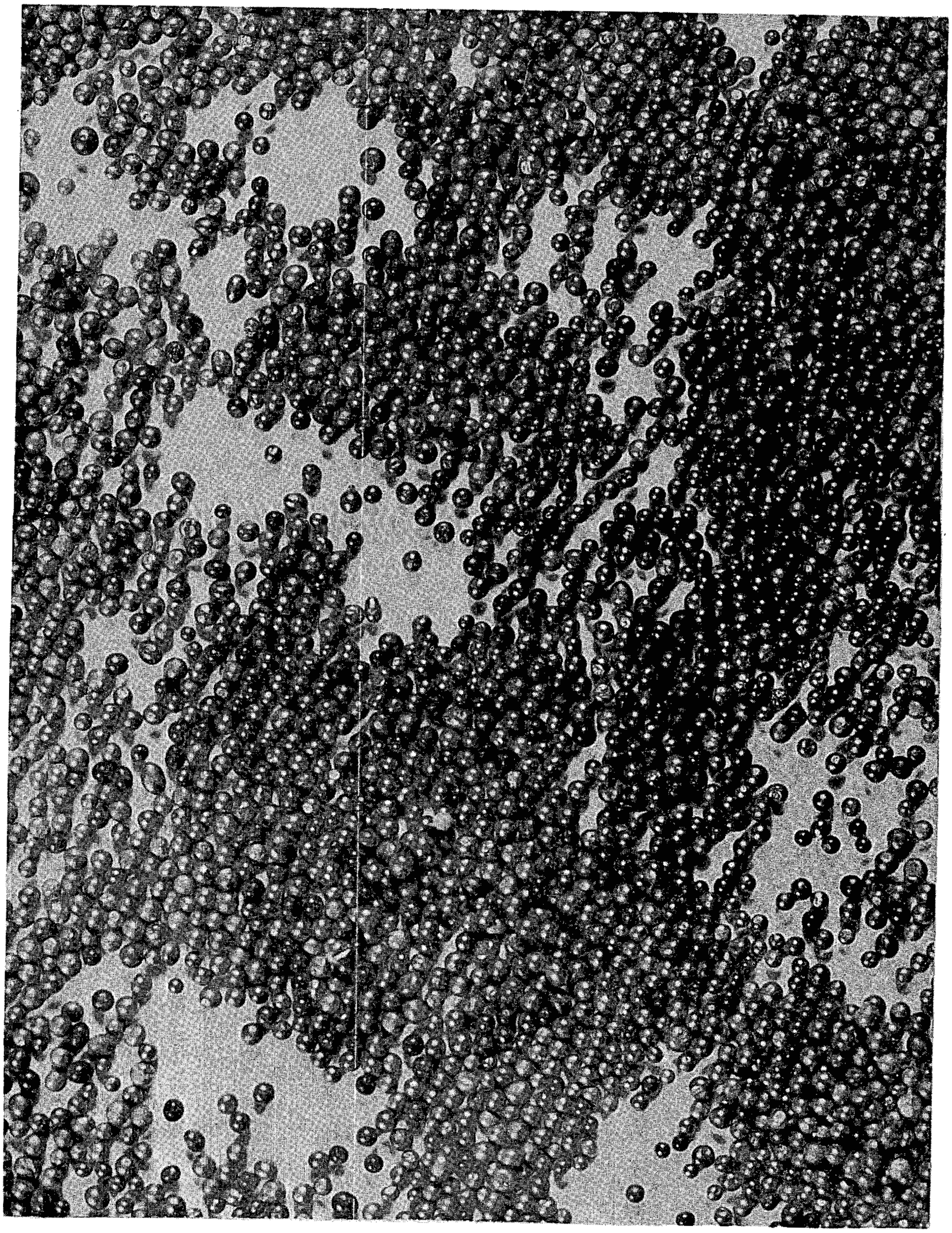

FIGURE 15-15 -20, +30 SIEVE SIZE SHOT (4X)

Solidification of the shot before it struck the furnace wall was essential for the preparation of acceptable shot. The horizontal trajectory space was 17 inches in all tests reported here.

Graphite and Porous Carbon Disks

Several of the concave disks investigated were fabricated of graphite to take advantage of graphite's property of thermal-shock resistance. The first graphite disk was designed to have an interior surface resembling the curve of a catenary, i.e., a very gentle slope near the center and a rapid increase in slope near the edge (Fig. 15-16). This should allow the molten metal to develop sufficient outward momentum (before it reaches the steeper slope of the catenary) to carry it up the slope, imparting a pronounced upward direction to the shot trajectory and allowing more time to chill the shot. Where the allowable horizontal trajectory is limited, as in the shot tank used for these tests, a vertical trajectory is especially desirable.

The graphite disk was brushed with two coats of magnesium zirconate to help decrease its thermal conductivity and was insulated from the metal holder. However, when the molten uranium reached the sharp slope, it slowed sufficiently to solidify on the periphery of the disk because of the relatively high heat capacity of the graphite. This, in turn, caused a decrease in the rate of rotation.

A similar disk was fabricated from porous carbon to take advantage of its better insulating properties. The pour temperature was raised from 2400°F to 2450°F. The buildup of uranium on the edge of the disk was less than that for graphite, but mechanical stresses broke up the porous carbon.

A saucer-shaped disk of graphite gave results similar to those for the graphite catenary disk: The uranium solidified along the rim of the disk. The saucer shape did not impart as much upward motion to the molten uranium particles as did the catenary. It was concluded that graphite and porous carbon are not suitable materials of construction for the disk.

Zirconia Disks

A bowl-shaped disk was made of zirconia, with a depth of 2½ inches. In operation, the molten particles left the bowl horizontally because the molten metal did not attain sufficient outward momentum to carry the shot upward. There was not the buildup of frozen metal that there was on the graphite disk.

The following data are typical of those derived from several subsequent experimental runs with an 8-inch-diameter flat zirconia disk:

Uranium metal charge	45 lb
Pour temperature	2425° to 2450°F

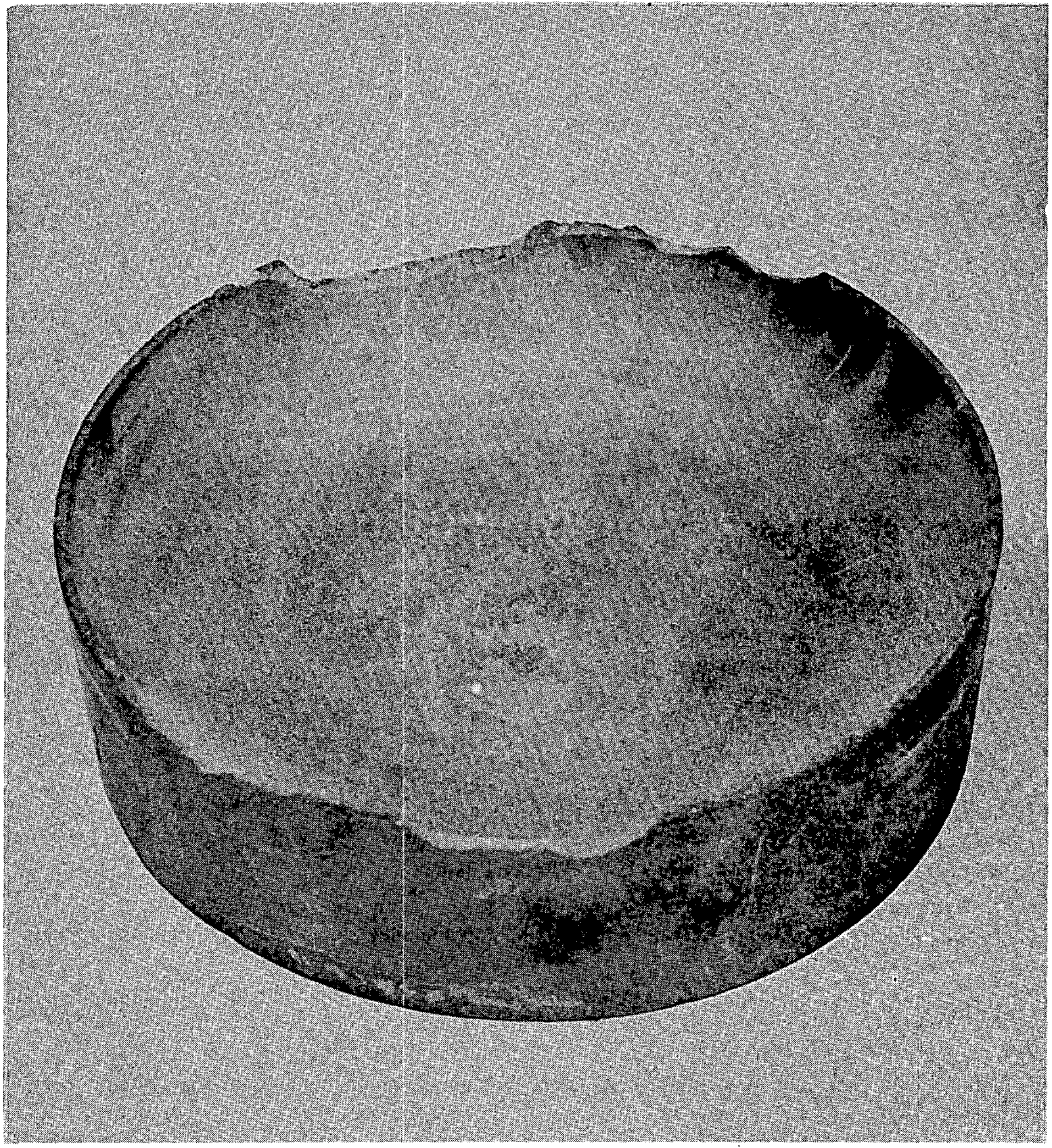

FIGURE 15-16 EIGHT-INCH-DIAMETER GRAPHITE CATENARY DISK

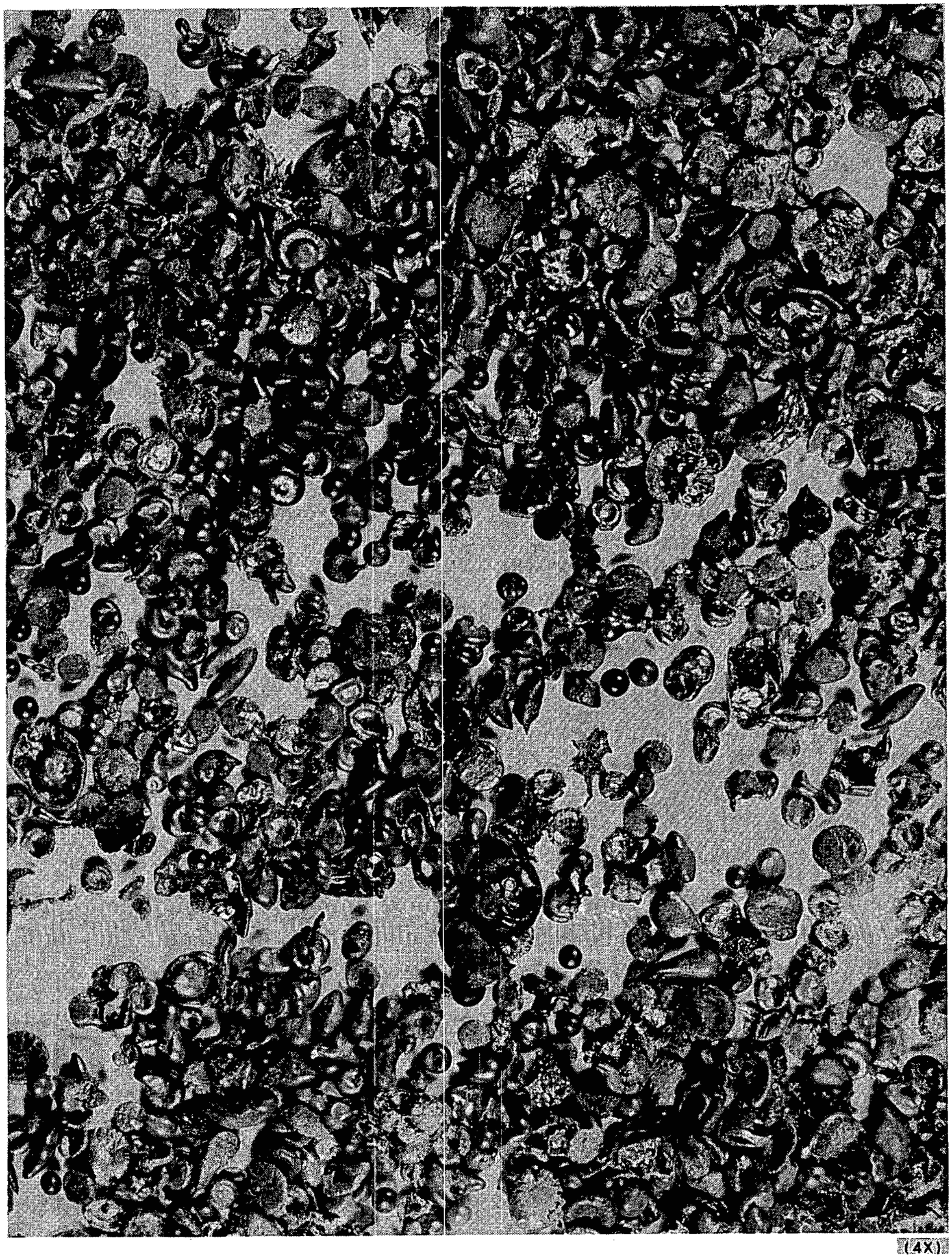

FIGURE 15-17 "FLATS" PRODUCED WITH INSUFFICIENT FREEZING TIME THIS TYPE OF PARTICLE IS PRODUCED WHEN DISKS SUCH AS THAT SHOWN IN FIGURE 15-19 ARE FORMED

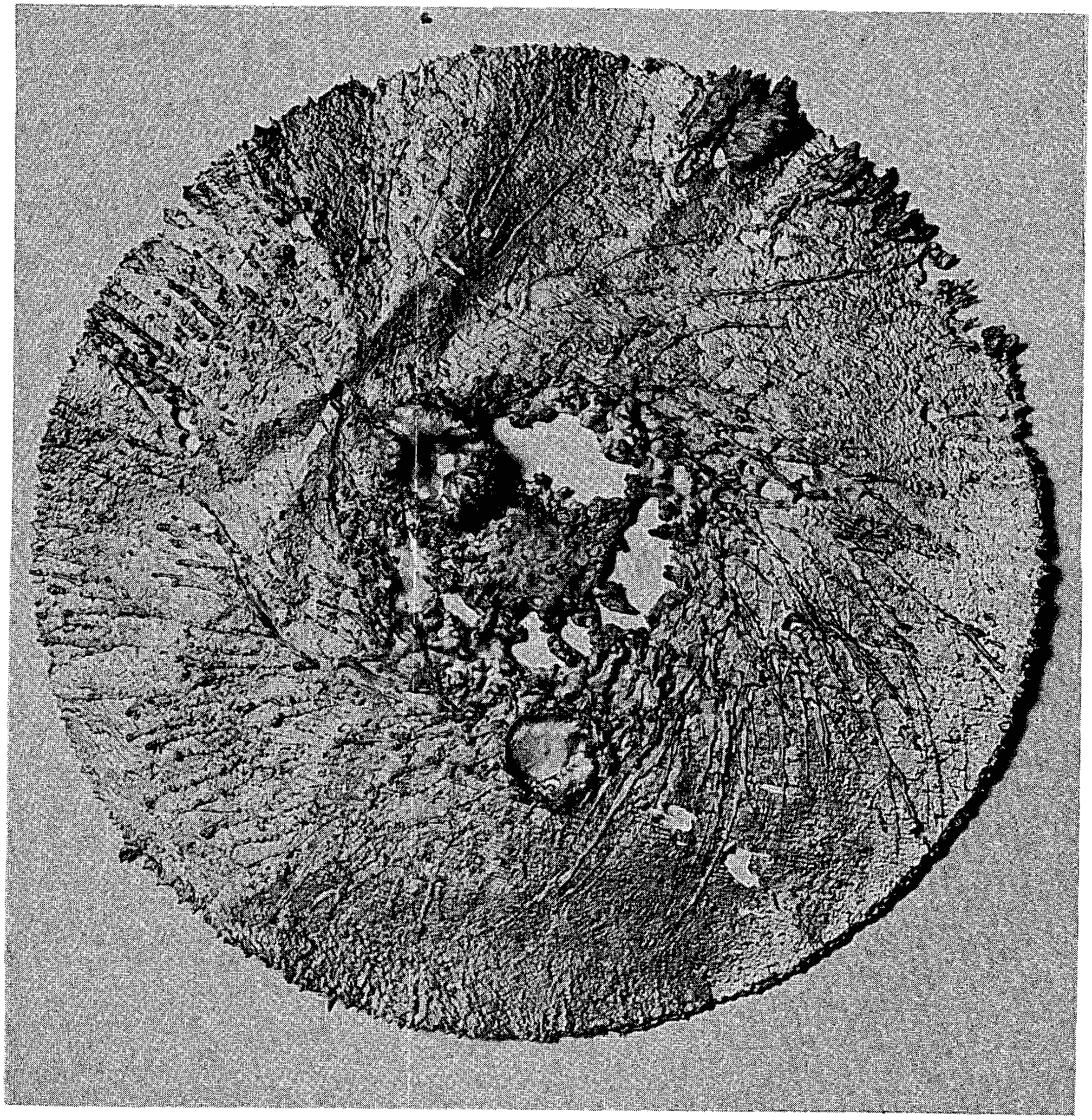

FIGURE 15-18 THIN METAL DISK FORMED ON THE SURFACE OF AN 8-INCH ZIRCONIA PLATE WITH NO BUILD-UP OF FROZEN METAL AT THE PERIPHERY. THE NEEDLE-LIKE LIGAMENTS AT THE PERIPHERY ARE GENERALLY ASSOCIATED WITH THE PRODUCTION OF SMALL-DIAMETER SHOT

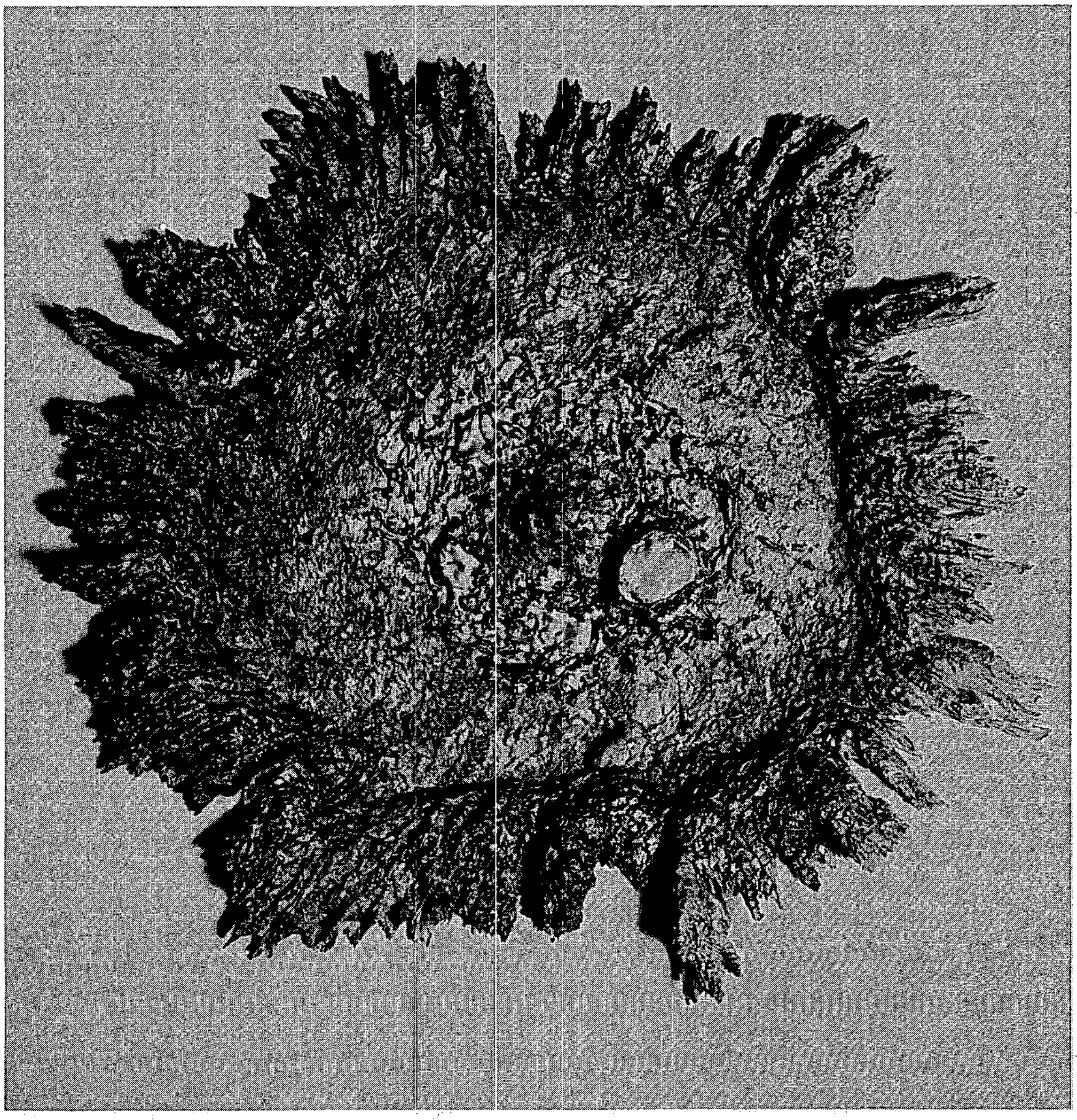

FIGURE 15-19 METAL DISK FORMED ON THE SURFACE OF AN 8-INCH ZIRCONIA PLATE WITH BUILD-UP OF FROZEN METAL AT THE PERIPHERY. LOW-TEMPERATURE POUR. THE COARSE LIGAMENT FORMATIONS AT THE PERIPHERY ARE GENERALLY ASSOCIATED WITH THE PRODUCTION OF LARGE DIAMETER SHOT.

Disk speed	800 to 1000 rpm
Pour rate	35 to 40 lb/min
Yield	20 to 40 per cent
Shot-size range	200 to 1500-micron
Packing density	11.6 g/cc

Results and Discussion

It is inferred that the yields can be increased with a greater free-throw distance, because a large number of flat, thin disks (Fig. 15-17) were formed by the molten shot striking the furnace wall. There was an increase in the "flats" produced at higher pour temperatures and slow disk speeds (below 800 rpm), the large particles having insufficient time to freeze.

The theory that the slower the disk speed, the larger the molten particles dispersed from the disk's periphery was confirmed by direct observation. The size of particle leaving the disk was characteristically indicated by the appearance of the periphery of the metal disk that remained on the zirconia disk (Fig. 15-18 and 15-19). The small needles at the periphery of the plate (Fig. 15-18) indicate ideal conditions for small shot.

On the basis of information obtained to date, a new shot tank was designed. Further work on shot preparation will be carried on in this tank shortly.

15.5 PRODUCTION CONTROL OF HYDROGEN CONTENT OF BARE FUEL ELEMENTS –

A. E. Guay

During the first quarter of 1956, routine observation of the rod heat-treating process has been continued. Previous reports[1,2] described the relationship that exists between the composition of the salt bath, the absolute humidity, and the hydrogen content of the uranium rod, i.e., the amount of hydrogen absorbed by uranium rod metal heat-treated in a salt bath. The data in these reports showed that the OH^- concentration of the salt bath is a measure of the amount of water vapor absorbed by the molten bath as the humidity changes. The absorbed water vapor is thought to react with uranium metal, resulting in the absorption of hydrogen gas by the uranium. It has been found that hydrogen absorption during the heat-treating process is controlled by adding CO_2 gas to the salt bath.

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[1] *Guay, A. E., Summary Tech. Rpt., pp. 126-132, NLCO-577, October 17, 1955.*

[2] *Griffith, R. L., Summary Tech. Rpt., Vol II, pp. 71-79, NLCO-601, January 16, 1956.*

Methods

A program is being carried out that is identical to the program previously described. The practice of adding CO_2 to the salt bath has been continued, but where previous control required the addition of a minimum of 50 pounds CO_2 per working shift from a temporary bottle manifold, a permanent 1½ ton CO_2 reservoir system has been installed.

In this program, the following types of data are collected:

1. Composition of the Salt Bath From daily samples, the OH^- concentration of the 46:54 Li_2CO_3:K_2CO_3 is determined.

2. Hydrogen Content of the Slug Metal Daily, a bare fuel element is chosen from among the fuel elements machined from heat-treated rods. The sample is analyzed to determine the amount of gas (calculated as hydrogen) evolved in a five-minute vacuum hot-extraction at 600°C. Too, measure is made of the total hydrogen evolved from the sample during a five-hour vacuum hot extraction at 820°C.

2. The Absolute Humidity From wet and dry bulb temperature readings, the average absolute humidity is calculated.

Data and Discussion

Figure 15-20 is a running plot of the weekly averages of salt bath alkalinity and hydrogen content of fuel elements. As our previous data have shown, there is remarkably good agreement between the OH^- concentration and the hydrogen content of the fuel element metal.

Figure 15-21 is a running plot of weekly averages of salt bath alkalinity, absolute humidity, and CO_2 additions. The data in this figure show a much lower absolute humidity than that encountered in the spring, summer, or fall. Coupled with this low humidity have been low values of OH^- concentration. Actually, the CO_2 additions made during the winter months have little effect, because of the low absolute humidity. Because the CO_2 additions were sporadic and nonuniform, the beneficial effects that normally would be shown in plots of this type are not apparent.

Reference is made to Table 15-1, which shows the hydrogen values that were obtained on samples derived from both NLO ingot metal and MCW ingot metal. The average total hydrogen content for the MCW metal is 1.85 ppm and the range is 0.85 to 3.19 ppm; the NLO-origin metal has an average total hydrogen content of only 1.57 ppm and a range of 0.94 to 2.17 ppm. This difference in hydrogen content is thought to be caused mainly by the difference in remelt charge: The MCW ingot metal consists almost exclusively of remelted derby metal (derby metal averages 3 to 5 ppm hydrogen), while NLO ingot metal is obtained by remelting some solid scrap and briquetted machine turnings.

~~CONFIDENTIAL~~

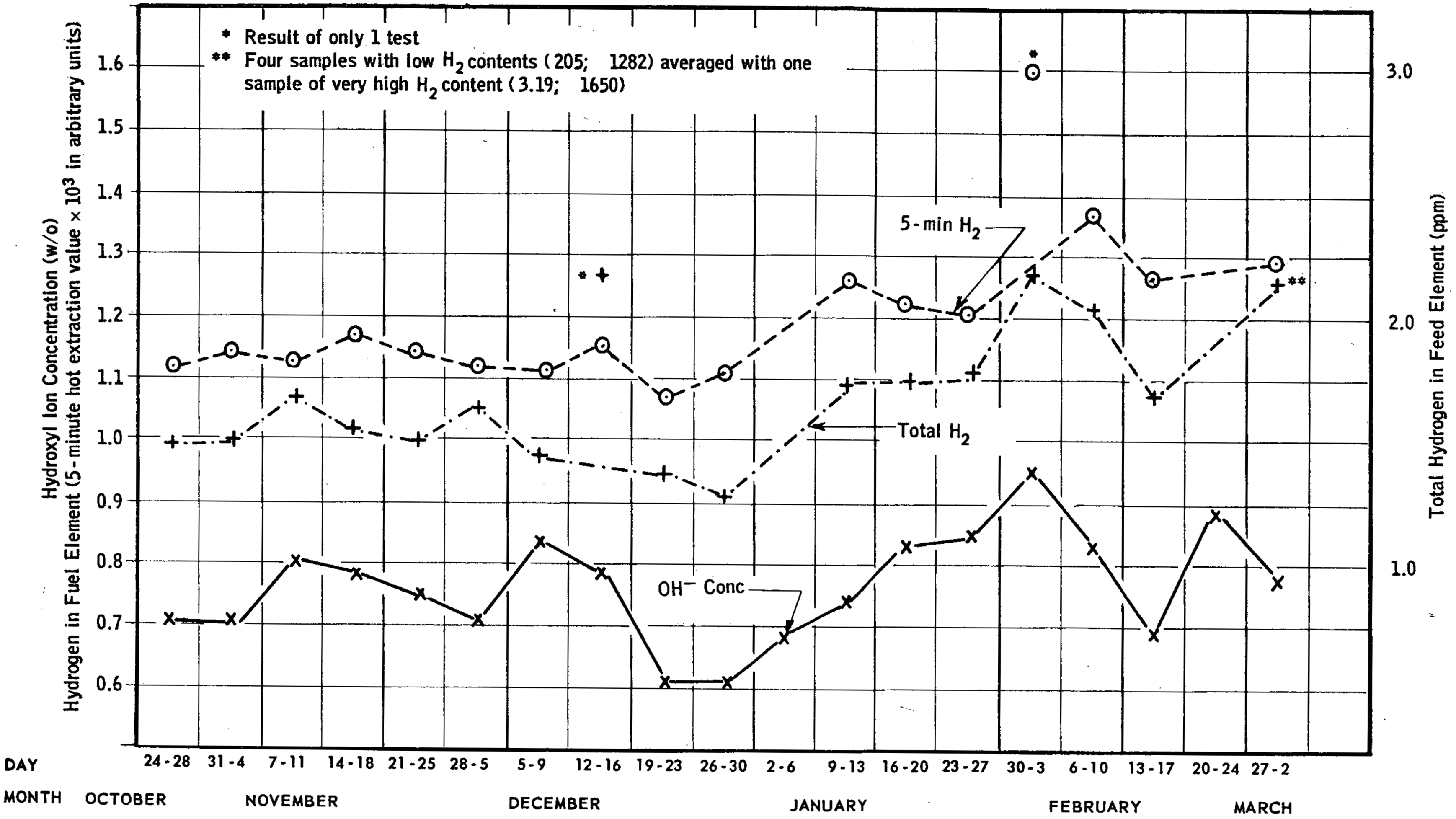

FIGURE 15-20 A RUNNING PLOT OF WEEKLY AVERAGES OF SALT BATH ALKALINITY AND THE HYDROGEN CONTENT OF FUEL ELEMENTS

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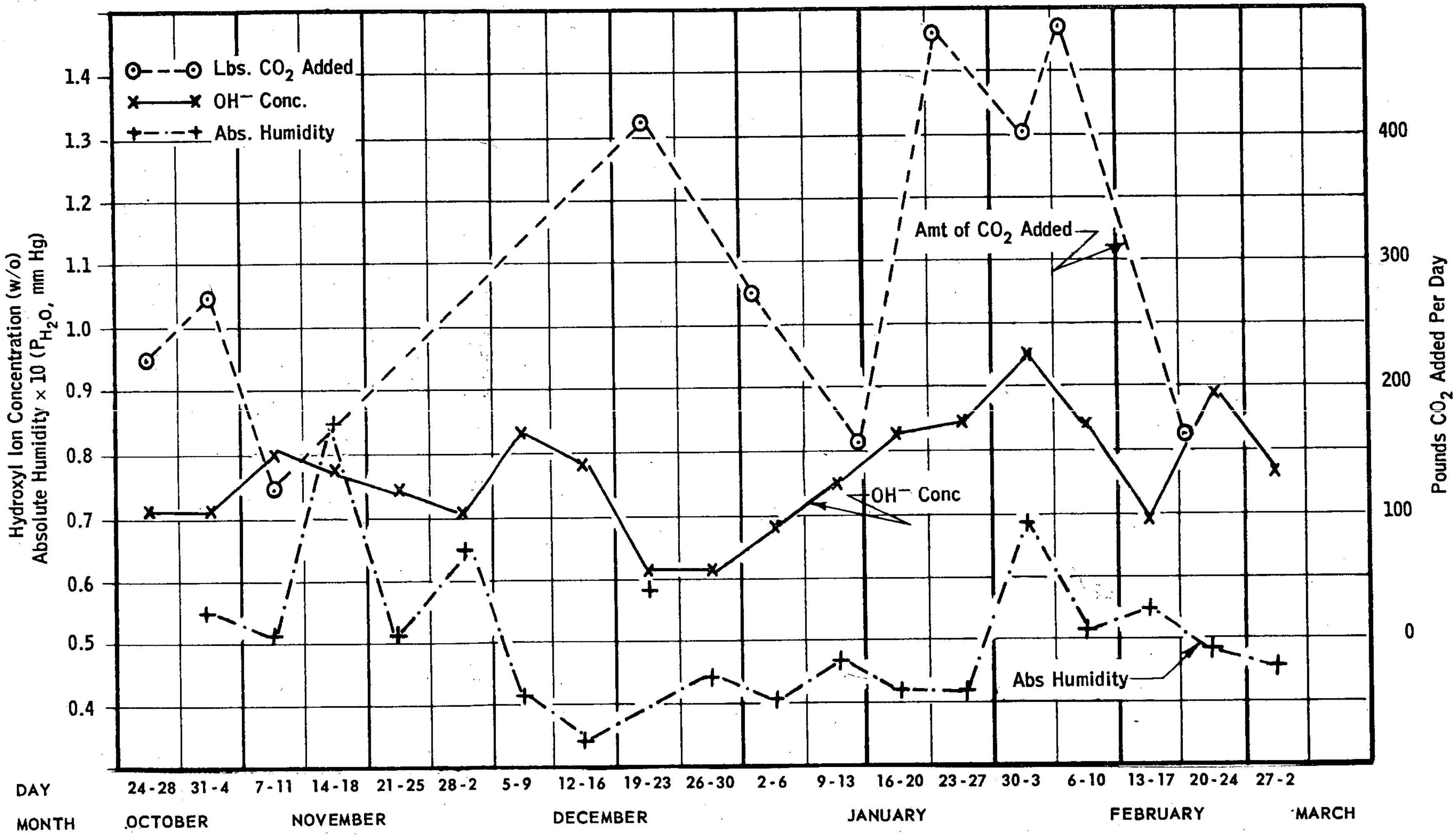

FIGURE 15-21 A RUNNING PLOT OF WEEKLY AVERAGES OF SALT BATH ALKALINITY, ABSOLUTE HUMIDITY, AND CO$_2$ ADDITIONS

TABLE 15-1

THE TOTAL HYDROGEN CONTENT OF NLO-ORIGIN METAL AND MCW-ORIGIN METAL

NLO Sample No.	Total H_2 (ppm)
7217-2-13	1.78
9931-3-13	1.63
7354-2-14	1.89
7449-1-13	1.26
7531-1-14	1.76
7544-4-14	1.35
6602-2-15	1.67
9916-4-20	1.38
8198-4-9	1.05
8238-3-10	1.88
8562-3-6	0.94
8658-2-12	2.11
8767-1-16	1.17
8519-4-20	1.14
8509-1-13	1.32
8524-3-20	1.32
14-3-18	1.10
190-2-10	1.44
250-3-4	1.13
786-1-10	1.79
283-3-12	1.44
936-4-5	1.13
924-1-21	1.28
1069-2-5	2.04
1377-3-10	1.54
1458-1-16	1.75
1435-2-25	1.76
1955-4-16	1.81
2298-1-12	1.90
2417-1-6	1.95
2347-2-18	1.14
2348-1-24	1.72
2730-4-3	2.17
F-2928-2-28	1.51
3258-1-19	1.93
3283-4-21	1.58
3408-4-16	2.10
3272-1-20	1.85
3742-3-7	1.38
4184-1-10	1.76
Avg	1.57
Range	0.94 to 2.17

MCW Sample No.	Total H_2 (ppm)
9438-1-15	0.85
9582-1-17	1.23
9900-1-13	1.53
9549-2-13	1.80
9950-1-9	1.68
569-1-17	1.58
580-3-8	2.01
626-4-15	1.48
527-1-14	1.63
828-2-20	1.92
969-1-25	2.17
1389-1-14	1.40
1674-2-24	1.91
1812-4-17	1.95
1856-2-19	1.74
1830-4-8	2.02
2162-2-4	1.96
2137-4-22	2.21
2166-1-22	2.49
2297-2-6	1.76
3508-3-4	2.05
2197-2-17	3.19
2584-2-19	1.92
Avg	1.85
Range	0.85 to 3.19

Conclusions

1. The present work has substantiated previous observations on the relationship of the salt bath composition to the amount of hydrogen gas that can be absorbed by uranium metal heat-treated therein.

2. Since the average hydrogen content of bare fuel elements should be below 2 ppm the heat-treating operation has been in good control.

Future Work

Work to determine the exact correlation of hydrogen absorption to salt bath composition has not been started. Realizing that establishment of this relationship would be worthwhile, the National Lead Company of Ohio has sponsored a development program at Battelle Memorial Institute which includes studies of the fundamental relationship of salt bath composition to hydrogen absorption for a number of salt systems. (The main objective of this development program is to perfect a cheaper salt bath having a lesser affinity for water vapor than has the present bath.) The recent monthly progress reports issued by Battelle Memorial Institute describe this work.

16. ANALYTICAL DEPARTMENT – "WET CHEMICAL" DEVELOPMENT

16.1 STEAM DISTILLATION OF CHLORIDES – R. Bonham and E. A. Brown

The turbidimetric method[1] for the determination of microgram quantities of chloride in various types of process solutions has been frequently used in this laboratory. However, the presence of sulfides, phosphates, and other interfering ions made difficult the direct application of this procedure to materials such as raffinate, digest slurries, and similar materials. Since a determination for fluoride is generally required on the same samples for which a chloride analysis is requested, tests were made to ascertain whether or not the distillate from the fluoride determination[2] could be employed in determining chloride.

A preliminary study of the distillation step as used in the modified fluoride distillation showed that chlorides are quantitatively removed at 160°C and tend to concentrate in the first few milliliters of distillate. Much of the chloride was found to be retained in the trap of the distillation apparatus. After the distillation apparatus was redesigned to eliminate the retention of water in the trap, satisfactory results were obtained.

Standards bearing known amounts of chloride and fluoride (in the order of 500 ppm) were carried through the regular distillation procedure for fluoride analysis and the distillate was analyzed for chlorides by the present turbidimetric method. From 88 to 102 per cent of the chloride added was recovered. The results were within permissible limits.

16.2 COULOMETRIC TITRATION OF CHLORIDES – N. Huey and E. A. Brown

In view of the increase in the number of samples for chloride analysis from the Refinery and Scrap Plant, some time was spent in investigating the ORNL coulometric method.[3]

Briefly, the coulometric titration is as follows: The sample containing chlorides is placed in a half cell which is equipped with a silver anode. Current is passed through the half cell, liberating silver ions from the anode which, in turn, precipitate the chloride. The end point of the titration is determined by the change in the EMF of another silver half cell placed in the solution. By measuring the elapsed time at known constant current, the chloride concentration may be calculated from the relationship:

$$\text{ppm Cl} = \text{Milliamperes} \times \text{Time in Seconds} \times \text{Factor}$$

Satisfactory results were obtained using a three-compartment titration cell with a 3-milliampere current. Excellent precision was obtained on standard samples; the results are given in Table 16-1.

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[1] *Rodden, C. J., "Analytical Chemistry of the Manhattan Project", p. 296, McGraw-Hill, New York, 1950.*

[2] *SP (CS) METH-171 (Microcard), Determination of Chloride in Uranium Tetrafluoride, Great Britain Springfields Works, Springfields, Lancs, England; Chief Chemist, Chemical Service Dept.*

[3] *ORNL Master Analytical Manual, CF-53-1-235, Method No. 90822011; February 8, 1955.*

TABLE 16-1

CHLORIDE RESULTS OBTAINED BY THE COULOMETRIC METHOD

Standard No.	Chloride Added (ppm)	Chloride Found (ppm)	
1	150	148	145
2	211	221	211
3	14	19	14
4	56	56	56
5	92	86	88
6	342	335	334
7	285	282	279

16.3 DETERMINATION OF THORIUM IN UO_3 – M. Jursik and E. A. Brown

In anticipation of the processing of thorium-bearing feed materials in the Refinery, some consideration was given to the analytical methods for determining traces of thorium in the presence of uranium. A literature survey of the procedures for determining microgram amounts of thorium showed the Port Hope method to be feasible for this work. In brief, the method consists of an initial precipitation of thorium as the fluoride from interfering ions, with lanthanum used as a carrier. After a fuming with perchloric acid to remove the fluorides, the thorium is determined colorimetrically, with thorin used as a chromogenic agent.

A preliminary study has been completed on the method. Standards were prepared by adding known amounts of thorium in the range of 20 to 70 ppm to 1-gram samples of orange oxide. The recovery was 89 to 96 per cent. The method is believed to be satisfactory for the determination of traces of thorium in uranyl nitrate and orange oxide.

16.4 DETERMINATION OF NIOBIUM IN URANIUM-NIOBIUM ALLOY – P. Hallbach and F. E. Jenkins

A study has been made to determine the precision of the analysis of uranium-niobium alloy for niobium.

The niobium is determined colorimetrically, using the peroxy-niobate complex.[1] In an anhydrous sulfuric acid solution that contains uranium, the peroxy-niobate complex is very stable, specific, and sensitive. The optical density versus concentration is a straight-line relationship over a substantial range of optical densities (0.000 to 1.500).

A standard sample of high-purity niobium metal is run with each group of determinations of niobium to eliminate the effect of variations in equipment and technique. The standard deviation for 40 standard determinations is 10.00 ±0.15% Nb.

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[1] *Patterson, J. F., Manual of Special Materials, Analytical Laboratory Procedures, p. 59, ANL-5410, March, 1955.*

It was observed that certain ingots varied in composition from top to bottom and, to a lesser extent, in the horizontal plane.

It is also significant to note that the fines obtained from screening drilled samples were somewhat higher in niobium concentration, as shown below.

A sample of drillings from uranium-niobium alloy was received for cooperative analysis. Another laboratory group had crushed the drillings and screened the particles through four sieves before analysis of the four fractions. The Analytical Department at National Lead analyzed the drillings without screening. The results obtained by the two laboratories are shown in Table 16-2.

TABLE 16-2

ANALYSIS OF A STANDARD URANIUM-NIOBIUM ALLOY SAMPLE BY NLO AND OFF-SITE ANALYTICAL LABORATORIES

NLO Drillings (As Received)	Other Lab Drillings (Crushed and Screened)	
% Nb	Mesh	Nb (%)
12.1	>20	12.1
12.2	>50	12.2
	>100	14.0
	<100	16.0

16.5 DETERMINATION OF OXYGEN IN MOLYBDENUM – C. Hall, F. Ford, and F. E. Jenkins

Several samples of finely divided molybdenum powder were submitted for the determination of oxygen. Two methods of analyses were used, hydrogen reduction and vacuum fusion.

Sidgwick[7] has reported that hydrogen will reduce molybdenum trioxide to the dioxide at 300° to 470°C, and to the metal at 500°C. A reduction train was set up that consisted of a hydrogen supply, a Vycor combustion tube, a tube furnace, and a water absorption weighing bulb. The sample was contained in a platinum boat. The hydrogen was passed through a preheater and into the combustion tube. At a temperature of 550°C, the hydrogen reacted with the molybdenum oxides of the sample and formed water, which was collected in an absorption bulb and weighed.

The samples were also analyzed by the vacuum fusion method. The molybdenum powders were wrapped in tin foil and were dropped into a degassed graphite crucible containing a molten iron bath at 1580°C. The oxygen was liberated as carbon monoxide, which was collected, converted

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[7] *Sidgwick, N. V., "The Chemical Elements and Their Compounds V. II", p. 1037, University Press, Oxford, England, 1951.*

to carbon dioxide by hot copper oxide, and measured with a calibrated McLeod gauge. According to Sloman,[1] oxygen is completely removed from the molybdenum in an iron bath at 1580°C in 2 minutes. Sloman's findings were verified.

Table 16-3 summarizes the results obtained by both methods of analysis. The agreement between methods is fairly good. The vacuum fusion analysis is probably the more accurate because a large volume of evolved gas is measured. The very small amount of water (in the milligram range) liberated in the hydrogen reduction method is weighed directly; therefore, this method is less sensitive. The vacuum fusion method requires at least ten times the man-hours required for the hydrogen reduction method.

TABLE 16-3

DETERMINATION OF OXYGEN IN MOLYBDENUM POWDER

Sample No.	Hydrogen Reduction Method (% O_2)	Vacuum Fusion Method (% O_2)
13M-339	0.12	0.16
	0.15	0.15
13M-469	0.34	0.37
	0.32	0.35
13M-470	0.12	0.12
	0.13	0.14

16.6 DETERMINATION OF ARSENIC IN PORT HOPE GRAVITY CONCENTRATE – E. Tieman, D. Valent, and B. Gessiness

Samples of Port Hope gravity concentrate have recently been received for the determination of arsenic content. This analysis had not been requested previously at NLO, so considerable development work was required to validate the procedure. The ore was known to contain both free and sulfide sulfur, so it was treated initially as arsenopyrite.

Procedure

The following procedure is recommended:

The ore is disintegrated, using low temperature oxidizing techniques. Arsenic is reduced with hydrazine sulfate and distilled from an excess of HCl as the trichloride. The distillate is titrated with standard iodine solution.

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[1] *Sloman, H. A., Harvey, C. A., and Kubaschewski, O., J. Inst. Metals, 80, 391 (1952).*

In detail, a 0.5 gram sample is transferred to a 250 milliliter beaker with a few beads and is digested for 20 minutes at room temperature with 20 milliliters of bromine water and 2 grams of KBr; 20 to 30 milliliters of HNO_3 is added and the sample is taken to dryness, keeping the temperature below 100°C (steam bath or asbestos-covered hot-plate). Then, 20 milliliters of H_2SO_4 (1:1) is added to the dry sample and the sample is again heated on the asbestos-covered hot plate until strong SO_3 fumes are evolved. When cool, it is slightly diluted with water and again taken to SO_3 fumes in order to eliminate traces of HNO_3.

The sample is transferred to the flask of a distilling apparatus and 3 grams of KBr and 5 grams of hydrazine sulfate are added. Thermometer, condenser, and adaptor are placed in position; a 500 milliliter Erlenmeyer flask, containing about 50 milliliters of water and a few drops of methyl red indicator, is used as a receiver and is placed so that the tip of the adaptor extends just below the surface of the water. This flask is kept in a cooling bath throughout the distillation. About 60 to 70 milliliters of HCl is introduced into the distilling flask through a dropping funnel. The contents of the flask are brought to a boil. When the first acid distillate forms, additional HCl is added to the distilling flask dropwise until about 100 milliliters has been added. Adding the bulk of the HCl in this manner not only controls the temperature of the distillate ($<108°C$), but also provides more complete distillation of all the arsenic with a minimum amount of acid. (The same effect was produced by adding the acid in 3 or 4 increments, but this reduced the temperature of the distillate with each addition and prolonged the distillation time.) The last traces of arsenic are removed by a final addition of 10 milliliters of hypophosphorous acid (H_3PO_2) and 50 milliliters of HCl. In order to avoid any serious suck-back, the receiving flask is continually lowered during the distillation so that the tip of the adaptor extends just below the surface of the distillate. Also, the distillate is continually neutralized with concentrated NH_4OH. (Since the distillate is already being cooled, this avoids the lengthy subsequent neutralization of the acid and a second tedious cooling.)

When the temperature of the distillate rises above 108°C (or after 400 milliliters of neutralized distillate has been collected), the receiving flask is lowered from the adaptor and the distillation is discontinued. The adaptor and the tip of the condenser are rinsed into the receiving flask, which is again neutralized with NH_4OH and then just acidified with HCl. Finally, about 10 grams of $NaHCO_3$ and 1 gram of KI are added, along with a few milliliters of starch indicator. The solution is then titrated with 0.05<u>N</u> iodine.

Data and Discussion

Preliminary work centered around the establishment of reagent blanks and optimum distillation conditions, with the recovery of standard arsenic solutions compared under varying conditions. The reagent blank was found to vary between 0.05 and 0.12 milliliter. To test the completeness of distillation, more H_3PO_2 and HCl were added, a second receiver was substituted, and a second distillation was performed that yielded a zero titration for blanks and standards and a titration of 0.05 to 0.07 milliliter for samples. Failure to subtract the reagent blank and to add the correction for the second portion of distillate would yield a maximum overtitration of 0.07 milliliter. However,

TABLE 16-4

ANALYSIS OF PORT HOPE GRAVITY CONCENTRATE FOR ARSENIC

1st Set: 20 ml 0.05N $As_2O_3 \hat{=} 18.32$ ml I_2 (Theoretical value: 18.22 ml I_2) Thus, 1 ml std $\hat{=}$ 0.92 ml I_2; reagent blank = 0.05 ml

Lab. No.	Sample Weight		Iodine Consumed (ml)	As (%)
1-1056 A	0.5001g		17.35	
		2nd Dist.	+ 0.06	
		Reagent Blank	− 0.05	
			17.36	7.14
1-1056 B	0.5006g		17.50	
		2nd Dist.	0	
		Reagent Blank	− 0.05	
			17.45	7.17
1-1056 C	0.5001g +		22.12	
		2nd Dist.	+ 0.05	
	5 ml std		− 4.60	
		Reagent Blank	− 0.05	
			17.52	7.21
1-1056 D	0.5001g +		26.49*	
	10 ml std		− 9.20	
		Reagent Blank	− 0.05	
			17.23	7.09

* Distillation interrupted about 10 minutes before completion.

2nd Set: Duplicate samples, no corrections for reagent blank or a second distillation

Lab. No.	Sample Weight	Iodine Consumed (ml)	As (%)
1-1057 A	0.5016g	22.07	9.05
1-1057 B	0.5004g	21.56	8.87
1-1058 A	0.5006g	25.65	10.54
1-1058 B	0.5015g	26.03	10.68

3rd Set: 20 ml new As_2O_3 std $\hat{=}$ 18.30 ml I_2 (Theoretical value: 18.22 ml I_2) Thus, 1 ml std $\hat{=}$ 0.915 ml I_2; reagent blank = 0.12 ml

Duplicate samples, no corrections for reagent blank or a second distillation

Lab. No.	Sample Weight	Iodine Consumed (ml)	As (%)
1-1072 A	0.5006g	25.45	10.46
1-1072 B	0.5000g	25.53	10.51
1-1073 A	0.5005g	21.93	9.02
1-1073 B*	0.4999g +	26.02	
	5 ml std	− 4.58	
		21.44	8.82**
1-1074 A	0.5000g	23.27	9.58
1-1074 B	0.5003g +	27.40	
	5 ml std	− 4.58	
		22.82	9.39**

** More acid (a total of 100 ml) was added initially to these two samples, with less (65 ml total) added through the dropping funnel in an attempt to reduce the distillation time. This procedure is not recommended.

0.3 milliliter of iodine would be required to alter the arsenic result by 0.1 per cent which is less than either the precision obtained for duplicates or the accuracy required for the determination. Hence, the blank and second distillate may be considered as cancelling one another. The experimental results are shown in Table 16-4.

The residue from sample 1-1056 D was filtered, washed, and analyzed spectrographically for arsenic. This residue represented 24 per cent of the initial sample and had the appearance of fine sand. It was reported to contain 500 ppm arsenic.

Conclusion

Thus, a reliable procedure has been developed for the determination of arsenic in Port Hope gravity concentrate.

16.7 EVALUATION OF BLACK OXIDE STANDARDS FOR VOLUMETRIC ASSAY WORK –

D. Valent, W. Steigerwalt, E. Ross, P. Ziegenfuss, and B. Gessiness

The NY-ST standard used by the Ores Laboratory has been re-evaluated. Uranium values for both NY-ST and a newly received U_3O_8 standard designated "No. 15" have been established by comparing these materials with freshly ignited (850° to 900°C) MS-ST, which has an established value of 99.94 per cent U_3O_8. (MS-ST was the original AEC standard black oxide whose assay value was validated by the National Bureau of Standards and Princeton University.)

The NY-ST was assayed, using both ignited and "as received" samples. The "as received" sample of No. 15 Standard was assayed. Each standard U_3O_8 was analyzed in triplicate by each of three analysts. Each analyst titrated duplicate aliquots of his own samples, as well as aliquots taken by the other two analysts in order to provide a cross-check on the sampling and the preparation of the dichromate.

Table 16-5 is a summary of the results, expressed in terms of per cent U_3O_8.

On the basis of this study, the NY-ST value used in this laboratory (99.90 per cent U_3O_8) has been 0.08 per cent high on the as-received basis. On the dry basis, the difference is 0.02 per cent. In September, 1953, when the NY-ST was compared with MS-ST, the value, 99.90, was obtained; in June, 1954, the value was found to be 99.91; and in December, 1954, 99.89, all on on the as-received basis. It appears that moisture absorption during 1955 could account for the shift in U_3O_8 content from 99.90 to 99.82 per cent.

TABLE 16-5

ASSAY OF STANDARD BLACK OXIDES

	Normality of $K_2Cr_2O_7$ based on ignited MS-ST*	U_3O_8 (%) NY-ST (Ignited)	 NY-ST** (As Received)	 New No. 15 Std† (As Received)
Analyst I	0.026973	99.936	99.804	99.892
Analyst II	0.026988	99.943	99.856	99.907
Analyst III	0.026964	99.913	99.812	99.857
		99.93 (avg)	99.82 (avg)	99.89 (avg)
U_3O_8 (Dry Basis)			99.88	99.91

* MS-ST[1] has a U_3O_8 content of 99.942%

** Loss at 110°C: 0.058%

† Loss at 110°C: 0.024%

16.8 EFFECT OF ATMOSPHERIC CONDITIONS ON THE MEASUREMENT OF THE MOISTURE CONTENT OF URANIUM ORE CONCENTRATES – D. Valent and B. Gessiness

It was shown in the previous quarterly[2] that there is an inverse relationship between moisture loss and relative humidity for uranium ore concentrates dried at 110° C. It would be advantageous to know whether or not these materials can be brought to a constant weight. Therefore, a study was undertaken whereby these materials were dried in a vacuum oven, through which dry argon was passed. Before that study is discussed, however, the uranium concentrate used will be described.

Behavior of South African Concentrate (Quality Control Sample)

The lot of South African concentrate used in this study had been dried at 110° C for 72 hours, bottled in a number of bottles, and sealed with tape (June, 1955). The sample from each bottle was used by the Analytical Quality Control group as a control sample – it was analyzed for uranium content and weight loss at 110° C along with production samples.

In Figure 16-1, Curve 2 represents the average uranium content of the as-received control samples analyzed during this study; Curve 1 represents the calculated uranium content of the control sample, based on the average uranium content of the as-received samples (Curve 2) and the loss at 110° C (Curve 5). Curve 4 represents the uranium content of the individual as-received control samples (as determined experimentally); Curve 3 represents the calculated uranium content of these control samples, based on the experimentally determined uranium content (Curve 4) and the loss

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[1] *Rodden, C. J., "Analytical Chemistry of the Manhattan Project", p. 55, McGraw-Hill, New York, 1950.*

[2] *Valent, D. and Gessiness, B., Summary Tech. Rpt., Vol. II, pp. 82-88, NLCO-601, January 16, 1956.*

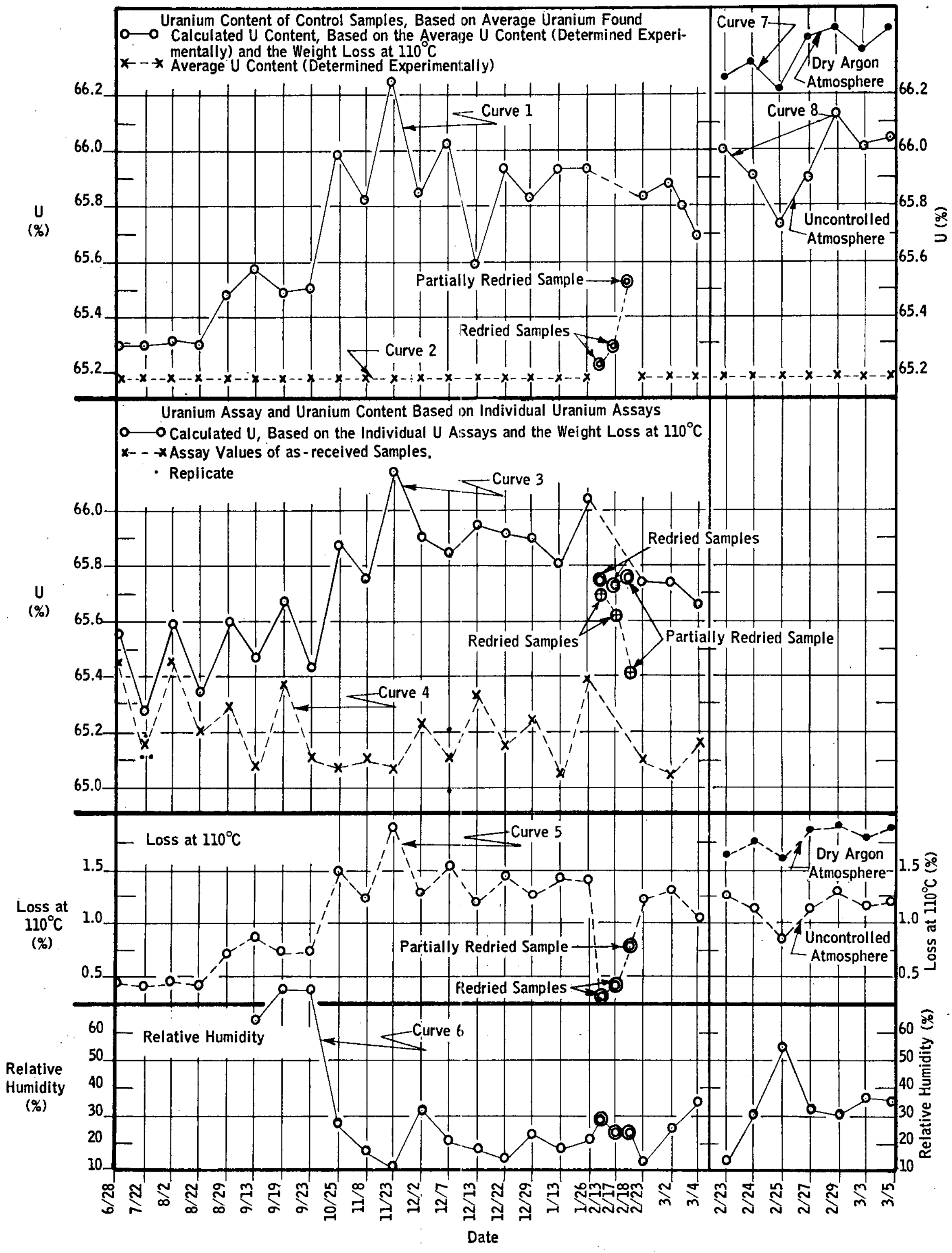

FIGURE 16-1 SOUTH AFRICAN CONCENTRATE (QUALITY CONTROL SAMPLE) – ASSAY COMPARED WITH RELATIVE HUMIDITY: RANDOM ATMOSPHERE AND CONTROLLED ARGON ATMOSPHERE

at 110° C (Curve 5). Curves 5 and 6 are self-explanatory. The curves adjacent to the right-hand margin are explained in the discussion of the heating study.

It was noted that the loss at 110° C (Curve 5), which should have remained constant for the sealed samples, had increased from 0.20 per cent on June 28 to 1.63 per cent on November 28. Between June and January, the average uranium assay of the as-received samples (Curve 4) remained at 65.18 per cent, with a standard deviation of 0.15 per cent. As a result, the calculated uranium content of the control sample (Curve 3) was 65.5 per cent from June through September, 65.9 per cent from November through December, and 65.7 per cent from January to the first week of March. The first three samples assayed in February were out of control, however. Two of the samples had been removed from the sample bottles and redried before being submitted for analysis; one sample had been partially redried. The points on the graph representing these samples are circled.

The results and control limits obtained by analysis of the as-received samples indicate that the samples were adequately sealed and did not absorb moisture. The weight loss curve, however, seems to indicate that the concentrate was "dry" under June conditions, but not under November to March conditions. The total effect on the uranium assay was approximately 0.7 per cent uranium (a June to September average of 65.49 per cent, when the relative humidity was 60 to 80 per cent, and a November maximum of 66.14 per cent, when the relative humidity was 11 per cent).

Heating Uranium Ores and Concentrates in a Dry Argon Atmosphere at 110° C

A vacuum oven was obtained in late February to determine whether the effect of atmospheric humidity can be completely overcome by "absolutely" drying the gas which enters the drying oven. The oven was used as a pressure oven rather than as a vacuum oven, so that if any undetectable leaks were present, dry gas would escape instead of air entering from the atmosphere. Argon was selected as the gas because it is inert and readily available. The drying tower consisted of indicating Drierite, to indicate at once (by a color change) whether the cylinder of argon was wet or dry; Ascarite, to eliminate any traces of carbon dioxide which could react with the concentrate; Anhydrone, to remove the bulk of nondetectable water vapor passing through the Drierite; anhydrous phosphoric acid and calcium metal, to remove the last traces of water vapor. (A change in the consistency of the phosphoric acid after 48 hours indicated that these precautions were not too elaborate.) A similar train was attached to the exit valve of the oven to preclude a back-rush of undried air in the event that the cylinder valve was accidently turned off or the tank was emptied overnight. Each time the oven door was closed, the oven was flushed with argon entering at a pressure of about three inches of mercury. The pressure was reduced to one-half inch and maintained at this level for the next 24 hours.

Two samples of South African concentrate were selected for a preliminary study: one was a regular control sample, the other was one of the redried control samples. About five grams of each was weighed in triplicate for the "argon oven" and a similar set was weighed for the oven in which normal air drying was to be carried out.

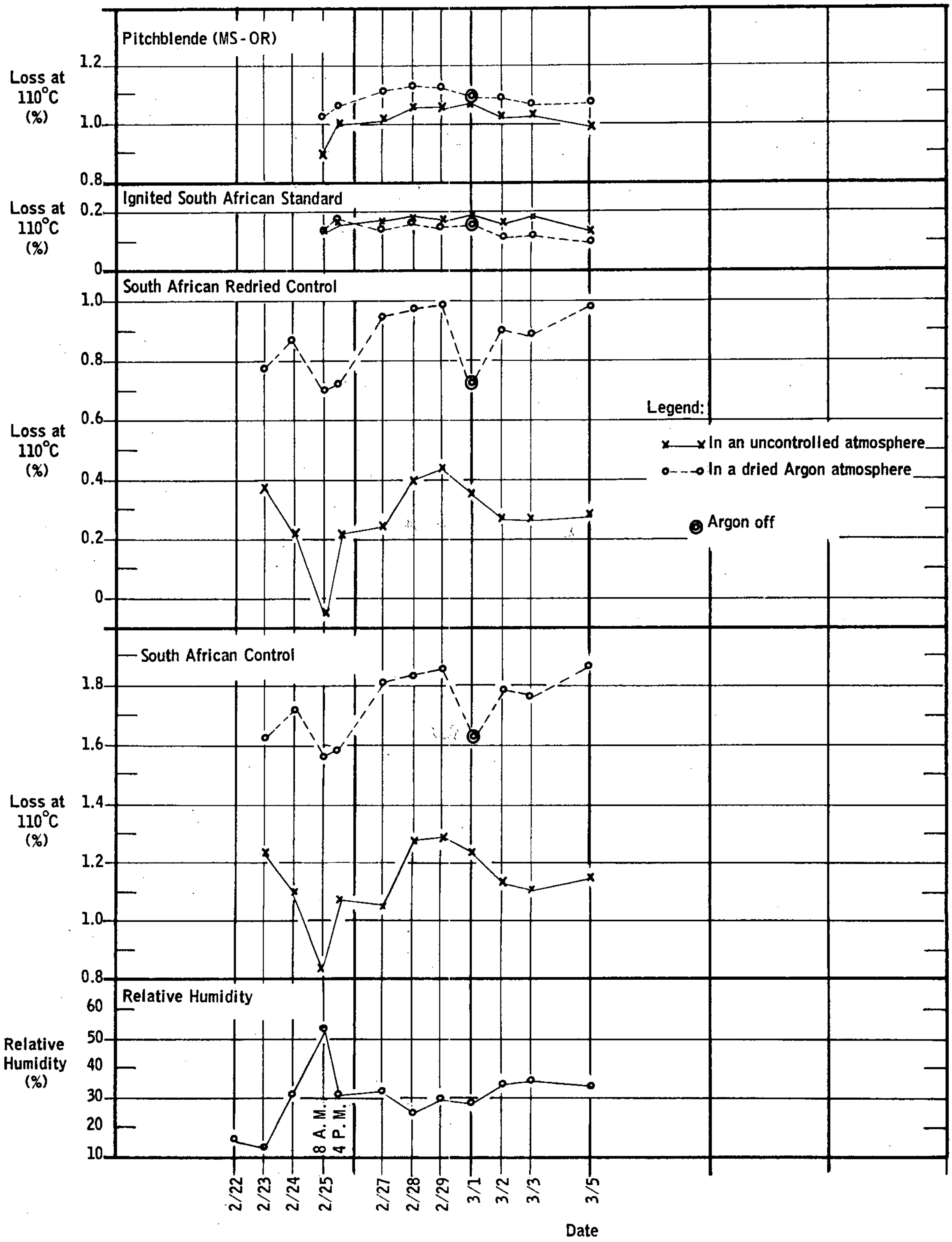

FIGURE 16-2 LOSS AT 110°C OF URANIUM ORES AND CONCENTRATES: ROUTINE PROCEDURE COMPARED WITH HEATING IN A DRY ARGON ATMOSPHERE

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TABLE 16-6

PRECISION OF "LOSS AT 110°C" DETERMINATION ON URANIUM ORES AND CONCENTRATES

(All Values given in %)

Sample	Type of Atmosphere	DATE										
		2/23	2/24	2/25A	2/25P	2/27	2/28	2/29	3/1	3/2	3/3	3/5
South African Control	Uncontrolled Atmosphere	1.24	1.10	0.82	1.07	1.06	1.28	1.29	1.24	1.13	1.10	1.14
		1.24	1.10	0.82	1.08	1.12	1.28	1.29	1.24	1.15	1.12	1.15
		1.24	1.10	0.83	1.07	1.04	1.27					
	Dry Argon Atmosphere	1.63	1.74	1.57	1.58	1.81	1.83	1.86	1.60	1.79	1.76	1.86
		1.62	1.71	1.56	1.57	1.82	1.83	1.85	1.64	1.79	1.75	1.88
		1.62	1.72	1.56	1.58	1.83	1.83					
South African Redried Control	Uncontrolled Atmosphere	0.39	0.23	−0.06	0.21	0.24	0.40	0.44	0.35	0.26	0.26	0.27
		0.37	0.22	−0.06	0.23	0.24	0.38	0.42	0.35	0.26	0.25	0.27
		0.35	0.19	+0.02	0.18	0.24	0.38					
	Dry Argon Atmosphere	0.78	0.87	0.70	0.73	0.97	0.98	0.98	0.73	0.91	0.90	0.98
		0.79	0.89	0.70	0.72	0.95	0.98	0.99	0.71	0.91	0.87	1.00
		0.75	0.86	0.69	0.70	0.94	0.96					
Pitchblende (MS-OR)	Uncontrolled Atmosphere			0.88	1.00	1.01	1.05	1.05	1.06	1.01	1.02	0.99
				0.89	1.00	1.01	1.05	1.05	1.06	1.02	1.03	1.00
	Dry Argon Atmosphere			1.01	1.06	1.10	1.12	1.11	1.08	1.08	1.06	1.07
				1.03	1.06	1.12	1.14	1.12	1.09	1.09	1.07	1.08
Ignited South African Standard	Uncontrolled Atmosphere			0.14	0.17	0.17	0.18	0.17	0.19	0.16	0.19	0.14
				0.13	0.16	0.16	0.18	0.17	0.19	0.17	0.19	0.14
	Dry Argon Atmosphere			0.14	0.17	0.16	0.17	0.15	0.16	0.12	0.12	0.10
				0.13	0.18	0.16	0.17	0.15	0.17	0.12	0.12	0.10

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Partial results for the regular control sample are included in Figure 16-1; the calculated uranium values (dry basis) obtained in the argon atmosphere (Curve 7) may be compared with the calculated uranium values obtained in the random atmosphere (Curve 8).

All of the results obtained after two weeks of drying are plotted on Figure 16-2. Also included on the graph are the averages for duplicate samples of pitchblende (MS-OR, the standard Q-11 sample) and the standard sample of Ignited South African Concentrate. Heating of the latter two samples began three days after heating of the first two. Average values for all samples are plotted on the figure.

Individual results are summarized in Table 16-6; the high degree of precision obtained for the triplicate and duplicate weighings precluded the use of replicates for this and subsequent loss studies.

This study is being continued with the drying of INX, Colorado Plateau black oxide, Eldorado orange oxide (both dry and hydrated), Blockson uranyl phosphate, and ammonium diuranate. The results will be summarized in a subsequent progress report.

16.9 ANALYSIS OF URANIUM – MOLYBDENUM ALLOYS

Samples of depleted uranium-molybdenum alloys received from the Pilot Plant and Metals Plant were analyzed for molybdenum. The molybdenum content ranged from 7 to 8 per cent.

Determination of Molybdenum – R. Scheer, E. Frank, and B. Gessiness

Molybdenum was determined gravimetrically, using α-benzoin oxime as precipitant. A study was made in order to determine the precision between analysts for this determination. Two analysts assayed punchings of alloy material and also determined the variability of aliquots from given stock solutions. The results of their work are shown in Table 16-7.

It was determined that the precision of the two analysts is not significantly different on the aliquots or punchings. It was also found that the variability of the results between punchings is significantly greater than the variability due to the analytical method.

Determination of Nickel – R. Scheer and B. Gessiness

Nickel was determined by the conventional colorimetric procedure, employing dimethylglyoxime as the chromogenic reagent. No apparent interference by molybdenum in the color development of the nickel dioxime was noted. However, a study was made to substantiate the accuracy of the determination by extracting the nickel dioxime with chloroform at a controlled pH. Results of this comparison are shown in Table 16-8.

TABLE 16-7

COMPARISON OF ANALYSES* FOR MOLYBDENUM BY DIFFERENT ANALYSTS

Lab No.	Punchings Analyst I	Punchings Analyst II	Aliquots from Stock Solutions Analyst I	Aliquots from Stock Solutions Analyst II
333	7.81 7.71	7.92		
	8.03 7.57	7.76 7.84	7.89 7.84	7.84 7.84
334	7.74 7.61	7.89		
	7.71 7.62	7.67 7.64	7.73 7.77	7.81 7.84
413		7.52		
	7.68 7.93	7.92 7.70	7.71 7.68	7.73 7.76
		7.61		
414		7.49		
	7.66 7.74	7.72 7.72	7.64 7.70	7.76 7.60
349	7.59 7.51	7.55		
350	7.60 7.59	7.72 7.81		
384	7.55	7.64		
385	7.52	7.49		

* All results are per cent.

TABLE 16-8

COLORIMETRIC DETERMINATION FOR NICKEL IN U-Mo ALLOYS

Lab No.	Nickel (ppm) Direct Colorimetric determination	Nickel (ppm) Extracted with Chloroform, followed by Colorimetric determination
333	125	112
334	123	120
357	37, 39	32
358	29	29
408	59, 59	51, 50
409	57	51

These values also compare favorably with those obtained by spectrographic analyses. If wet-chemical analysis of this material for nickel is required, the direct determination is satisfactory for routine work.

Determination of Iron – E. Tieman and B. Gessiness

An investigation was made in order to determine the optimum conditions for the colorimetric determination of iron in the alloys, using o-phenanthroline. Preliminary studies indicated interference by molybdenum in the ferrous-phenanthroline color development. In an effort to overcome this hindrance and to induce a more stable color formation, numerous variations in the standard procedure were attempted.

It was indicated that a direct colorimetric procedure could be used with no separation of molybdenum provided the amount of molybdeum present is limited to 8 milligrams; this prevents effective interference from molybdenum.

It was also indicated that reliable results could be obtained by passing a sulfuric acid solution of the alloy through an ion-exchange column containing Dowex-1 resin. The resin (in the sulfate form) does not adsorb trivalent iron from a 0.3M sulfuric acid solution but will adsorb quantitatively both molybdenum and uranium. The iron is then determined by the usual colorimetric procedure. Excellent precision was obtained by replicate analyses. Furthermore, quantitative recovery of iron was obtained in spiked samples. Further examination of the two methods will continue.

16.10 ANALYSIS OF MISCELLANEOUS FEED MATERIALS FOR URANIUM – B. Gessiness

During the past quarter, samples of Q-11, INX, South African and Australian concentrates, and Blockson phosphate were analyzed volumetrically for uranium. Eldorado orange oxide was assayed gravimetrically. Also, several miscellaneous feed materials were received whose analysis necessitated modification and deviation from the standard volumetric procedure. The assay of these materials is discussed in the following sections.

Assay of Port Hope Gravity Concentrate – W. Steigerwalt and D. Valent

When this material was first assayed for uranium in December, 1953, it was found that the then newly adopted "thioacetamide procedure" for removing the heavy metal sulfide group was only partially effective because of the high arsenic content (about 10%). Too much thioacetamide reagent was required in order to complete the precipitation; this was accompanied by the additional problem of excessive foaming. The number of samples to be assayed, however, was small so the problem was substantially by-passed by making an additional precipitation with gaseous H_2S and checking the filtrate for completeness of precipitation after removal of the sulfide group.

Upon the receipt of recent shipments of this material at NLO, it was decided to resolve this problem. The primary objective of the study was to determine whether thioacetamide alone would suffice as precipitant, thus excluding the use of H_2S entirely from the Ores Laboratory. (Thioacetamide has been successfully substituted in the analysis of all other ore concentrates.)

The problem apparently could be resolved in the amount of arsenic to be precipitated could be lessened without using so small a sample that the accuracy of the uranium assay was drastically affected. Since the uranium content was approximately 10 per cent, any size sample above 0.1 gram that resulted in a titration greater than 10 milliliters of $K_2Cr_2O_7$ should give a sufficiently accurate uranium assay (±0.2% U). A 0.5 gram sample (one-half to two-thirds the size sample normally taken for material that assays in the range of 10 per cent) would yield a titration of approximately 15 milliliters. This reduction in sample size helped considerably, but nevertheless some samples precipitated additional sulfides when the filtrate was tested by further addition of thioacetamide. Foaming was controlled by frequently turning off the electric heaters on the shaking hotplate.

Volatilization of some of the arsenic by boiling with HCl was also investigated. Addition of 50 milliliters of HCl at the same time as addition of the sulfuric and nitric acids was only partially successful in eliminating a second thioacetamide precipitation. However, when the HCl was added after the samples had first been fumed with HNO_3 and H_2SO_4 to SO_3 fumes, considerable arsenic was evidently volatilized as $AsCl_3$ (the samples, of course, were again taken to SO_3 fumes to eliminate the HCl). Very little foaming occurred while the sulfides were being precipitated and no sample treated in this manner produced any precipitation when the filtrate was tested with additional thioacetamide. This, then, is the recommended procedure that will henceforth be followed for the assay of all samples of high-arsenic feed material. Results of the assays for this material by the recommended procedure are shown in Table 16-9.

TABLE 16-9

ASSAY OF PORT HOPE GRAVITY CONCENTRATE

Laboratory No.	Uranium (%)	
1-1078	9.39	9.35
1-1079	10.07	9.95
1-1080	9.28	9.24
1-1081	9.32	9.32
1-1090	9.80	9.89
	9.79	9.87
1-1091	10.47	10.51
1-1120	9.34	9.31
1-1121	10.04	10.04

Assay of International Minerals Green Salt – W. Steigerwalt

Three lots of International Minerals green salt were assayed. No difficulties were encountered; however, 0.7-gram samples were taken for assay rather than the usual 1.5-gram samples because of the very low density of the material. The results obtained for the assay of this material are shown in Table 16-10.

TABLE 16-10

ASSAY OF INTERNATIONAL MINERALS GREEN SALT

Sample (Official Dried)	U As-Recd (%)		Loss at 110°C (%)	U Dry Basis (%)	
FMPC 1290	36.08	36.18	0.26	36.17	36.27
FMPC 1291	43.05	43.01	0.23	43.15	43.11
FMPC 1292	32.17	32.20	0.25	32.25	32.28

Assay of Canadian "Pronto" Ore – W. Steigerwalt

Problems associated with the assay of the first lot of this material were discussed in a preceding progress report.[1] The second lot of "Pronto" ore was received and assayed during the past month. The official "as is" sample was found to contain 52.17 and 52.14 per cent uranium by duplicate analysis. The loss value at 110°C was 5.21 per cent. This compares with the first lot of material, which assayed 55.13 and 55.27 per cent uranium and had a loss value of 5.36 per cent.

The material is now being assayed for thorium by the gravimetric oxalate procedure.

16.11 TURBIDIMETRIC METHOD FOR DETERMINING SULFATES IN ORANGE OXIDE –

W. Ellis, T. Keefe, and E. A. Brown

Recent reports[2,3] on the analytical method for determining sulfates in orange oxide (UO_3) indicated that the turbidimetric determination of sulfate is not feasible in the presence of uranium. Objections were based on the interference of the uranyl ion color in the turbidimetric measurement, as well as the tendency of uranium to form a sulfate complex. A preliminary ion-exchange or solvent extraction separation to remove the uranium was recommended. This study indicates that these objections may be sufficiently overcome, through modifications in the procedure, to permit the use of the turbidimetric determination as a routine control method.

In Figure 16-3 is shown the effect of uranium content on the optical density of standard solutions prepared by adding 500 micrograms of SO_4 to sulfate-free UO_3. The color effect of the uranium solution was overcome by the blank and wave length used. Some reduction in the intensity of the turbidity with increased uranium concentration is evident. However, it is possible to overcome this interference by making SO_4-UO_3 standards containing various uranium concentrations and then plotting a calibration curve for each UO_3 concentration. Typical calibration curves using 5-centimeter cells will be found in Figure 16-4. The absorbance of the uranyl ion color may be minimized through the use of a wave length of 535 mu.

A substantial savings in analytical time is possible through the use of this simplified procedure, based on direct turbidimetric measurements in the presence of the uranyl ion. Satisfactory precision was obtained.

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[1] *Valent, D., Gerhardt, E., and Gessiness, B., Summary Tech. Rpt., Vol. II, pp. 88-90, NLCO-601, January 16, 1956.*

[2] *MCW-1380, Quarterly Progress Report.*

[3] *Gerhardt, E. and Gessiness, B., Summary Tech. Rpt., p. 141, NLCO-577, October 17, 1955.*

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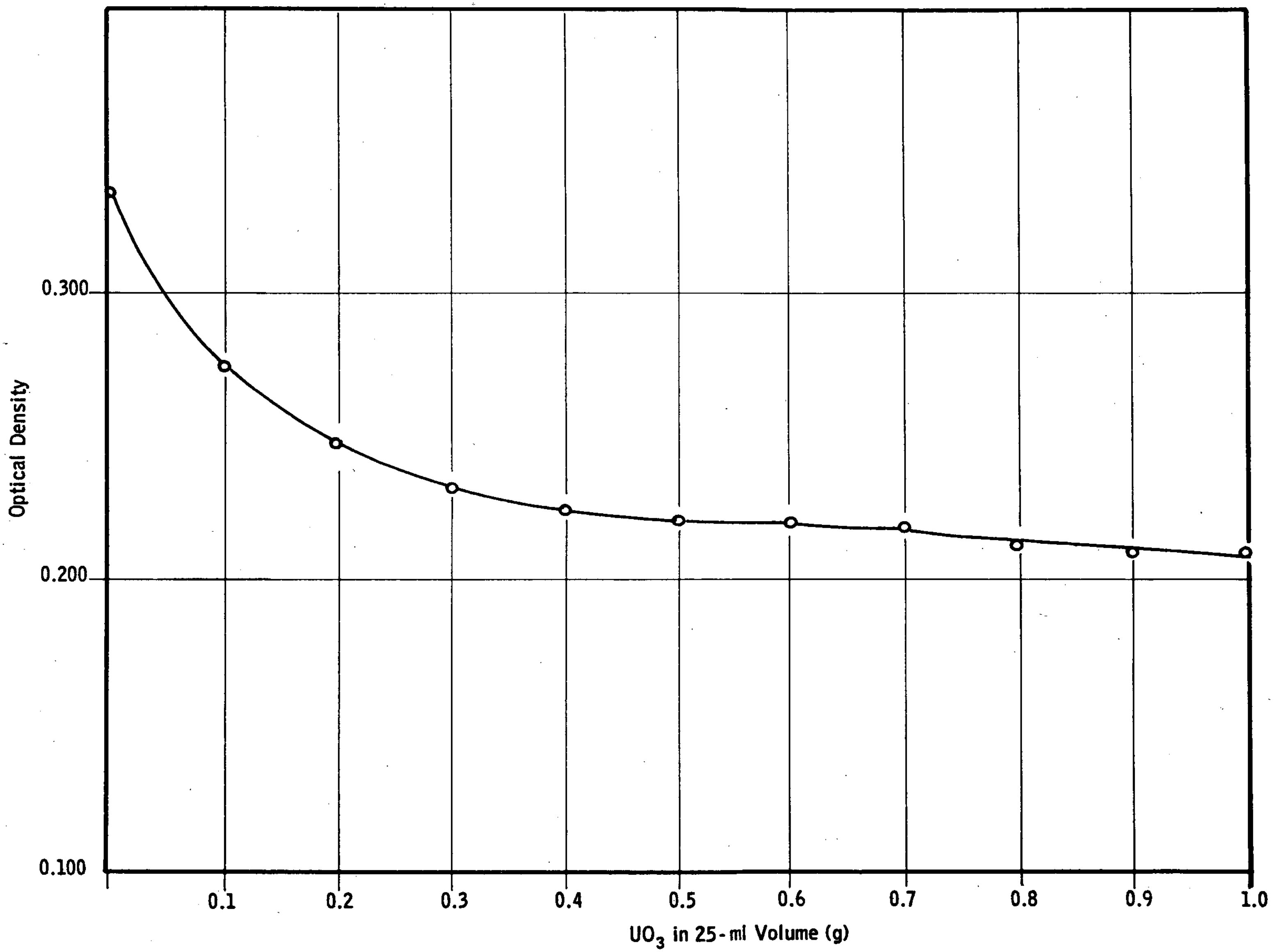

FIGURE 16-3 EFFECT OF URANIUM CONTENT ON $BaSO_4$ PRECIPITATION (500 γ SO_4 IN 25 ml; WAVE LENGTH: 535 mμ)

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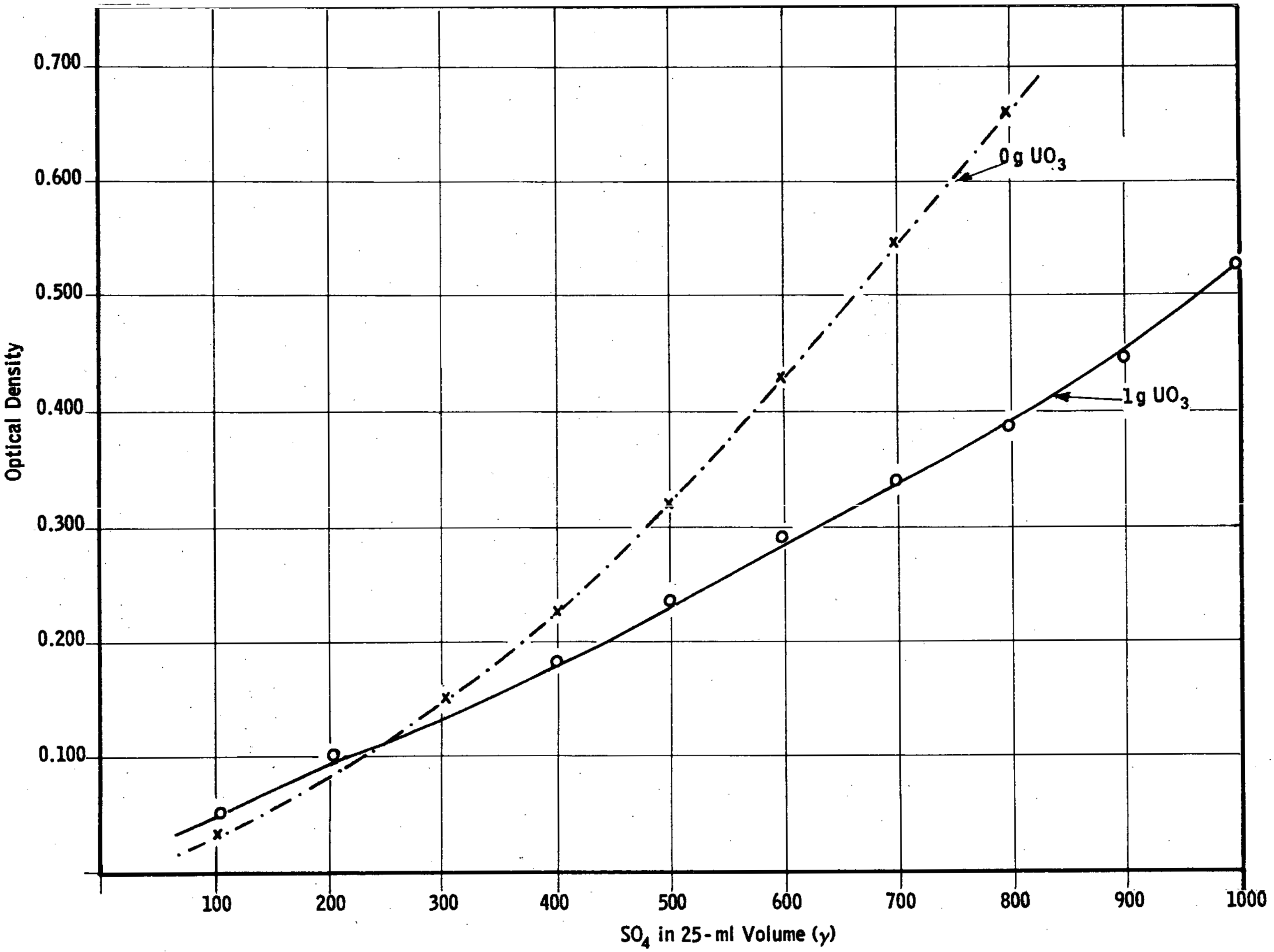

FIGURE 16-4 CALIBRATION CURVES FOR THE DETERMINATION OF SULFATE IN A URANIUM-CONTAINING SOLUTION (WAVE LENGTH: 535 mμ)

17. ANALYTICAL DEPARTMENT – SPECTROCHEMICAL DEVELOPMENT

– G. L. Stukenbroeker

The development projects in the Spectrochemical Group this quarter continue to center about the further refinement of analytical methods associated with the impurity analysis of uranium and thorium materials and ore concentrates.

17.1 CHEMICAL SEPARATION OF RARE EARTHS FROM URANIUM ORES – M. G. Atwell

The use of many different types of uranium ore and concentrates at the FMPC has necessitated the development of analytical methods for the determination of the rare earth content of such ores. Previous work on similar problems was on material which contained a high uranium content and a comparatively high rare earth content.[1] The use of ores containing less uranium and rare earths required some modifications of this procedure.

Great Bear Lake Gravity Concentrate

The Great Bear Lake gravity concentrate assays approximately 10 per cent uranium. The procedure for separation of rare earths which is used at the FMPC is as follows: A 1.000-gram sample of the concentrate is dissolved with $8\underline{N}$ HNO_3 and filtered. This filter paper (containing the residue) is treated with 48 per cent HF and is evaporated to dryness with the aid of a steam bath. (This step removes the silicon which is present in the concentrate.) The filtrate is transferred to the dish containing the residue, and 100 micrograms of thulium is added in order to serve as a monitoring element to check the efficiency of the chemical extraction of the rare earths.

A few milliliters of 48 per cent HF is next added, and the material is stirred and allowed to stand for at least three hours. The sample is then filtered and the filtrate is discarded. (This step of the procedure removes iron and other elements having fluorides which are soluble in HF.)

The precipitate in the filter paper is then transferred to an evaporating dish and a few milliliters of concentrated H_2SO_4 is added. The material is heated until the white fumes cease to be given off. The sample is then transferred to a Fisher burner and ignited until all organic material is destroyed. More sulfuric acid is added and the sample is again heated until the white fumes cease. (This procedure converts the fluorides to their sulfates.)

After the sample has cooled, five milliliters of HCl is added and the material is warmed. It is then diluted to a volume of approximately 25 milliliters and again is warmed to dissolve the residue. If the material will not go into solution, it is necessary to filter off the residue and to treat it again with H_2SO_4 to complete the dissolution procedure.

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[1] *Atwell, M. G., Summary Tech. Rpt., p. 144, NLCO-577, October 17, 1955.*

The solution containing the rare earths is diluted to about 100 milliliters and is extracted with an 8-hydroxyquinoline-chloroform solution to remove other interfering elements.[1] The rare earth elements are then precipitated as quinolates at pH 8.5, filtered off, and ignited to their oxides. These oxides are redissolved with a little 1:1 HCl, diluted to a volume of 100 milliliters, and then are subdivided into 10-milliliter, 30-milliliter, and 60-milliliter portions. This subdividing of the sample permits a greater range of concentrations to be covered in the individual analyses of the rare earth elements.

Each of the three solutions is diluted to 60 milliliters and one milligram of lanthanum is added to each to serve as a precipitation carrier. The rare earths are precipitated with NH_4OH, filtered, and ignited to RE_2O_3. The rare earth residue is excited spectrographically for the quantitative determination of the individual rare earths.

Canadian Pronto Ore

The procedure for the chemical separation of the rare earths from Pronto Ore is similar to that given for the gravity concentrate, but the problem is slightly complicated by the lower rare earth content and high uranium concentration of the ore.

Due to the low concentration of rare earths in Pronto Ore, a 20.000-gram sample is used. This material is treated with 75 milligrams of $8\underline{N}$ HNO_3 containing $0.02\underline{N}$ HF and is warmed. The residue is filtered, washed and transferred to a platinum dish and then is processed exactly as is the residue of the Gravity Concentrate. The resultant filtrate is then extracted with three 100-milliliter portions of a pentaether-HNO_3 solution (150 ml pentaether, 100 ml HNO_3), and the aqueous layer is recombined with the residue after the removal of silicon. This extraction with pentaether-HNO_3 removes the bulk of the uranium.

The remainder of the procedure is the same as that used for the Gravity Concentrate except that the sample is not subdivided at the end. The low rare earth concentration present makes this unnecessary.

In future work, TBP-kerosene will be substituted for pentaether-HNO_3 in the extraction of uranium in the Pronto Ore. It may also be necessary to add a treatment with KIO_3 to remove calcium, which is the carrier through the entire procedure.

17.2 SPECTROGRAPHIC IMPURITY ANALYSIS OF URANIUM-NIOBIUM ALLOYS –

C. A. Haberle and C. E. Pepper

The excitation conditions for the standards prepared by the dry grinding of the oxides of uranium and niobium were described previously.[2]

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[1] *ibid.*

[2] *Haberle, C. A., Summary Tech. Rpt., Vol. II, p. 99, NLCO-601, January 16, 1956.*

Difficulty has been encountered in matching the excitation conditions of the unknown metal alloy oxides with those of the prepared standards. The oxide obtained from uranium-niobium metal by direct ignition of the metal does not have the same excitation properties as the standards material. Samples of the 10 per cent alloy that have been ignited at 850°C for two hours produce oxide material that is approximately 75 per cent soluble in HNO_3.

The 25 per cent of the sample which is insoluble in HNO_3 will decompose partially upon fuming with $HClO_4$ and the oxides derived from this treatment have the same excitation characteristics as the spectrographic standards. However, the $HClO_4$ offers contamination of B and Cu to the sample.

The U-Nb metal is very nearly dissolved by aqua regia and H_2O_2 or by HCl and H_2O_2, but the oxides which are prepared from these solutions compare more nearly to those obtained by direct ignition of samples than to the standards.

New standards are being prepared from UNH and a solution of $NbCl_5$. It is thought that these oxide standards may have the same excitation properties as the oxides from samples treated with aqua regia and hydrogen peroxide.

Work on this project will continue in an effort either to prepare standards with excitation characteristics similar to those of the oxides obtained from samples or to convert samples in a manner which will result in oxides similar to the present set of standards.

17.3 SPECTROGRAPHIC IMPURITY ANALYSIS OF URANIUM-MOLYBDENUM ALLOYS –

E. R. Barker and C. E. Pepper

The production of a 7.5 per cent uranium-molybdenum alloy at the FMPC initiated a request for the spectrographic impurity analysis of the alloy metal.

Normally, molybdenum is excited as one of the common impurities in the spectrographic analysis of U_3O_8. Molybdenum present at a 7.5 per cent level not only produces a matrix effect but also an abundant undesirable spectra of molybdenum. An acceptable method of eliminating this interfering spectra without a chemical separation has not yet been found.

As a temporary measure, the alloy at first was ignited directly to the oxide in a muffle at 900°C with frequent grindings of the sample. This type of conversion was discontinued due to the difficulty of completely converting a one-gram sample to the oxide in less than three hours. The alloy is now dissolved in a minimum of HNO_3, taken to dryness, and ignited to the oxide at 900°C.

A pedestal-type electrode containing 50 milligrams of the sample oxide (carrier: 15% AgCl) is excited in a 14-ampere d.c. arc for 60 seconds. The spectra is recorded on a spectrographic plate (SA-I emulsion) and presently is compared visually to a standard plate. The alloy standards containing 7.5 per cent molybdenum were prepared in solution, ignited to the oxide, and ground. Analyses for the following elements are routinely reported: B, Be, Bi, Cd, Co, Cr, Cu, Fe, Mn, Ni, P, Pb, Si, V, and Zn.

Comparison of spectrographic values with results determined colorimetrically, show excellent agreement for approximately 20 samples analyzed to date.

Investigations of excitation conditions, carrier materials, electrode size, crater sizes, and improved conversion of the alloys to their oxides are presently in progress. This work is expected to provide methods of analyzing for Al, Mg, and Sn, as well as to lower the limits of reportable values.

17.4 SPECTROGRAPHIC DETERMINATION OF BERYLLIUM IN AIR SAMPLES – C. E. Pepper

In the production of U-Mo alloys at the FMPC, slurries of beryllium oxide are used to coat the reactor liners. Due to the toxicity of beryllium and beryllium compounds, the Health and Safety Division required that the air around such operations be sampled. The air filter samples were submitted to the spectrographic group with an urgent request for beryllium analysis.

The spectrographic method that was developed basically follows the procedure of Cholak and Hubbard[1,2] with several modifications. Essentially, the filter paper is digested with HNO_3 and $HClO_4$, taken to complete dryness, and the residue is redissolved with a minimum of HCl and 50 milliliters of water. Two milligrams of $CaHPO_4$ (in solution) are added, and the solution is made ammoniacal to phenol red. The precipitated $CaHPO_4$ and beryllium are filtered and ignited to the oxide. This sample oxide is then mixed with 9 milligrams of graphite and completely excited in a 3/16-inch electrode. The spectrum is visually compared to that of a prepared standard plate, using the Be 2348A line.

Standards covering the range 0.001 to 10 micrograms of beryllium were prepared by "spiking" clean filter papers and processing them as described above.

The precision and accuracy obtainable from this procedure are illustrated by the control results given in Table 17-1.

TABLE 17-1

RECOVERY OF BERYLLIUM FROM SPIKED SAMPLES

Beryllium Added*	Beryllium Found*	Beryllium Added*	Beryllium Found*
0	<0.001	0.04	0.05
0	<0.001	0.04	0.06
0	<0.001	0.04	0.05
0.004	0.004	0.4	0.4
0.004	0.005	0.4	0.3
0.004	0.006	0.4	0.35

* **All results are given in micrograms of beryllium.**

Precision and accuracy will be improved with the introduction of densimetric techniques.

It was determined that all chemical equipment must be kept scrupulously clean and segregated. Special care must be exercised during the spectrographic analysis to avoid contamination. Twenty filter-paper samples can be analyzed in one man-day.

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[1] *Cholak, J. and Hubbard, D. M., Anal Chem, 20, 73 (1948).*

[2] *Cholak, J. and Hubbard, D. M., Anal Chem, 20, 970 (1948).*