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SUMMARY TECHNICAL REPORT FOR THE PERIOD JULY 1, 1955 TO SEPTEMBER 30, 1955

UNITED STATES ATOMIC ENERGY COMMISSION
Technical Information Extension, Oak Ridge, Tennessee

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SUMMARY TECHNICAL REPORT
FOR THE PERIOD
JULY 1, 1955, TO SEPTEMBER 30, 1955

EDITED BY
JOHN W. SIMMONS

F. L. CUTHBERT, DIRECTOR
TECHNICAL DIVISION

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

Date: **OCTOBER 17, 1955**
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DEPARTMENT HEADS

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CONTENTS

1.0 ABSTRACT

The activities of the Technical Division of the National Lead Company of Ohio are reported for the period of July 1, 1955, to September 30, 1955.

2.0 INTRODUCTION

Activities carried on by Technical Division personnel during the past quarter included the following types of studies:

The determination of more nearly optimum process conditions in order to increase the yield and throughput of existing equipment.

The evaluation of a low-HNO_3 feed in the Refinery for use when high-grade ores are being processed. If feasible, this will lower nitric acid consumption.

Equipment modifications aimed at increasing production capacity.

The testing of less expensive grades of process chemicals as substitutes for presently used grades.

Testing of the effect of process conditions on the contaminant level in order to obtain an improved product.

Improvement of methods of recovering uranium from scrap materials in order to return uranium to the process stream more quickly.

The evaluation of new feed materials to determine whether they can be processed to meet specifications by the use of the FMPC process.

Testing of materials of construction in order to determine their performance (from a corrosion standpoint) in equipment being planned for new construction.

Determination of the feasibility of using a moving bed reactor for the production of green salt.

Development of techniques for the centrifugal casting of slugs. Centrifugally cast uranium alloy slugs will be evaluated as to their suitability as fuel elements.

Development of alternative steps in the thorium process in order to reduce costs and improve the quality of thorium.

Determination of process conditions that will eliminate secondary pipe in production ingots.

Modification of standard analytical methods for use in analyzing new types of FMPC samples.

Evaluation of presently used analytical methods.

3.0 SUMMARY

4.1 Variability of analysis caused by liquid sampling techniques was determined for South African ore concentrates, using either gravimetric or volumetric methods.

5.1 A laboratory investigation indicates that a two to one blend of No. 1 Special Pilot Mill uranium concentrate and black oxide can be processed through the NLO Refinery with complete uranium extraction.

5.2 A pilot plant evaluation has shown that Anaconda Bluewater uranium concentrate is suitable for processing through the NLO Refinery.

6.1 Plant-scale tests have shown that the 33.5 per cent TBP flow sheet can be adapted to refinery conditions and that the anticipated production increase can be realized. A 5.7/1 scrub ratio and an AP specific gravity of 1.000 were determined to be optimum values. Under these process conditions, the acidity of the uranyl nitrate product stream was 0.035 to $0.040\underline{N}$, its iron level was maintained below 10 ppm, and its uranium content was 90 to 95 g/l.

6.2 Excellent uranium extraction results were obtained by using a low-acid ($0.5\underline{N}$ HNO_3) concentration with an UNH feed material.

6.3 Pilot Plant studies showed that higher throughput can be obtained by operating the scrub column with the organic phase continuous when water is the scrubbing medium. If the column is to be operated with the aqueous phase continuous, a high-density scrubbing medium allows higher throughput.

6.4 Stainless steel types 347, 304-ELC, 309, 316, and 304 would be satisfactory materials of construction for use in the sparge tank (which generally contains 100 per cent uranyl nitrate hexahydrate at 245°F).

8.1 Green salt containing controlled amounts of UO_2F_2 was produced in the uranium hexafluoride reduction reactor by the addition of small quantities of UF_6 through the discharge screw conveyor. Derby yields were increased by this addition of small percentages of UO_2F_2 to the UF_4.

Slag liners were satisfactory when used in the reduction of green salt made from hexafluoride.

8.2 Inconel proved inferior to Monel as a reactor tube material for the hexafluoride reduction reactor because of nickel contamination in the UF_4 product.

9.1 A bank of reactors in the Green Salt Plant has been modified for equipment and process development work. In shakedown operations, the equipment changes were shown to be improvements over present production facilities.

9.2 Green salt (UF_4) was sintered and pulverized, resulting in a density equal to or greater than the density of green salt now used in uranium production.

10.1 A series of development test runs on the MBR Pilot Plant reduction reactor has resulted in 27 hours of sustained steady state operation at an average feed rate of 555 lb/hr, giving a product whose hourly assays averaged 97.6% UO_2. Development work is continuing on improving reduction reactor control, evaluation of hydrofluorination reactor performance, and development of economical pelleting techniques.

10.2 Laboratory thermal balance studies concerned with the moving bed reactor indicated that enhanced UO_3 reactivity can be attained by the use of casting-belt pellets of relatively high water content.

11.1 Commercial magnesium proved satisfactory for UF_4 reduction. Iron and manganese impurities were increased, but the cost advantage is significant.

11.2 Green salt densification was tested by two methods, sintering and prilling. Ground, sintered green salt and ground, prilled green salt both allowed about an eight per cent heavier reduction pot charge than the standard production green salt charge.

12.1 Investigations were conducted to determine the effects of mold insulation and mold geometry on the structure and soundness of uranium ingots cast in vacuum furnaces.

13.1 Uranium was successfully water-leached from sulfated sludge and recovered from the leach liquor by either (1) precipitating it with ammonium hydroxide or (2) reducing it with aluminum and precipitating it with orthophosphoric acid.

13.2 In HF recovery tests, a sulfate roast volatilized 55 per cent of the available HF from a static bed of MgF_2 slag in three hours.

13.3 A maximum tolerance for phosphate was determined for the TVA hydrochloric acid used in leaching uranium from C-oxide.

13.5 Of several materials of construction tested, only Teflon and tantalum showed adequate resistance to a synthetic digestion solution (925 cc H_2O; 77 cc HCl; 75 g/l $CaCl_2$; 75 g/l $MgCl_2$; 1.5 g/l MgF; 1.6 g/l $KClO_3$).

14.1 Several modifications of the method of making thorium chloride by the chlorination of thorium oxalate pellets were tested.

14.3 The production of 6-1/8-inch-diameter finished thorium ingots by consumable arc-melting of dezinced derbies is described.

14.4 Decontamination of off-specification thorium metal (by dissolution in HNO_3 NaF solution, followed by precipitation of thorium as the oxalate) resulted in satisfactory removal of all metal contaminants except zirconium.

14.5 Hydrated lime, sodium hydroxide, and magnesium oxide were compared as thorium sump precipitants. Hydrated lime was the most economical from a reagent cost standpoint and the use of magnesium oxide resulted in the fastest filtration rate.

14.6 Preliminary studies indicate that reduction and dezincing steps in the thorium process can be modified so as to make fabrication of primary electrodes by welding unnecessary.

15.1 A small quantity of uranium shot was made by pouring molten metal through a small nozzle into a 22-foot tube cooled with helium.

15.2 Heat-treating times for the beta transformation of 1.4-inch-diameter uranium rods were determined at 685°C, 695°C, and 715°C. in a molten salt bath of 46:54 w/o Li_2CO_3:K_2CO_3.

15.3 Annealing beta-treated uranium at 640°C for 20 minutes resulted in no correlation between grain structure before and after annealing.

15.4 Absolute humidity above the (45% Li_2CO_3, 55% K_2CO_3) molten salt bath was related to the hydrogen content of heat-treated uranium fuel elements. Sparging with CO_2 gas or covering the salt bath with a layer of CO_2 gas are thought to be effective methods of offsetting the effects of humidity.

15.5 Dilute zirconium, silicon, and molybdenum alloys of uranium have been centrifugally cast at various temperatures and mold speeds. Excellent internal soundness and smooth surfaces have been obtained.

16.2 The digestion time used in determining HCl-insoluble in orange oxide was varied, resulting in wide differences in the HCl-insoluble values.

16.3 A versene-bismuth method for the determination of zirconium has been modified satisfactorily for the analysis of zirconium in uranium-niobium-zirconium alloy.

16.4 It was shown that interference from niobium and zirconium was not significant in the estimation of molybdenum in uranium-zirconium-niobium-molybdenum alloy.

16.5 Excessive cooling of hydrous hydrofluoric acid samples before assay was shown to be inadvisable, as it results in the crystallization of hydrated molecules of hydrofluoric acid on the sides and bottoms of the containers and thus in nonrepresentative sampling.

16.6 The uranium content of Virginia-Carolina green salt was determined to be 18.46 to 18.50%.

16.7 Eldorado orange oxide was assayed for uranium content by three analysts. The precision of analysis was consistently good.

16.8 A method has been developed for determining sulfate in orange oxide in concentrations of 100 to 1000 ppm.

16.9 A colorimetric procedure, using thiocyanate as the chromogenic reagent, has been successfully adapted for the determination of molybdenum in ores.

16.10 Progress is being made in the determination of boron in thorium-base materials.

17.1 In the chemical separation of rare earths from thorium materials, better recovery is attained by keeping the pH below 4.0 during the 8-hydroxyquinoline-chloroform step.

17.3 A residue of rare earths that was very free of uranium and impurities was separated from Q-11 ore.

17.4 A spectrographic method was used to determine potassium, lithium, and sodium in calcium metal to a low limit of 5 ppm or less.

4.0 SAMPLING PROCESS

4.1 SAMPLING ORE BY WET SAMPLING TECHNIQUES - C. W. Taylor, S. Cseplo, and H. J. Davies.

This study was initiated to compare the relative accuracy of dry sampling techniques and wet sampling techniques. A total of 12 different lots, representing two complete shipments (boatloads) of South African concentrate, were evaluated.

Samples of South African concentrate were split by riffling. A four-ounce dry sample was taken from one of the riffled half-samples from each lot and was analyzed by the standard Plant 1 method. The other half-samples were analyzed by a liquid sampling technique after being placed in a tank and dissolved.

The uranium content of the first seven lots (1 boatload) was determined by a volumetric method, i.e., the uranium content of a representative sample of the slurry and the volume of the slurry were determined. From that, the per cent uranium in the original sample was calculated. A comparison of the analyses obtained by the volumetric and standard methods is presented below:

LOT NO.	STD. PLANT 1 METHOD (% URANIUM)	VOLUMETRIC METHOD (% URANIUM)	DIFFERENCE (%)
199	65.38	64.59	-0.79
200	65.11	62.37	-2.74
201	64.84	62.89	-1.95
202	64.73	64.98	+0.25
203	64.36	64.09	-0.27
204	65.82	62.04	-3.78
205	63.87	62.90	-0.90

Comparison of the results obtained by the two sampling methods shows that the analyses obtained by liquid sampling were low for six out of seven lots. These results indicate that at best the accuracy of volume measurement of tank contents was ±1 gallon, which represents a variation of ±0.8 per cent in the uranium analysis. For ore assaying 65 per cent uranium, diluted to an 80-gallon volume, the assay variation should be no greater than ±0.10 per cent. This is equivalent to an accuracy of ±1/8 gallon in measuring the slurry volume.

There were large differences between the analyses by volumetric and standard methods for Lots 200, 201, and 204. A possible reason for this discrepancy is the fact that the slurry level did not become steady until five minutes after mixing was discontinued.

The second series of tests utilized both gravimetric and volumetric techniques. In the gravimetric method, the specific gravity of the slurry is determined, as well as the slurry weight. The volume of the solution is then calculated and this, plus the uranium content of a representative slurry sample, is used to calculate the per cent uranium in the original dry sample.

In the second series of tests, five South African ore samples (representing one boatload) were riffled as described above. One set of half-samples was again riffled and these halves were analyzed by either gravimetric or volumetric methods. The results of the analyses are presented below:

LOT NO	STD PLANT 1 METHOD (% URANIUM)	GRAVIMETRIC METHOD (% URANIUM)	VOLUMETRIC METHOD (% URANIUM)
235	66.90	66.61	67.29
236	66.79	65.97	66.46
237	66.32	66.74	66.83
238	65.71	65.88	66.78
239	66.54	66.90	67.11

These results indicate good agreement between the averages of the gravimetric and the Plant 1 standard method, with 66.44 per cent versus 66.45 per cent average assays. The volumetric results were biased on the high side, with an average assay of 66.89 per cent, which is within the expected limits of ±0.4 per cent. Since the volumetric method was not expected to be any more precise than this with existing equipment, the results were encouraging in that the maximum variation from either Plant 1 or gravimetric results was one per cent. After correcting for the bias of 0.45 per cent, the standard deviation between the volumetric analyses and the average of the gravimetric and Plant 1 analyses on each lot was only 0.3 per cent. The results from Lots No. 199 to 205, inclusive, did not exhibit this accuracy, but had a maximum variation of 3.78 per cent.

The Pilot Plant investigation of liquid sampling (wet) techniques has indicated that either gravimetric (tank on weigh scales) or volumetric methods are feasible for South African ore concentrates. The gravimetric technique is favored, since the volume is more easily and accurately obtained by this technique than by direct volume measurement. A specially designed volumetric container could provide improved accuracy.

It was recommended that the sampling plant consider whether installation of a liquid sampling system is advisable.

5.0 FEED MATERIAL EVALUATION

5.1 LABORATORY EVALUATION OF NO. 1 SPECIAL PILOT MILL URANIUM CONCENTRATE - E. J. Beer and T. J. Collopy

A laboratory investigation of the digestion and extraction characteristics of an advance sample of No. 1 Special Pilot Mill uranium concentrate was performed. The results indicate that a two to one blend of this material and black oxide can be processed through the NLO Refinery with complete uranium extraction. The low uranium assay of this material necessitates blending with a high assay material in order to achieve the feed slurry specification in regards to uranium and residual solids content.

No. 1 Special Pilot Mill concentrate was produced by the caustic neutralization of a sulfuric acid leach liquor. The advance sample received was ground, and a representative portion was sent to New Brunswick Laboratories for analysis. The results, given in Tables 5.1-1 and 5.1-2, show sulfate and ammonia content, in excess of Refinery tolerance limits, and a uranium content that is too low for routine processing. The information received with this sample stated that with increased filtering and cake washing, these two features would be greatly improved.

TABLE 5.1-1

CHEMICAL ANALYSIS OF NO. 1 SPECIAL PILOT MILL*

COMPONENT	ANALYSIS**	COMPONENT	ANALYSIS**
Al_2O_3	6.70	Rare Earth Oxides	N.D.
Ca	0.11	SiO_2	0.46
Cl	0.01	SO_4	36.49
CO_3	0.03	U_3O_8	7.05
F	0.06	V	5.33
Fe	12.86	Loss at 1100°C (Moisture)	2.38
Mg	0.33	Loss on Ignition at 750°C	55.36
Mo	0.01	Loss on Ignition at 1000°C	55.51
NH_4	11.7		
P_2O_5	0.05		

* *Analyses performed by New Brunswick Laboratories.*

** *Analyses reported in weight per cent on as-received basis.*

N.D. Not Detected

TABLE 5.1-2

SPECTROCHEMICAL ANALYSIS OF NO. 1 SPECIAL PILOT MILL*

COMPONENT	ANALYSIS**	COMPONENT	ANALYSIS**
Ag	2-10	Mg	0.2-1%
Al	1-5%	Mn	0.5-2%
As	500-2000	Mo	200-1000
B	2-10	Ni	<500
Bi	N.D.	P	0.2-1%
Cd	N.D.	Pb	<100
Co	<200	Sb	N.D.
Cr	<500	Si	1000-5000
Cu	500-2000	Sn	10-50
Fe	> 5%	V	2-10%
		Zn	<500

* *Analyses performed by New Brunswick Laboratories*

** *Values are ppm except where noted otherwise. Estimations are based on 1:10 and 1:100 dilutions of the sample with pure U_3O_8.*

N.D. Not Detected

Two low temperature, dilute nitric acid digestion tests were made in the laboratory, using a blend of one part black oxide to two parts No. 1 Special Pilot Mill. The digestion of this material produced little foaming or fuming but the temperature rise was rapid during ore addition. After digestion, the slurry was acid-stable and had a low solids content. The results of the digestion experiments are presented in Table 5.1-3.

TABLE 5.1-3

DILUTE NITRIC ACID, LOW TEMPERATURE DIGESTION OF 2 TO 1 BLEND (NO. 1 SPECIAL PILOT MILL TO BLACK OXIDE)

TEST NO.	TEMP. OF DIGESTION (℃)	DIGESTION TIME (hr)	VOLUME CHANGE (V_i/V_F)	ACID CONSUMPTION (EQ.HNO_3/g ORE)	FINAL SLURRY CONC. U(g/l)	FINAL SLURRY CONC. HNO_3(N)
1	35-56	2	0.885	0.0100	200	3
2	42-69	2	0.885	0.0100	201	3

The slurry from digestion test No. 1 was extracted by batch extraction techniques. Table 5.1-4 presents the stage data for the batch shakeout. The results indicate that the uranium can be efficiently extracted from the No. 1 Special Pilot Mill material.

TABLE 5.1-4
BATCH SHAKEOUT OF FEED SLURRY FROM 2 TO 1 BLEND*
(NO. 1 SPECIAL PILOT MILL TO BLACK OXIDE)
(AQUEOUS TO ORGANIC VOLUME RATIO = 1 TO 1)

STAGE	U IN AQUEOUS PHASE (g/l)	U IN ORGANIC PHASE (g/l)
Feed	200	
1E	117	83
2E	48	71
3E	5	34
4E	0.252	3.45
5E	0.012	0.205
6E	0.004	0.010

* *From Test No. 1 (Table 5.1-3)*

5.2 PILOT PLANT EVALUATION OF ANACONDA BLUEWATER URANIUM CONCENTRATE

T. J. Collopy and C. W. Huntington

The pilot plant evaluation of Anaconda Bluewater uranium concentrate demonstrated that this material is suitable for processing through the NLO Refinery.

The laboratory evaluation which was previously reported[7] indicated that the uranyl nitrate product (CP) obtained from the processing of this material would not meet the NLO purity specification regarding cadmium. This product contamination was not duplicated employing Pilot Plant pulse plate column conditions and an organic/aqueous scrub ratio of 10.4/1.

The material used for Pilot Plant testing was a composite of four drums from Lot 75 and was used as-received, since grinding was unnecessary.

A low-temperature dilute nitric acid digestion was made on this feed material. Table 5.2-1 gives the digestion conditions and results. The results indicate that only minor foaming difficulties would be encountered under refinery conditions.

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[7] *Beer, E. J. and Collopy, T. J., Summary Tech Rpt., pp. 37-41, NLCO-565, July 15, 1955.*

TABLE 5.2-1
DIGESTION – BATCH NO. 366

Weight of Ore (lb)	1270	Fume System	Fan on
Plant Acid (gal)	190	Digestion Time (hr)	1.25
Plant Water (gal)	200	Temp during Digestion (hr at °F)	1.25 at 155°F
Initial Volume (gal)	390	Analysis of Slurry after Adjustment	
Initial Acid Concentration (N)	7.12	U (g/l)	204
Initial Temp. (°F)	150	HNO_3(N)	3
Rate of Ore Addition (lb/hr)	615	Final Slurry Volume (gal)	550
Temp. during Ore Addition (°F)	150-166		

The conditions listed in Table 5.2-2 were employed in processing the uranium from this digested feed material. The results obtained during extraction, scrubbing, and re-extraction show that this material would present no problem under refinery conditions.

TABLE 5.2-2
OPERATING CONDITIONS FOR PILOT PLANT EXTRACTION TESTS

A. Stream Compositions
- AF: 200 g/l; 3N HNO at 100-110°F
- AX: 22.5% TBP in kerosene diluent, 0N HNO
- BS: Deionized water at room temp.
- CS: Deionized water at 150°F

B. Pulse Conditions
- A column: 1 in. amplitude, 50 cpm frequency
- B column: 0.11 in. amplitude, 68 cpm frequency
- C column: Jet mixer

C. Continuous Phase

A column	Organic
B column	Aqueous
C column	Organic

D. Flow Ratios

Feed/Organic/Scrub recycle	4.75/13/1.25
Organic/Scrub	13/1.25
Strip water/Organic	1.1/1

E. Flow Rates (gph)

AX	104	BS	10
AF	38	CS	114

F. Total Throughputs (gsfh)

A column	760	C column	1090
B column	570		

G. Solvent Cleanup System
- Na_2CO_3 wash, followed by water wash.

Filtered samples of the aqueous uranyl nitrate product were examined for purity. Table 5.2-3 gives the spectrochemical results. These results show that under pulse column conditions an organic to scrub water ratio of 10.4/1 yields a product which meets purity specifications.

TABLE 5.2-3

SPECTROCHEMICAL ANALYSIS OF AQUEOUS UNH PRODUCT(CP)*
(SAMPLES TAKEN FROM RUN 274 AFTER 12 HOURS ON STREAM)

ELEMENT	ANALYSIS	ELEMENT	ANALYSIS
Ag	<0.1	Mn	<4
Al	<4	Mo	<4
B	<0.2	Ni	<2
Bi	<1	P	<20
Cd	<0.2	Pb	<1
Co	<2	SiO_2	<20
Cr	<4	Sn	<1
Cu	<1	V	<20
Fe	<4	Zn	<20
Mg	2		

* *ppm on uranium metal basis.*

6.0 REFINERY PROCESS (URANIUM)

6.1 PLANT-SCALE TEST OF THE 33.5 PER CENT TRIBUTYL PHOSPHATE (TBP) EXTRACTION FLOW SHEET - C. W. Huntington, T. J. Collopy, J. R. Nelli, E. J. Beer, and E. J. Fasnacht.

A plant-scale test program is currently in progress to evaluate the 33.5 per cent TBP flow sheet previously reported.[1] Two phases of this program have been completed. They have shown that the 33.5 per cent TBP flow sheet can be adapted to refinery conditions and that the anticipated production increase can be realized. A final test remains to be made.

The first series of Refinery tests utilized the flow sheet essentially as it had been developed in the Pilot Plant program.[2] The specific gravity of the organic product stream (AP) was maintained at 1.000 ± 0.005. The scrub ratio (organic to aqueous) was 9 to 1, and the strip ratio (organic to aqueous) was 1 to 1. Under these conditions, it was found that an aqueous uranyl nitrate product stream (CP) containing 100 to 105 g/l uranium could be produced at an extraction column throughput of 895 gsfh. At these rates, no overloading of the extraction, scrub, or re-extraction columns occurred with respect to column throughput. The nitric acid (0.035 to 0.045<u>N</u>) and iron (17 to 25 ppm) concentrations in the aqueous product stream (CP) exceeded present specifications for these impurities, however.

The second phase of the test program was concerned with the development and modification of the flow sheet for optimum Refinery application, with special emphasis on product purity problems. Briefly, this period involved the adjusting of process conditions at extraction column throughputs of approximately 785,910 and 1000 gsfh.

Several major changes in organic saturation were tested. An AP specific gravity of 1.000 ± 0.005 was shown to be the maximum value that can be utilized which provides a safety factor against excessive losses of uranium in the raffinate. This specific gravity corresponds to a uranium concentration of 105 to 110 g/l U in the AP stream. Raffinate losses of TBP remained within tolerable limits.

In an attempt to reduce iron and nitric acid contamination in the CP stream, scrub ratios (AX to aqueous) ranging from 9/1 to 5/1 were used. At an AP specific gravity of 1.000, it was found that a scrub ratio of 5.7/1 is necessary in order to consistently maintain the iron level below 10 ppm. At this scrub ratio, the uranium concentration in the CP stream was 90 to 95 g/l. The lowest acidity obtained in the CP stream was 0.035 to 0.040<u>N</u>. This value is slightly in excess of the hydrolytic acid concentration of 0.028<u>N</u>; however, during sustained operation impurity levels of the orange oxide (UO_3) remained within specification. This indicated that the excess acidity did not cause excessive equipment corrosion in the evaporation and boildown operations.

A final plant-scale test will be conducted in the near future to determine accurately operating data for optimum utilization of the 33.5 per cent TBP system.

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[1] *Huntington, C. W., Collopy, T. J., Taylor, C. W., and Cseplo, S., Summary Tech. Rpt., pp. 42-44, NLCO-565, July 15, 1955.*

[2] *ibid.*

6.2 LOW-ACID EXTRACTION OF URANIUM - S. Cseplo and C. W. Taylor.

The major portion of the free acid present in the extraction column feed acts only as a salting agent and subsequently comes out with the raffinate stream. Therefore, a study was conducted to determine the extractability characteristics of a low-free-acid flow sheet using a 33½% TBP, 66½% Amsco 125-90W solvent for high-grade ores with a low nitric-acid-soluble salt content.

This project was initiated as a plant assistance study, since a considerable saving could be made in the main refinery area if good extraction characteristics were obtainable without a large excess of free acid in the initial feed slurry. A lowering of the feed slurry free-acid concentration would also mean that the load on the raffinate calciner and acid absorption tower would be reduced, resulting in a more economical and trouble-free operation. In fact, the raffinate evaporator and calciner could probably be by-passed entirely, since the acid content of the raffinate would be too low for economical recovery.

Since the extraction characteristics of 200 g/l U, $3.0\underline{N}$ HNO_3 feeds are established, the study was limited to a uranium concentration of 200 g/l U and a range of free nitric acid concentrations between $0.25\underline{N}$ and $2.0\underline{N}$. All of the runs were made using a uranyl nitrate tetrahydrate (UNH) feed, except one that was made with a slurry type ore. The runs were made using the Pilot Plant six-inch extraction, scrub, and strip columns under conditions closely simulating Refinery conditions (Table 6.2-1).

Product purity for all of the runs was excellent with respect to contaminants, regardless of acid concentration and F/O/S ratio. Table 6.2-2 gives typical spectrographic results of the final product (CP).

The preliminary conclusions reached on the basis of the runs made so far are:

1. When the feed material is pure UNH or a similar low-impurity feed solution, excellent extraction characteristics are obtainable with as low a free acid concentration as $0.5\underline{N}$ HNO_3 using an F/O/S ratio of 4.5/9/1. Lowering the free acid content to $0.25\underline{N}$ HNO_3 results in raffinate losses, however, indicating that $0.5\underline{N}$ HNO_3 free acid is the lowest feasible concentration consistent with good extraction efficiency.

2. Raising the F/O/S ratio to 4.75/9/1 and keeping the feed solution at 200 g/l U and $0.5\underline{N}$ HNO_3 results in raffinate losses, due to a high uranium scrub reflux.

3. It appears, on the basis of one slurry run, that 200g/l U, $0.5\underline{N}$ HNO_3, and an F/O/S ratio of 4.5/9/1 are the limiting conditions for a slurry type extraction run.

Several more slurry feed runs are contemplated so that the study may be completed and firm conclusions can be reached.

TABLE 6 2-1

LOW-ACID EXTRACTION FLOW SHEET (SOLVENT. 33½% TBP, 66½% AMSCO 125-90W)

RUN NO.*	FEED SLURRY CONCENTRATION (g/l U)	FEED SLURRY CONCENTRATION HNO_3 (N)	F/O/S RATIO	RAFFINATE CONCENTRATION (g/l U)	RAFFINATE CONCENTRATION HNO_3 (N)
289	200	2.0	5/9/1**	14	1.75
290†	200	2.0	5/9/1	16	1.60
291	200	1.5	5/9/1	18	1.30
292	200	1.5	4/9/1	0.002	1.25
293	200	1.1	4/9/1	0.002	0.80
294	200	1.0	4.5/9/1	0.003	0.95
296	200	0.5	4.5/9/1	0.004	0.45
297	200	0.25	4.5/9/1	1.2	0.18
298	200	0.55	4.75/9/1	0.20	0.42
299	200	0.51	4/9/1	0.04	0.46
			4.5/9/1	0.06	0.46
			4.75/9/1	0.4	0.44

* *UNH was used as feed except in Run 299, when a 1 to 1 mixture of black oxide and Anaconda Bluewater ore was used.*

** *The F/O/S ratio was cut to 4/9/1 with the result that the AR loss was reduced to 0.005 g/l. U*

† *This run was made to check Run 289 results*

TABLE 6.2-2

TYPICAL SPECTROCHEMICAL ANALYSIS* OF FINAL PRODUCT (CP)

COMPONENT	ANALYSIS RUNS 289 TO 298**	ANALYSIS RUN 299†	COMPONENT	ANALYSIS RUNS 289 TO 298**	ANALYSIS RUN 299†
Ag	<0.1	<0.1	Mg	<1	<1
Al	<4	<4	Mn	<4	<4
As	<5	<5	Mo	<4	<4
B	<0.2	<0.2	Ni	<2	<2
Bi	<1	<1	P	<20	<20
Cd	<0.2	<0.2	Pb	<1	<1
Co	<2	<2	SiO_2	<20	<20
Cr	<4	<4	Sn	<1	<1
Cu	<1	<1	V	<20	<20
Fe	<4	<4	Zn	<20	<20

* *All values are given in ppm, based on the uranium content*

** *UNH feed*

† *Slurry feed*

6.3 PILOT PLANT STUDY OF SCRUB COLUMN THROUGHPUT RATE - S. Cseplo and C. W. Taylor.

The scrub column capacity limits the amount of uranium processed through the Refinery. A study was initiated to determine what variables would result in the desired 750 to 800 gsfh rate throughput in the Refinery scrub column.

Variables which were investigated included:

1. Temperature of the inlet streams.
2. Composition of the scrub solution.
3. Concentration of acid in the scrub solution.
4. Pulse amplitude and frequency.
5. Use of organic phase continuous or aqueous phase continuous.

An important specification that had to be met at the increased throughput rate was: An acid normality of the final OK liquor (CP stream) of $<0.03\underline{N}$ HNO_3.

Conclusions and Recommendations

The scrub column should be operated with the organic phase continuous when water or a liquid of similar density is to be used as the scrubbing medium. Under these conditions, throughput rates will provide the desired scrub column capacity.

If it is advantageous to run the scrub column with the aqueous phase continuous, the scrubbing medium should have a high density (high uranium concentration) and a low acid concentration.

Whichever phase is made continuous, it is anticipated that the OK liquor produced under the optimum process conditions found in this study will have an acceptable acid concentration and be within tolerances with respect to contaminants.

Equipment and Procedure

Because the former "B" column (scrub column) pulser in the Pilot Plant gave erratic performance, the initial tests were made using "A" column as the scrub column. The physical geometry of both A and B columns was the same, and the "A" column pulser could be adjusted through a wide range of amplitude and frequency. After the installation of a large Milton-Roy pump as the B column pulser, all further scrub tests were made using the normal three-column setup, i.e., A-column for extraction, B-column for scrub and C-column for strip.

Both UNH (uranyl nitrate hexahydrate) and mixed ores were used as feeds, and the O/A scrub ratio was kept at 9/1.

The experimental procedure used for the evaluation program consisted of making a normal extraction-system run and increasing the throughput rate until the scrub column emulsified or flooded. When this occurred, the streams entering the scrub column were heated to 150°F and the pulse conditions (amplitude and frequency) were changed in order to eliminate the emulsion and permit higher throughput rates. After the maximum throughput rate was reached with this procedure, additional tests were made, varying the type and concentration of the scrubbing medium so as to find the maximum throughput rate. Further tests were made to see if acceptable scrubbing performance could be obtained by running the column with organic-continuous or aqueous-continuous and also to see whether the choice of continuous phase had any effect on throughput rates.

Data

Summaries of the experimental runs are compiled in Tables 6.3-1, 6.3-2, and 6.3-3.

With the aqueous phase continuous and water used as the scrubbing medium, the required throughput rate was not attained (Table 6.3-1). High-acid-concentration scrubbing medium was tried, but resulted in an OK liquor acid concentration that was too high (Tables 6.3-1 and 6.3-2). Therefore, a fraction of the OK liquor stream was concentrated to a specific gravity of 1.20 (Run 279) and was used as the scrubbing medium. This resulted in the OK liquor acid concentration being reduced nearly to within specification. Figure 6.3-1 shows how HNO_3 concentration of the OK liquor is related to HNO_3 concentration of the scrub solution.

Runs 282B, 283, 287, and 288 are duplicate runs, performed to verify the results of using recycled OK liquor (spiked with 0.2<u>N</u> HNO_3) as a scrubbing medium. These runs also verified the relationship between scrub solution density and the throughput rate (Fig. 6.3-2).

Runs 284, 285, and 286 were made with the organic phase continuous and with water used as the scrubbing medium. Here, it was possible to operate at 900 gsfh with the likelihood that higher rates would have been possible without flooding or emulsification. The OK liquor HNO_3 concentration ranged from 0.02 to 0.06<u>N</u>, which is only slightly above specifications.

The purity of the OK liquor was determined by spectrographic analysis (Table 6.3-3) and was found to be within specifications.

Summary

1. With the aqueous phase continuous and with water used as the scrub medium, operation at increased temperatures does not increase throughput appreciably.

TABLE 6.3.1

OPERATING CONDITIONS FOR SCRUB COLUMN RUNS

Run* No.	Type of Feed	Organic Solvent Conc. (% TBP)	Scrub Solution Conc.	Specific Gravity	Contin Phase	Pulse Conditions		OK Liquor Acid Conc. (N)	Maximum Throughput Rate (gsfh)
						Freq. (cpm)	Ampli. (in)		
275	UNH	33.5	deionized water	1.00	Aqueous	25	¾	<0.03	550
276	UNH	33.5	60 g/l U Water Solution	1.082	Aqueous	25	¾	<0.03	600
278	UNH	33.5	5N HNO_3	1.160	Aqueous	25	¾	0.26	800**
279	UNH	33.5	143 g/l U 0.5N HNO_3	1.210	Aqueous	25	¾	0.06	900**
281	UNH	33.5	0.2N HNO_3 (150° F)	1.007	Aqueous	25	¾	0.05	600
282A	UNH	33.5	0.2N HNO_3 (150° F)	1.007	Aqueous	25	1	0.05	650
282B	UNH	33.5	100 g/l U 0.2N HNO_3	1.140	Aqueous	25	¾	0.04	700
283	UNH	33.5	100 g/l U 0.2N HNO_3	1.140	Aqueous	25	3/8	0.045	700 750**
284	UNH	33.5	deionized water	1.000	Organic	25	3/8	0.06	900**
285	Anaconda Bluewater, South African Concentrate, and Black Oxide	33.5	deionized water	1.000	Organic	30	5/8	0.03	900**
286	Synthetic Carnotite and Black Oxide	33.5	deionized	1.000	Organic	60	1	0.02	900**
287	Synthetic Carnotite and Black Oxide	33.5	92 g/l U 0.25N HNO_3	1.133	Aqueous	25	½	0.03	700
288	Synthetic Carnotite and Black Oxide	33.5	95 g/l U 0.28N HNO_3	1.138	Aqueous	25	3/8	0.03	700

* *For all runs, the O/A scrub ratio was 9/1*

** *These throughput rates may have been increased if they had not been limited by the "A" column capacity.*

TABLE 6.3-2

AVERAGE ANALYSES* OF THE COLUMN STREAMS

RUN NO.	AF	AX	AR	AP	BP	BR	BS	CP	CR
275	N.A.	N.A.	N.A.	N.A.	102	N.A.	—	8.2	N.A.
	N.A.	N.A.	N.A.	N.A.	0.035	N.A.	Water	0.027	N.A.
276	N.A.	N.A.	N.A.	N.A.	107	100	60	95	N.A.
	N.A.	N.A.	N.A.	N.A.	N.A.	1.50	0.02	0.03	N.A.
278	N.A.	N.A.	N.A.	N.A.	94	18	0	76	0.11
	N.A.	N.A.	N.A.	N.A.	0.31	4.6	5.00	0.26	0.00
279	N.A.	N.A.	N.A.	N.A.	108	21	143	95	0.12
	N.A.	N.A.	N.A.	N.A.	0.07	2.5	0.50	0.06	0.00
281	N.A.	N.A.	N.A.	N.A.	96	110	—	87	0.15
	N.A.	N.A.	N.A.	N.A.	0.05	1.3	0.20	0.05	0.00
282A	N.A.	N.A.	N.A.	N.A.	97	120	—	88	0.20
	N.A.	N.A.	N.A.	N.A.	0.05	1.8	0.20	0.05	0.00
282B	210	0.10	0.004	117	109	158	100	102	0.07
	3.10	0.00	2.7	0.18	0.04	1.30	0.20	0.04	0.00
283	198	0.05	0.02	122	110	200	100	97	0.12
	3.50	0.00	2.8	0.12	0.05	1.0	0.20	0.045	0.00
284	206	0.006	0.002	120	99	190	Water	90	0.10
	2.95	0.00	2.6	0.12	0.10	0.60		0.06	0.00
285	200	0.08	0.02	116	98	194	Water	86	0.05
	3.0	0.01	2.6	0.17	0.04	0.80		0.03	0.00
286	206	0.10	0.004	120	101	200	Water	90	0.01
	3.15	0.00	2.8	0.18	0.04	0.90		0.02	0.00
287	195	0.03	0.004	110	107	140	92	99	0.06
	3.2	0.00	2.8	0.21	0.04	1.50	0.25	0.03	0.01
288	215	0.09	—	114	106	222	95	93	0.05
	3.06	0.00	2.6	0.17	0.12	0.80	0.28	0.03	0.00

***NOTE:** The top figure is g/l U; the bottom figure is HNO_3 normality.*

N.A. - Not available

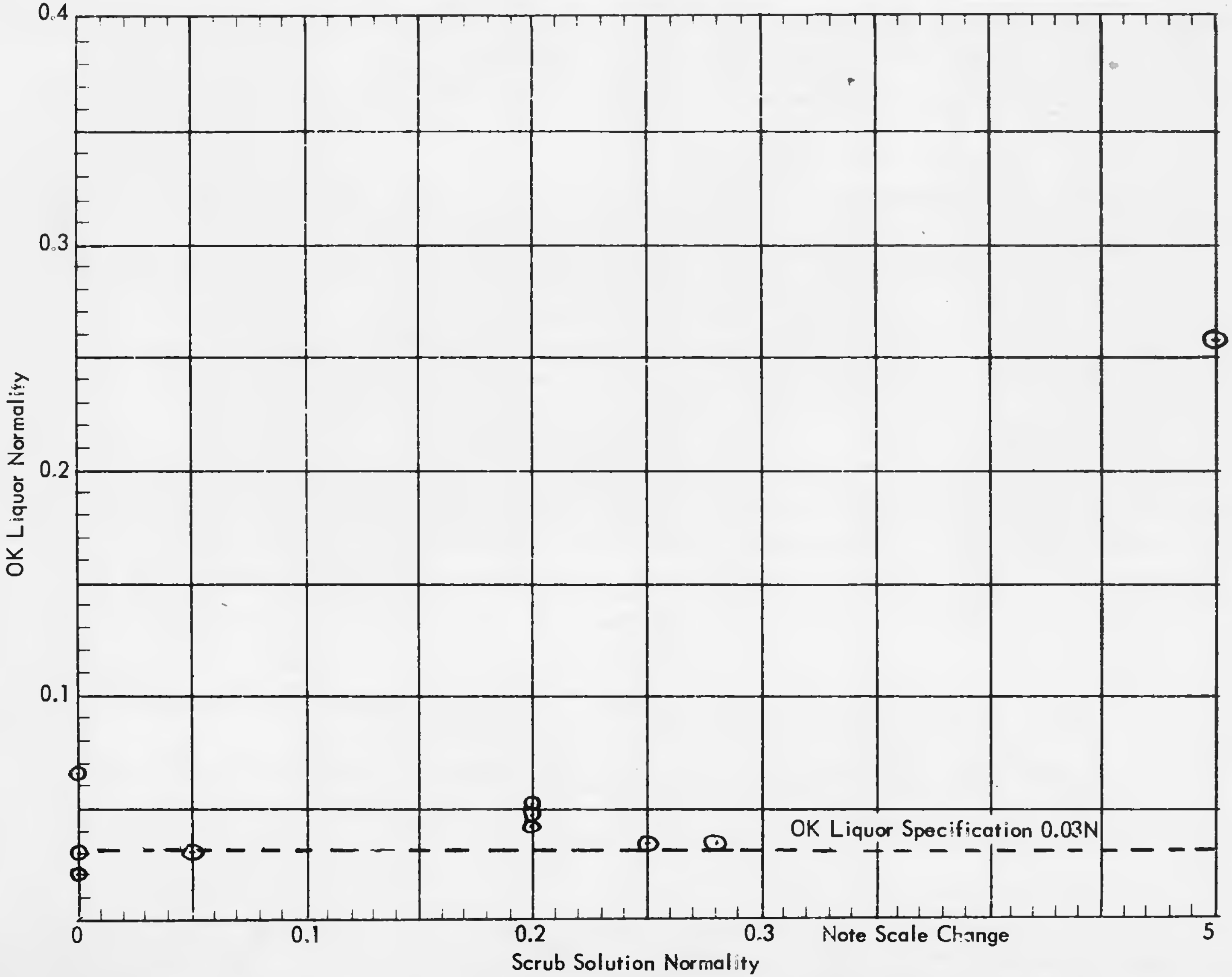

FIGURE 6.3-1 VARIATION OF FINAL OK LIQUOR NORMALITY WITH SCRUB SOLUTION ACID NORMALITY

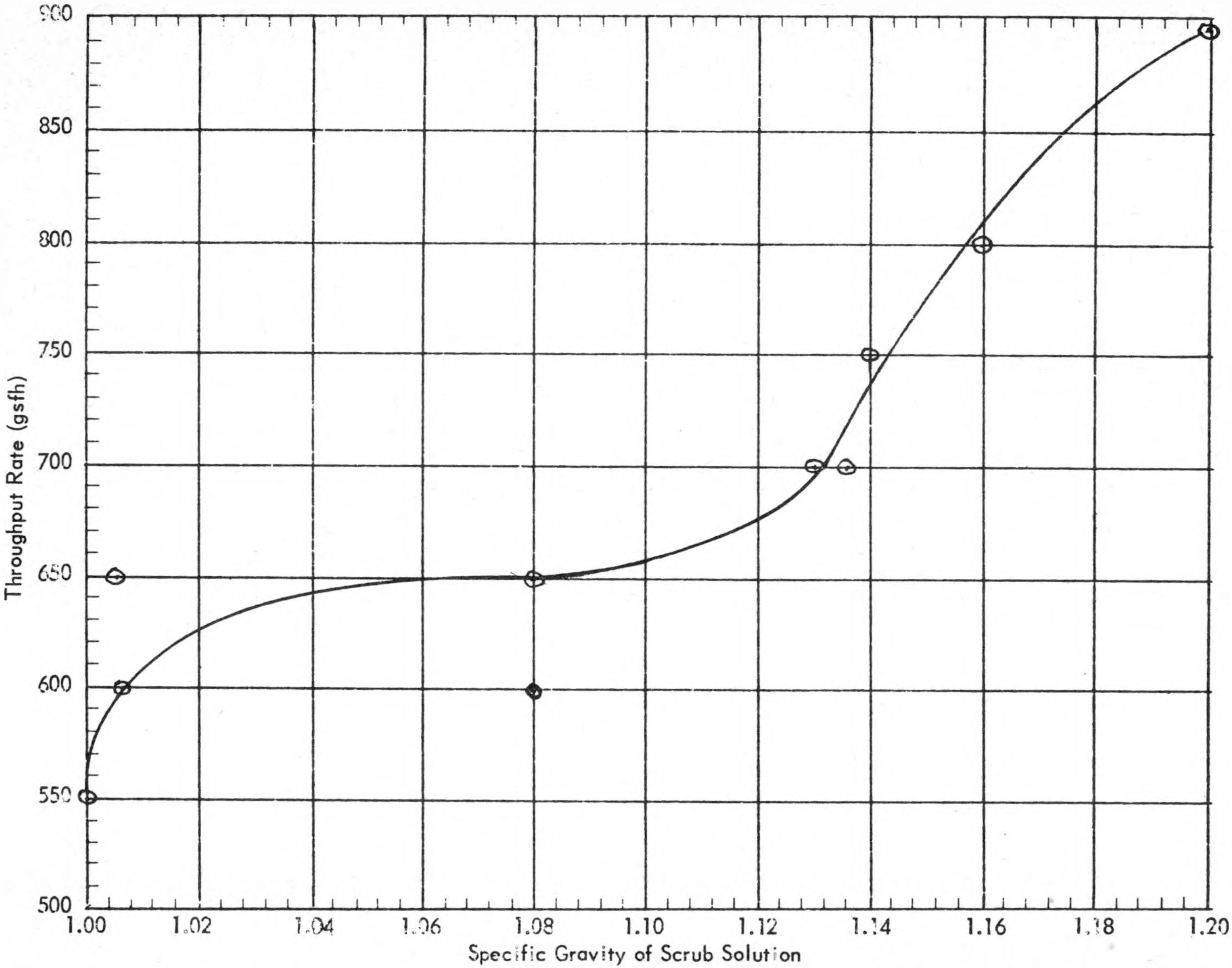

FIGURE 6.3-2 THROUGHPUT RATES VS. SPECIFIC GRAVITY OF THE SCRUB SOLUTION

TABLE 6.3.3

SPECTROGRAPHIC ANALYSIS* OF THE OK LIQUOR (ALL RESULTS GIVEN IN ppm)

COMPONENT	ANALYSIS	COMPONENT	ANALYSIS
Ag	<0.1	Mn	<4
Al	<4	Mo	<4
B	<0.2	Ni	<2
Bi	<1	P	<20
Cd	<0.2	Pb	<1
Co	<2	SiO_2	<20
Cr	<4	Sn	<1
Cu	<1	V	<20
Fe	<4	Zn	<20
Mg	<1		

***** *All analyses for all runs (275, 276, 278, 279, 281, 282, 283, 284, 285, 286, 287, 288) were at the lower limit of analysis except that the Fe analysis was < 5 for Run 285 and the Mg analysis was < 2 for Run 286 and <4 for Run 287.*

2. With the aqueous phase continuous, use of a high-density, low-acid concentration scrubbing medium will result in maximum throughput rates and acceptable acid concentrations of the OK liquor.

3. The optimum pulse conditions in the scrub column were found to be:

    A. <u>Aqueous phase continuous</u>
    Amplitude: ½ inch
    Frequency: 25 cpm

    B. <u>Organic phase continuous</u>
    Amplitude: 1 inch
    Frequency: 60 cpm

4. By running the organic phase continuous rather than the aqueous phase continuous, better results were obtained with respect to acid concentration of the OK liquor. The maximum scrub column throughput rate could not be determined because at 900 gsfh scrub throughput, "A" extraction column facilities were running at maximum capacity.

6.4 CORROSION STUDIES IN THE ORE REFINERY

F. H. Meyer and N. N. Peters

A continuous program for corrosion testing of possible constructional materials for nitric acid concentrator service has been pursued since March of 1954. Previous work has been reported in two previous quarterlies.[1,2] Welding recommendations made in NLCO-565 were adopted by the Mechanical Department and have led to much longer service life of reboiler tubes in the nitric acid

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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. 52-54, NLCO-565, July 15, 1955.*

recovery area. The combination of 304 ELC stainless steel base metal with 308 ELC stainless steel weld rod has proved superior to 347 stainless steel welded with 347 welding rod. The recommended alloys also are being used in new construction in the nitric acid recovery and raffinate areas. Heliarc welding is now used within these areas, rather than tungsten arc welding. Also adopted by the Mechanical Department are the tube sheet designs recommended by Hanford Metallurgical Research Subsection Welding Unit. These are expected to minimize crevice and end grain corrosion.

In-process Evaluation Tests of Materials of Construction In Ore Refinery Starge Tank

To determine rates of corrosion in the boildown area of the Ore Refinery, a rack containing various grades of stainless steel was exposed for one year in a sparge tank. (The sparge tank is constructed of 304 ELC stainless steel with internal steam coils fabricated of 347 stainless steel.) The sparge tank generally was at 245°F and contained 100 per cent uranyl nitrate hexahydrate (UNH).

Table 6.4-1 summarizes the data obtained.

TABLE 6.4-1
AVERAGE RATES OF CORROSION OF STAINLESS STEEL IN 100% UNH AT 245° F (ONE-YEAR EXPOSURE)

STAINLESS STEEL TYPE	CORROSION RATE (mils/yr PENETRATION)
347	0.35
304-ELC	0.23
309	0.35
316	0.54
304	0.26

From the data obtained, it appears that any of the stainless alloys would be excellent for the indicated service. Therefore, the sparge tank should suffer very little corrosion. This assumption has been borne out by the results of Ultrasonic Audigage thickness tests.

7.0 DENITRATION-ACID RECOVERY PROCESS

7.1 DRYING OF RAFFINATE CONCENTRATE IN A DRUM DRYER - A. Whitman, J. F. Blum, and T. J. Collopy

Based upon exploratory work in the NLO laboratory,[1] tests were conducted in the Buflovak laboratory, Buffalo, New York, on drum drying of concentrated raffinate. A laboratory-scale twin-drum dryer (6-inch-diameter by 8-inch-long drums) was used, with 85 psig steam as a source of heat. A dry product was produced that contained 5 to 10 per cent moisture but was granular and essentially free flowing. Free nitric acid and water were removed from the raffinate during drying, but there was essentially no denitration. Some difficulty was encountered with wear of the carbon steel doctor blade (both erosion and corrosion) used for removal of the dried product from the drum. This condition was greatly improved by the substitution of a stillite blade.

The product from the drum dryer tests was calcined in a laboratory-scale indirect-fired rotary kiln at the Bartlett & Snow Company, Cleveland, Ohio. At temperatures ranging from 1200° to 1500°F and kiln retention times of 7 to 12 minutes, a product containing less than 0.05 per cent nitrates was produced. At a temperature of 1200°F and a kiln retention time of 3.8 minutes, a residue containing less than 0.4 per cent nitrate was produced. Some evidence of sintering tendencies was observed at the higher temperatures.

Plans are being made for the installation of a pilot-scale twin-drum dryer-calciner system at NLO for further testing of this process.

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

8.0 URANIUM HEXAFLUORIDE REDUCTION PROCESS

8.1 PILOT PLANT STUDY OF THE EFFECTS OF UO_2F_2 CONTENT ON THE REDUCTION OF UF_6-SOURCE UF_4 - S. L. Reese, W. E. Palmer, and S. O. Samoriga

The UF_4 produced by the reduction of UF_6 with H_2 is characteristically low in uranium compounds other than UF_4. In the metal production plant, the average derby yield from this UF_4 is normally several percentage points lower than that of UF_4 produced from hydrofluorinated UO_2. A recent study(1,2) of the effects of UO_2F_2 in the production-scale reduction of UO_2-source UF_4 provided substantial evidence of increased derby yield when a small quantity of UO_2F_2 is present in the UF_4.

Since it appeared possible to increase derby yields by adding UO_2F_2 to UF_6 source UF_4, a program was initiated. It was necessary first, to develop a method of producing UF_4 containing controlled quantities of UO_2F_2 and second, to evaluate the reduction to metal of such UF_4. The reactor used is described in referenced reports.(3,4)

To evaluate the use of slag liners in the reduction of UF_6 source UF_4, the program was broadened to include the use of both dolomite and slag liners in the reduction pots.

Addition of Water or Air to the UF_6 and H_2 Gas Streams

In early attempts at producing UO_2F_2, water vapor (with N_2 as the carrier) was fed into the top of the reactor and directed toward the UF_6 - H_2 inlet. The reaction mechanism postulated was:

$$UF_6 + 2H_2O \rightarrow UO_2F_2 + 4HF$$

At the inlet temperature of the gases, this reaction evidently proceeded as indicated, since UO_2F_2 scale was observed when water was injected into the premixing chamber where the feed gases enter. Nevertheless, although the water feed was increased during several runs to a maximum of 1600 cc/hr (corresponding to 10 per cent UO_2F_2 content), the UO_2F_2 content of the product was found to be 0.33 per cent or less. The water content of the product was found to be as high as 1.3 per cent. Evidently, UO_2F_2 is not stable at the higher temperatures inside the reactor (about 1500°F). Either UO_2F_2 is not formed initially or, if formed, it is reduced to UO_2 and hydrofluorinated to $UF_4 + H_2O$.

At the high water feed rates, there was fouling of the product dust-collecting system from water carry-over.

In several runs, air was fed in the same manner as water vapor. The reaction was probably the same, except that it was preceded by the reaction of oxygen (present in the air) with hydrogen, giving water.

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1 *Natwick, J.W. and Dunning, D.N., Summary Tech Rpt., pp. 66-73, FMPC-475, October 15, 1954.*

2 *Titmuss, R.J., Summary Tech Rpt., pp. 87-93, NLCO-565, July 15, 1955.*

3 *Spenceley, R.M., Pilot Plant Scale Reduction of Uranium Hexafluoride to Uranium Tetrafluoride, T.C. Runion, ed., FMPC-176, March 30, 1953.*

4 *Heineke, H., Kraus, H.A., and Palmer, W.E., Summary Tech. Rpt., pp. I-72 to I-76, FMPC-404, April 15, 1954.*

Conversion to Metal

As the UF_4 product from water and air feeding was low in UO_2F_2, it was sent to the production plant for conversion to metal. This UF_4 contained some moisture. It is likely that the magnesium in the charge reacted with the moisture, giving a MgO coating on the magnesium, which inhibited initiation of the reaction. It is also likely that there was a greater HF content than usual, as the water probably acted as a carrier for the HF as it passed through the UF_6 reactor. HF would form a MgF_2 coating on the magnesium and would also inhibit initiation of the reaction.

This material reduced quite well and showed an improvement on derby yields. Production personnel reported no evidence of excessive pressure or blowouts from H_2 of H_2O gas when this material was used.

Since water addition would be economical and easy to handle, a test is scheduled, to establish its merits and whether or not it must be fed to the UF_6 reactor or whether addition to the UF_4 would be satisfactory.

Addition of UF_6 to the UF_4

Several runs were made with UF_6 gas fed into the bottom zone (E zone) of the reactor. This method was successful in that the product contained the desired UO_2F_2. The UF_6 contacted the UF_4 over only a three-foot distance of free fall, however, which was not sufficient for complete adsorption. Some UF_6 was carried into the off-gas system.

UF_6 was then added at the end of the product screw conveyor, with excellent results. The equipment consists of a small cylinder of UF_6 maintained in a hot-water bath. The entire setup is placed on a scale and the UF_6 is weighed into the screw conveyor via a steam-traced line. A steam-water mixture is fed into the conveyor cooling mechanism to maintain a conveyor temperature of 180°F. The UF_6 flows through the conveyor toward the off-gas line of the reactor, contacts the UF_4 coming from the reactor and is adsorbed, giving a dark-green UF_4. The contact distance with the UF_4 is slightly over 6 feet (the length of the conveyor). No UF_6 reached the off-gas system at any rate of UF_6 addition used.

The actual conversion of the UF_6 to UO_2F_2 occurs during pulverizing and other handling, when the material is exposed to atmospheric moisture. (If the exposure time during pulverizing, packaging, and blending with magnesium is short, the UF_4 probably contains some free UF_6 when charged to the furnace pot.) UF_4 was produced with UO_2F_2 contents ranging from 0.3 per cent (in the case where no UF_6 was fed to the product) to 3.3 per cent in 0.5 per cent increments.

This apparatus was easy to operate within the limits of the feed rate accuracy. A permanent setup will consist of a steam-traced line from the UF_6 surge tank, which tank will be at constant pressure. This line will flow to a fluorethene flowmeter and into the screw conveyor. A nitrogen purge line and necessary metering valves will also be included.

Conversion to Metal

The material was reduced in standard 14-inch pots. A 7/8-inch-thick liner prepared by the two-mandrel method was used in all Pilot Plant reductions. A 400-pound UF_4 charge and a 4 per cent excess of magnesium were used throughout.

Half of the runs were made with dolomite liners and half with slag liners. At least one run was made at the 1140°F control temperature for each UO_2F_2 level, to show the increase in firing time with increased UO_2F_2 content. (Fig. 8.1-1) The remaining runs were made at 1140°F or higher, to determine optimum reduction conditions. Six runs were made in each type of liner for each lot of UF_4. In addition, several lots were sent to production facilities for reduction evaluation. This latter material was reduced in dolomite liners.

At a constant reduction-furnace control temperature, firing time increased with UO_2F_2 content.

An extremely short firing time is not recommended; if it were used, the necessary heat input would be at a minimum, the reaction would not trigger as well over the entire mass, and the ultimate temperature of the mass would not be sufficiently high to give consistently clean slag-metal separation. Apparently, no detrimental side reactions were experienced with prolonged firing times, since yields were high.

The samples of UF_4 to be analyzed for UO_2F_2 content (Fig. 8.1-2) were exposed to air to permit complete conversion, and although the UF_4 charged to the reduction furnace pot would not be identical to the samples, the samples (having been completely converted in every case) would show more accurately the changes in UO_2F_2 content as related to changes in UF_6 feed.

HF and UF_6 in the Reduction Charge

The quantity of free HF and UF_6 in the UF_4 is certain to vary, depending on the time of exposure to atmosphere and the atmospheric moisture content. This variation should not be detrimental, since the range of UO_2F_2 for optimum reduction conditions is quite wide, being approximately 1 per cent (Fig. 8.1-2). This range permits less exacting feed rates for the addition of UF_6 to the UF_6-source UF_4.

The fumes from the UF_4 were not excessive. Some slight HF evolution was noticed in handling, and a black liner cap was apparent at derby breakout. This evidences some reactive material, probably UF_6, reaching the cap. The fact that residual HF and unreacted UF_6 are present in the UF_4 reduction charge may be beneficial in that they would tend to coat the Mg particles with MgF_2, as well as coating the UF_4 with UO_2F_2. (This should permit the use of lower "UO_2F_2" concentrations.)

Use of Slag Liners

The 7/8-inch-thick slag liner used was not sufficient to withstand the greater heat from the longer firing times. Three pots burned through at the slag-derby interface and derbies produced using slag liners were enlarged as much as 1¼ inches in diameter over the original liner diameter. Figure 8.1-3 shows the increase in derby diameter with increased UO_2F_2 content when slag liner was used. Figures 8.1-4 and 8.1-5 illustrate the effect of liner melting on derby appearance. Seven per cent of the slag liner runs melted through the 7/8-inch-thick liner.

A 1¼-inch liner is recommended as providing adequate insurance against melting through the liner. Since the heat is concentrated in the metal-slag area low in the furnace pot, it is intended to use a liner tapered to a ¾-inch thickness at the top.

Conclusions and Recommendations

(1) Controlled quantities of UO_2F_2 can readily be produced in the UF_4 product by feeding UF_6 vapor into the discharge end of the product screw conveyor in the UF_6 reduction process. Feed rates used are necessarily slightly less than theoretical, since the unit inherently produces some UO_2F_2.

(2) Derby yields increase with the addition of small percentages of UO_2F_2 to the UF_4. Figures 8.1-3 and 8.1-6 show the improved appearance of derbies with UO_2F_2 in the UF_4. UF_6 addition to the green salt product should be incorporated into the UF_6 to UF_4 process to produce a UO_2F_2 content of 1.5 ± 0.3 per cent.

(3) Slag liner is satisfactory as a liner material in the reduction of UF_6-source UF_4 to metal. The 14-inch-furnace-pot side liner should be 1¼ inches thick at the bottom and should taper to a ¾-inch thickness at the top.

(4) The reduction furnace control temperature should be approximately 1180°F for UF_4 containing 1.5 per cent UO_2F_2.

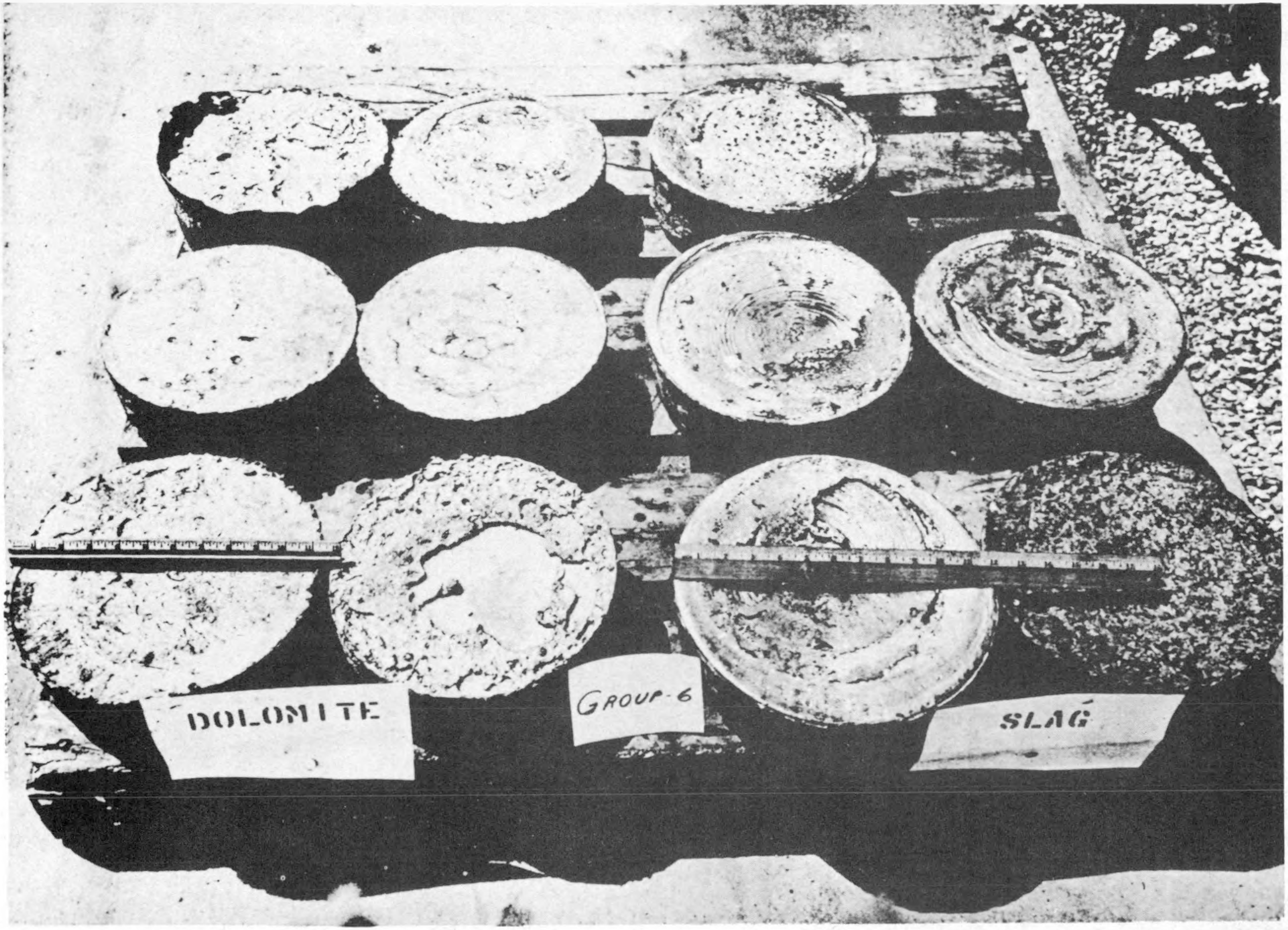

FIGURE 8.1-3 DERBIES FROM UF_4 CONTAINING 2.5% UO_2F_2

FIGURE 8.1-4 SLAG LINER DERBY SHOWING FLOW LINES OF MELTED LINER

FIGURE 8.1-5 DERBY FROM DOLOMITE LINER, SHOWING NO EVIDENCE OF LINER FLOW

UNCLASSIFIED

FIGURE 8.1-6 DERBIES FROM UF_4 CONTAINING 0.5% UO_2F_2

8.2 PILOT PLANT STUDY OF MATERIALS OF CONSTRUCTION FOR THE UF_6 REDUCTION REACTOR - S. L. Reese and W. E. Palmer.

A study is in progress to compare Inconel with Monel as a material of construction for the UF_6 reduction reactor. Compared were operating characteristics, product contamination and corrosion and fatigue of reactors made of each material. These reactors are continuously exposed to temperatures of 1300°F and above, being controlled at 1300°F in the upper four to six feet with the temperature decreasing to 800°F at the bottom.

Monel Reactors

Until this study was begun, all of the reactors used for the hydrogen reduction of UF_6 to UF_4 were fabricated from Monel. Monel, composed of 67% Ni, 30% Cu, and 1.4% Fe, is recommended for operation at 1000°F and is stated to be suitable for some operations up to 1500°F.[1] The Monel reactors were fabricated from standard 10-inch pipe with a 0.375 inch wall.

Inconel Reactor

An Inconel reduction reactor was fabricated and put into service. (Inconel, composed of 80% Ni, 14% chromium and 1.4% iron, is generally recommended for temperatures in excess of 1500°F.)[2] This reactor consists of a 10-inch ID pipe, 17 feet long and with a wall thickness of 0.5 inch. It is enclosed in resistance heaters. It also has facilities for air-cooling the outside walls. The reactor is flanged at both ends, with a product hopper at the bottom and with the reaction gases entering at the top. It has been on stream intermittently for 443 hours and has been subjected to varied experimental operating conditions.

Operating Characteristics

The larger mass of the Inconel tube (0.5-inch wall thickness versus 0.375 inch for the Monel tube) necessitated a control temperature increase of 100° to 150°F over that used in the Monel tube.

Product Contamination

As shown in Table 8.2-1, product contamination in Monel reactors is considerably less than that in Inconel reactors, and so Monel is recommended where product specifications limit the nickel and chromium content. Nevertheless, nickel contamination in excess of 200 ppm and copper in excess of 65 ppm have, on occasion, appeared in the product from the Monel reactors (especially in product from de-slagging operations).

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[1] *Lyman, T., "Metals Handbook", p. 1049, A.S.M., Cleveland, 1948.*

[2] *ibid., p. 1057.*

TABLE 8.2-1

OPERATING DATA - INCONEL AND MONEL REACTORS IN THE PILOT PLANT

Reactor Material	Time on Stream (hr)	UF Produced (tons)	Original Wall Thickness (in.)	Final Wall Thickness (in.)	Corrosion Rate (in./ton of product)	Average Impurity Concentration (ppm) Ni	Cu	Cr	Fe
Monel	2200	398	0.37	0.12	0.0006	40	20	4	5-10
Monel	2400	408	0.37	0.06	0.0008	32	24	4	5-10
Inconel	443	53	0.50	0.43	0.0013	>200	–	>40	15

Reactor Fatigue and Corrosion

After long use, the Monel reactors showed fatigue in the form of extensive bulges. The Monel reactors were then supported at their tops by the use of counterweights, which reduced physical deformation.

Since the Inconel reactor is comparatively new, the effect of fatigue deformation on its life is not yet known. It was noted, however, that a slight concavity has appeared along the weld seam in the upper zone of the Inconel reactor.

Corrosion, accompanied by weld cracks, occurred in the reaction zone of the Monel reactor and was the main cause of reactor failure. The thickness of small areas of the wall was reduced to as little as 1/16 inch. In addition, considerable external corrosion and scaling occurred on the Monel reactor (Fig. 8.2-1). In one instance, sufficient scale flaked off to cause a short circuit in the external heaters.

The internal corrosion rate for Inconel is twice that for Monel (Table 8.2-1), but oxidation of the outer surface of Inconel reactors is negligible at the temperatures used. Nevertheless, the life of the Monel reactor should be considerably longer because of the high rate of internal corrosion of the Inconel reactor.

Conclusions and Recommendations

The preponderance of data indicates a decided advantage in the use of Monel as a UF_6 reduction reactor material.

It is recommended that a non-oxidizing external atmosphere be provided to reduce external corrosion of Monel reactors.

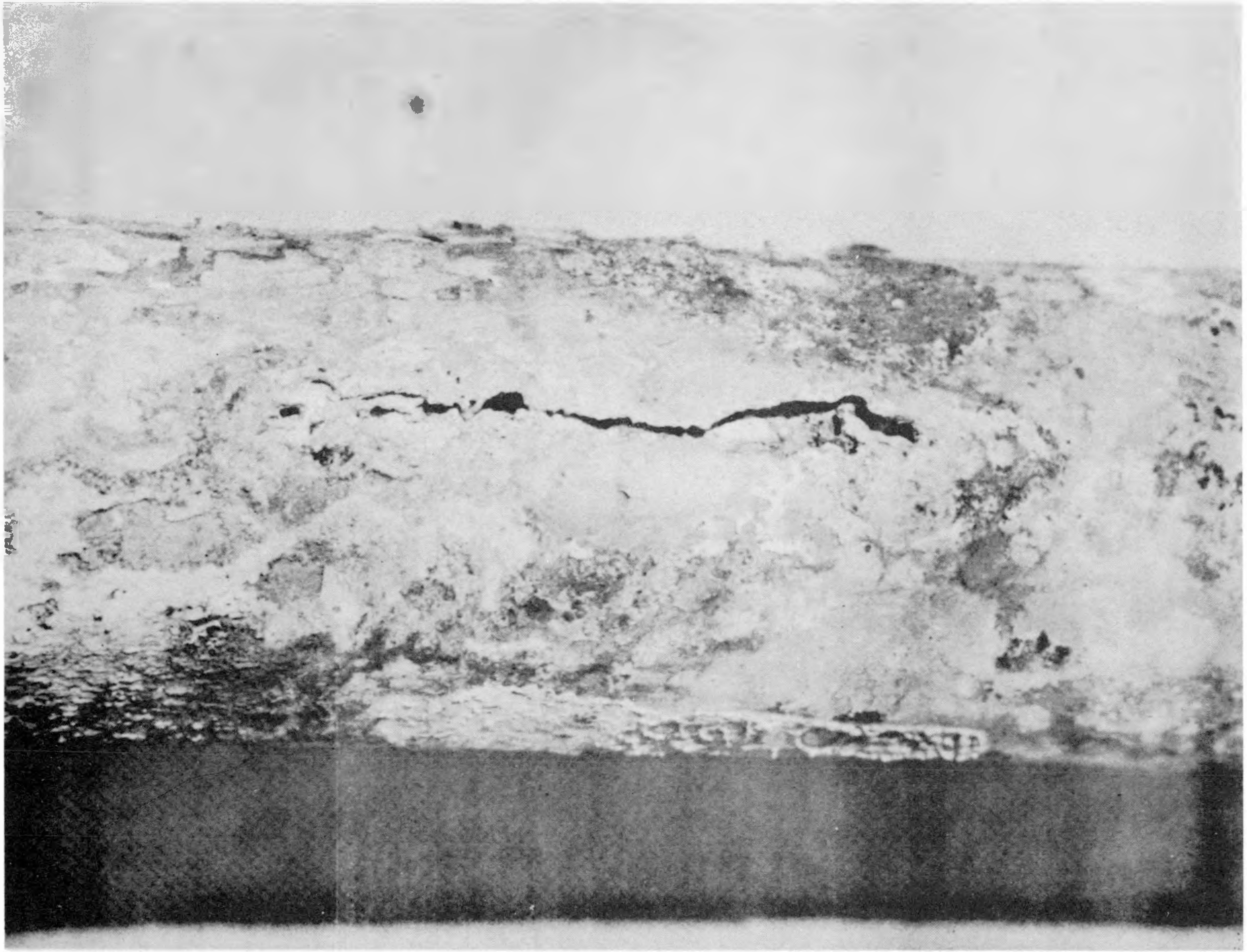

FIGURE 8.2-1 CORROSION OF A MONEL REACTOR. NOTE FISSURE.

9.0 GREEN SALT PROCESS

9.1 PLANT MODIFICATIONS FOR HIGHER PRODUCTION CAPACITY IN THE UO_3 TO UF_4 PROCESS - W. Burkhardt, R. L. Maddox, E. W. Mautz, and J. Schonberger

A bank of reactors in the Green Salt Plant has been devoted to the experimental development of optimum conditions for using activated feeds in the plant. Equipment modifications have been made in order to reduce operational difficulties such as reactor plugs, corrosion, and loss of powder-gas seals when operating at high feed rates. Changes which have been made include:

1. Installation of a new design seal hopper with a built-in bridge breaker and level indicator between the reduction and hydrofluorination reactors
2. Installation of a cyclone separator in the off-gas line from the hydrofluorination reactor
3. Incorporation of a recycle system to return the cyclone product to the first hydrofluorination reactor
4. Alteration of the feed weighing system to provide better control of the UO_3 feed rate to the reduction reactor
5. Use of a Republic Flow Meters Company differential pressure transmitter (instead of the present unit) across the Adams carbon tube filter in the hydrofluorination off-gas system for better pressure measurement.

In addition to these changes, provisions are being made to measure gas flow rates and gas and internal reactor temperatures more accurately than has been possible in the past.

Operation of this bank of reactors has been on a shakedown basis to date. However a number of items of importance have been observed. These are:

1. Performance of the new design seal hopper has been satisfactory and has maintained a powder seal at gas pressures higher than those normally encountered in plant operation.
2. Use of the cyclone has significantly minimized the number of times it is necessary to discharge accumulated powder from the Adams carbon tube filter. This has resulted in a more uniform product from the first hydrofluorination reactor by avoiding interruption of reactor operation.
3. The revised feed weighing system has been demonstrated to be a considerable improvement over the existing production installation.

Evaluation of equipment changes is being continued. Normal plant orange oxide is being used, to provide a basis of comparison for operation with activated feeds.

Detailed process studies will be made in the experimental reactor bank in order to provide a better basic understanding of the reduction and hydrofluorination processes. From these, means of reactor and reaction control will be developed to accommodate the high feed rates expected with activated feeds.

9.2 THERMAL DENSIFICATION OF GREEN SALT - W. Burkhardt, R. L. Maddox, B. C. Doumas, and T. F. Rupert

Following previous sintering tests,[1] a one-ton lot of normal green salt produced in the NLO Green Salt Plant was sintered batch-wise in electrically heated muffle furnaces at Y-12, Oak Ridge. Roughly 20-pound batches of the material were charged in Hastelloy C boats, with a bed depth ranging up to about two inches. After charging, the furnace was heated as rapidly as possible until the muffle wall temperature reached approximately 950°F. This required approximately six hours. The furnace was then air-cooled externally to about 200°F. (This required about two hours.) Except for initial and final nitrogen purges, an anhydrous hydrogen fluoride atmosphere was maintained during the cycle. Excessive corrosion of the boats and the muffles occurred, resulting in contamination of the product green salt.

The sintered green salt was crushed in a jaw crusher and pulverized in a Denver grinder in the NLO laboratory to achieve high bulk densities. Screen analyses, bulk densities, and tap densities of various cans of this lot of sintered, crushed and pulverized green salt are presented in Table 9.2-1. Sieve data for the sample from the control lot (that is, the material prior to sintering) are also included, as is data on one of the cans of magnesium used in the reduction of the sintered green salt.

The sintered and pulverized green salt and the control lot of green salt were reduced to metal in the NLO Pilot Plant (Section 11.2 of this report). The charge weight of green salt-magnesium mixture was increased approximately 9 per cent by virtue of the densification.

This test has demonstrated the ability of the sintering technique to produce a green salt of density equal to or greater than that now used in uranium production. This will permit a realistic investigation of various green salt activation techniques that have previously been found to produce an excessively low-density green salt.

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[1] *Maddox, R. L. and Burkhardt, W., Summary Tech. Rpt., p. 72, FMPC-540, April 15, 1955*

TABLE 9.2-1

PARTICLE SIZE AND DENSITY OF GREEN SALT

Drums 1-15:	Densified green salt (sintered, crushed and pulverized).
Drum 16:	Control lot (from NLO production before sintering)
Drum 17:	Grab sample from NLO production
Drum 18:	Green salt produced by hydrogen reduction of UF_6
Drum 19:	Pulverized green salt prill
Drum 20:	Prilled green salt
Drum 21:	Grab sample of magnesium used for reduction

DRUM	PARTICLE SIZE: U.S. MESH NO. (CUMULATIVE%)						BULK DENSITY	TAP DENSITY
NO.	+12m	+20m	+40m	+60m	+100m	+325m	(g/cc)	(g/cc)
1.	0.56	4.44	14.95	29.85	48.51	85.50	3.21	4.45
2.	0.12	3.81	15.74	31.60	48.87	89.31	3.40	4.54
3.	0.08	3.80	16.95	32.22	49.77	97.49	3.35	4.50
4.	0.08	3.24	14.67	31.44	53.47	98.06	3.23	4.42
9.	0.08	3.93	16.51	31.83	48.41	91.19	3.40	4.47
10.	0.07	3.31	13.98	26.02	38.85	75.62	3.45	4.61
11.	0.13	3.48	14.19	27.64	41.98	84.29	3.25	4.37
13.	0.17	3.96	15.32	29.96	46.24	93.67	3.41	4.51
14.	0.07	3.14	13.52	27.70	51.68	94.44	3.20	4.33
15.	3.43	12.70	27.22	37.70	48.08	73.58	3.48	4.47
16.	----	0.17	1.50	4.65	9.29	24.36	2.54	3.53
17	----	----	2.46	6.52	13.29	96.05	2.46	3.51
18.	----	0.73	2.54	4.72	19.84	93.36	2.96	4.35
19.	----	----	4.67	23.90	49.59	82.97	3.74	4.92
20	53.27	92.97	98.89	99.51	99.75	-----	3.80	4.32
21.	13.47	72.39	97.64	98.99	99.66	100.	0.74	0.88

10.0 MOVING BED REACTOR (MBR)

10.1 PELLETING, REDUCTION RUNS 25, 26, AND 27, AND HYDROFLUORINATION RUN 28 (SEE ALSO SECTION 10.2 OF THIS REPORT) - W. Burkhardt, P. W. Henline, A. J. Klee, D. J. Loudin, H. F. Muhlhauser, R. H. Sisson, D. C. Stephan, and F. M. Teetzel

During the past quarter, efforts have been concentrated on developing techniques and equipment for sustained steady-state production of uniform, high-quality UO_2. During this period, reduction reactor product that assayed less than 95 per cent UO_2 was considered unsatisfactory for hydrofluorination tests and was scrapped as UO_2. From the results of each reduction reactor test run, modifications of reactor equipment and procedural techniques were devised, applied, and then evaluated in the succeeding test run.

Attention was also devoted to the development of more suitable pelleting techniques (reactor feed fabrication) and to correlation of laboratory and reactor process data.

Pelleting[1,2]

Revision of the pellet casting technique resulted in the production of 100 pounds of pellets per hour on a 12-inch-wide belt. These pellets had an appreciably lower water content (5 to 7% compared to 12%) than those produced by previous casting and seemed to be less reactive. The revisions consisted of (1) using a belt with shallower holes (3/16 inch compared to 3/8 inch) but of the same diameter and (2) substituting a direct hot air stream over the belt for the steam chest formerly used for heating (drying and setting) the pellets.

A new type of casting belt, which uses a larger portion of the belt surface for pellet formation, has been ordered and is scheduled for delivery early in October.

A newly tested method for handling fast-setting orange oxide paste involves discharging the paste directly onto the Proctor and Schwartz dryer (without extrusion) and then milling the hard "clumps" after a 24 hour cure. This procedure has been termed "clump pelleting" and has yielded a reactor feed (+6 mesh) fraction of about 50 per cent, based on the weight of the starting material. Such a method can be used for preparing aggregate from a feed which has rapid setting characteristics, but the method is handicapped by the low yield.

The most encouraging pelleting development thus far has been a successful batch-mix continuous-extrusion using small amounts (2 to 7%) of ammonia in the orange oxide-water paste. The quantity of ammonium hydroxide added is varied with temperature changes to give a continuous "sandy" consistency to the paste about to be extruded. The pellet yields have been approximately 65 per cent, based on the weight of starting material.

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[1] *Burkhardt, W., et al., Summary Tech. Rpt. pp. 50-53, FMPC-540, April 15, 1955.*

[2] *Burkhardt, W., et al., Summary Tech. Rpt., pp. 80-82, NLCO 565, July 15, 1955.*

To date, pellet preparation by both extrusion and casting has utilized batch mixing of the orange oxide and water, as efforts to mix the orange oxide and water in the pug mill section of the Bonnot extruder have been unsuccessful. Since batch mixing requires excessive manpower, work has been initiated on the development of suitable equipment and procedures for continuous mixing of the orange oxide-water paste as a separate operation.

Reduction Run 25 (Using Sulfated Casting Belt Pellets)

Since the previous reduction operation (Run 23) had indicated that the use of steam in the feed gas moderated reaction temperatures and reduced gas channeling,[7] steam was employed in Run 25 to substantiate the data obtained in Run 23.

The objective of Run 25 were:

1. To determine the ease of reaction temperature control when a steam-dissociated ammonia(DA) mixture was fed to the bottom of the reactor.

2. To reduce gas channeling by the use of steam in the inlet DA stream (by increasing the turbulence of gas flow in the reactor bed).

To parallel the conditions used in Run 23, casting belt pellets made from sulfated UO_3 were air-dehydrated and then reduced. A solids feed rate of 400 pounds per hour and a gas rate of 30 per cent excess hydrogen were specified. Approximately 80 pounds per hour of steam was introduced with the inlet DA.

The results of the run were:

1. Reaction temperature control was erratic, and temperatures often exceeded the specified limits of 1400°F.

2. Gas channeling was not appreciably reduced from that noted in previous reduction operations.

3. Inability to control the reaction satisfactorily resulted in nonuniform reactor conditions, and the average product assayed less than 90 per cent UO_2.

4. Product assay was not improved by a second pass through the reactor at 600°F; therefore, the product was scrapped.

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[7] *Burkhardt, W., et al., Summary Tech. Rpt., p. 82, NLCO-565, July 15, 1955.*

Reduction Run 26 (Using Nonsulfated Pellets)

Starting with Run 26, bed temperatures and pellet compositions were measured across several diameters within the reduction reactor. The radial temperature gradients were obtained with multiple bare thermocouples. Solids composition gradients were obtained from samples taken with a sampling probe. This probe may be inserted in any one of the six sampling ports.

The objectives of Run 26 were:

1. To obtain quantitative data on gas channeling and radial temperature gradients by the use of the newly installed sampling ports and thermocouples.

2. To compare extruded and casting-belt pellets from the standpoint of reduction reactivity.

3. To determine the effect of nonsulfated feed on reactor control and operation.

Extruded and casting-belt pellets made from the same lot of nonsulfated UO_3 were blended together and air-dehydrated at 570°F to 700°F.

For reduction, the solids feed rate was approximately 400 pounds per hour with a gas (DA) rate of 10 to 20 per cent excess hydrogen. Fifty to one hundred pounds per hour of steam was fed to the reactor with the DA.

The run lasted 22 hours; with an over all product assay of less than 90 per cent UO_2. Yellow, unreacted pellets were found in the product throughout the run, and as a result the product was scrapped.

The results of this test led to the following conclusions:

1. The thermal and composition gradient data definitely showed the existence of large variations in temperature and pellet composition from the center of the reactor to the reactor walls.

2. The use of nonsulfated feed hindered reaction control.

3. Due to the poor conversion of both extruded and cast pellets, no conclusion as to their relative reactivities could be drawn.

Reduction Run 27 (Using Sulfated Pellets)

A new DA feed gas distributor was installed in the reduction reactor to reduce the tendency toward gas channeling indicated by the results of Run 26. In addition, the sampling system was modified to permit (1) the sampling of pellets closer to the reactor walls and (2) obtaining gas samples.

The objectives of Run 27 were:

1. To determine the effect of the newly installed gas distributor on reactor operation.

2. To explore the effect of higher solids and gas flow rates on gas channeling.

The "clump" and the ammonia treated pellets made with sulfated UO_3 were air-dehydrated at 570°F to 750°F and were fed separately to the reactor. An average solids feed rate of 555 pounds per hour was used during reduction operations, with a DA gas rate of 30 per cent excess hydrogen.

Initially, a DA-steam feed mixture was introduced at the bottom of the column. However, reaction control was erratic and unconverted pellets were found in the product samples. Therefore, the gas feed was changed to undiluted DA and after several hours of operation high quality UO_2 was being produced and reaction control was improved. The reaction zones occurred at different levels in the sectors of the reactor monitored by the three thermocouple banks, as had occurred in previous reduction runs. During a period of 27 hours of operation with undiluted DA, hourly product assays averaged 97.6 per cent UO_2.

The following results were achieved in this test:

1. A period of sustained steady-state operation was achieved in which the product assay was superior to that obtained in any recent reduction run.

2. The use of the new gas distributor, higher solids feed rates, and undiluted DA appreciably enhanced reaction control and product quality.

3. Additional development work on the reduction reactor is needed in order to facilitate reactor control. Very close manual control was needed in this test.

4. No difference in reactor performance or product quality was observed between "clump" pellet and ammonia-inhibited pellet feeds.

Hydrofluorination Run 28

Since the last hydrofluorination run, the reactor system has been modified to provide a feed of anhydrous HF to the reactor at temperatures in excess of 1000°F. For better heat transfer, the HF heating tank has been replaced with one containing baffle plates. The line leading from the tank to the reactor has been wired for electrical heating to minimize heat losses

The manifold system on the reactor has been changed so that cold HF can be used for cooling the various reaction zones. Such cooling should permit reactor operation within the range of maximum conversion rates indicated by data developed by the New Brunswick Laboratory.

The purpose of Run 28 was to determine the operability of the reactor system when using HF at 1000°F or more at the bottom of the reactor and cold HF for temperature control. The run had just been started when the HF heating tank failed. Therefore, the run has been postponed until necessary repairs are completed (estimated to be the first week of October).

Conclusions and Recommendations

A successful technique has been developed for sustained steady-state reduction reactor operation, using sulfated feed and separate dehydration and reduction. High grade UO_2 has been produced by the use of this technique.

Additional work is needed in order to develop reactor control procedures and detailed data for reactor design which would be satisfactory for routine production operation.

Hydrofluorination of the high-grade UO_2 produced in the latest reduction reactor operation has been delayed by failure of the HF heater. Following the hydrofluorination of this lot of high-grade UO_2 pellets, an intensive program will be conducted to develop a practical and economical method of reactor feed fabrication (pelleting).

10.2 THERMAL BALANCE INVESTIGATION OF REACTION RATES DURING REDUCTION AND HYDROFLUORINATION OF PELLETIZED MATERIALS FROM MBR RUNS 25, 26, AND 27 - J. W. Votaw, G. G. Briggs, D. E. Richards, R. C. Abbott, and J. D. Drew

During the past quarter, the laboratory thermal balance[1] has been used to determine the reactivity of pelletized material which had been prepared for MBR Runs 25, 26, and 27. These studies included not only the original hydrated feeds prepared for these runs, but also pellets dehydrated in the MBR and samples of the UO_2 produced in the MBR. In addition, pellets which had been prepared experimentally in the plant and in the laboratory (see Section 10.1 of this report) were studied in order to evaluate different pelleting techniques when applied to the same lots of UO_3 powder. Types of hydrated UO_3 pellets investigated with the thermal balance included:

1. Casting-belt pellets prepared in the plant.

2. Extruded pellets prepared in the plant.

3. Screened clumps prepared in the plant by (a) mixing the paste in the pug mill section of the extrusion machine, (b) discharging the paste as large lumps into the Proctor and Schwartz dryer, (c) milling to break up the hydrated lumps, and (d) screening to remove oversize and fines.

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[1] *Briggs, G. G., Votaw, J. W., and Richards, D. E., Summary Tech. Rpt., p. 83, NLCO-565, July 15, 1955*

4. Spherical pellets prepared experimentally in the plant in a rotating drum.

5. Cubical pellets prepared in the laboratory by cutting up a ¼-inch-thick layer of the UO_3-water paste as it set.

The plant-produced casting-belt pellets, extruded pellets, and screened clumps constituted feed for the MBR runs. The cubical pellets were included because these can be prepared conveniently in the laboratory under more reproducible conditions (particularly with respect to water content); it is assumed, therefore, that their reactivities (time rates of reduction and hydrofluorination) best reflect differences caused by using different lots of UO_3 powder.

Procedure

Hydrated UO_3 pellets were dehydrated overnight in the laboratory oven at approximately 750°F. These were then suspended in the reaction chamber of the thermal balance, which had been preheated to 1200°F. Reduction with hydrogen was then completed at the setting of 1200°F. After the temperature was lowered to 1100°F, the pellets were hydrofluorinated until the reaction either was essentially complete (97 to 98%) or had been continued for 90 minutes. The observed weight loss or gain, expressed as a percentage of the calculated total weight loss or gain was plotted against time. The curves obtained were compared with similar curves for the reaction of standard cubical pellets prepared in the laboratory from a Mallinckrodt UO_3. To present the data in tabular form, the "hydrofluorination time ratio" was calculated at several conversion levels. More specifically, this is the ratio of the time required for hydrofluorinating the sample to a given per cent conversion to the time required for the standard to reach the same per cent conversion. Tables 10.2-1, 10.2-2, and 10.2-3 present the data for the three MBR runs. At the time of writing, analysis of the pellets from Run 27 was not complete.

Summary of Results

1. Large differences in reactivity were associated with the UO_3 powders from which the pellets were prepared. However, if each MBR run is considered alone, the reactivities of the hydrated feeds prepared from at least two lots of UO_3 for that run did not differ greatly. The large variations were between powders used in different MBR runs.

2. Sulfated feeds were employed in MBR Runs 25 and 27, whereas the feed for Run 26 was not sulfated. In general, the sulfated lots of UO_3 produced the more reactive feeds, as had been expected. The best evidence of this fact was the laboratory measurements of reactivity for the feeds of MBR Run 25 and for the cubical pellets prepared from lots of UO_3 used in Runs 26 and 27.

3. The thermal balance results for MBR Runs 25 and 27 indicate that the reactivities of sulfated feeds can vary greatly.

TABLE 10.2-1

LABORATORY HYDROFLUORINATION OF PELLETS PREPARED FOR RUN 25

SAMPLE*	HYDROFLUORINATION TIME RATIO** AT INDICATED CONVERSION LEVEL						DEHYDRATION WEIGHT LOSS (%)	ANALYSIS OF HYDROFLUORINATED PELLETS (%)		
	60%	70%	80%	90%	95%	97%		UF_4	UO_2	UO_2F_2
A. UO_3 Lot 3E-16-389 (PE 99013) Dehydrated in Laboratory	0.71	0.69	0.70	0.70	0.74	0.77	13.35	99.0	0.4	0.6
B. UO_3 Lot 3E-16-389 (PE 99013) Dehydrated in MBR	0.67	0.64	0.62	0.60	0.58	0.64		99.0	0.5	0.5
C. UO_3 Lot 3E-16-393 (PE 99015) Dehydrated in Laboratory	0.60	0.55	0.52	0.46	0.44	0.47	13.84	98.8	0.3	0.9
D. UO_3 Lot 3E-16-393 (PE 99015) Dehydrated in MBR	0.74	0.69	0.63	0.57	0.51	0.51		99.7	0.2	0.1
E. Hand-Picked Yellow Pellets. Not redehydrated†	0.67	0.63	0.61	0.51	0.55	0.63		98.1	0.9	1.0
F. Hand-Picked Yellow Pellets. Redehydrated in Laboratory†	0.64	0.61	0.59	0.56	0.55	0.57	2.83	99.3	0.5	0.2
G. Hand-Picked UO_2 Pellets from MBR Reduction Step	0.87	0.88	1.01	1.34	2.06	3.25		97.3	1.6	1.1

* *All pellets were prepared in the plant from sulfated UO_3 by the casting-belt technique*

** *Ratio* = $\dfrac{\textit{Time required for hydrofluorination of sample to indicated per cent conversion.}}{\textit{Time required for hydrofluorination of standard to indicated per cent conversion.}}$

† *Pellets consisting essentially of UO_3 which had passed through the reduction reactor of MBR without being reacted. These were scattered throughout the product.*

TABLE 10.2-2

HYDROFLUORINATION OF FEED AND EXPERIMENTAL PELLETS (RUN 26)

SAMPLE*	HYDROFLUORINATION TIME RATIO** AT INDICATED CONVERSION LEVELS						DEHYDRATION WEIGHT LOSS (%)	ANALYSES OF HYDROFLUORINATED PELLETS (%)		
	60%	70%	80%	90%	95%	97%		UF_4	UO_2	UO_2F_2
A. UO_3 Lot 3E-16-556 (PE 99016) Dehydrated in Laboratory.										
1. Casting-belt	0.95	1.04	1.16	1.52	2.38	–	6.48	98.3	1.5	0.2
2. Casting-belt	0.70	0.76	0.81	0.91	1.07	1.23	10.5	98.8	0.7	0.5
3. Extruded	1.05	1.08	1.13	1.18	1.63	–	5.72	97.8	1.9	0.3
4. Rotary Drum	2.30	2.56	3.00	–	–	–	8.54	90.7	9.1	0.2
5. Cubical†	1.05	1.08	1.16	1.34	1.57	1.85	11.24	98.9	0.8	0.3
B. UO_3 Lot 3E-16-556 (PE 99016) Dehydrated in MBR										
1. Casting-belt	1.20	1.36	1.91	3.57	–	–	–	–	–	–
2. Extruded	1.70	2.00	2.75	–	–	–	–	86.6	12.1	1.3
C. UO_3 Lot 3E-16-555 (PE 99017) Dehydrated in Laboratory										
1. Casting-belt	0.80	0.84	0.97	1.57	–	–	5.6	95.0	4.9	0.1
2. Extruded	1.10	1.16	1.16	1.25	1.95	–	5.6	96.9	2.9	0.2
3. Cubical†	1.20	1.24	1.28	1.39	1.70	2.06	10.5	98.7	0.9	0.4
D. UO_3 Lot 3E-16-555 (PE 99017) Dehydrated in MBR										
1. Casting-belt††	2.65	3.00	3.56	–	–	–	–	–	–	–
2. Casting-belt‡	1.44	1.57	1.88	3.51	–	–	–	93.5	6.1	0.4
3. Extruded	1.05	1.36	2.41	–	–	–	–	87.2	12.5	0.3
Standard MCW Pellet Dehydrated in Laboratory‡‡	0.80	0.84	0.81	0.75	0.71	0.72	10.71	–	–	–
E. UO_2 Produced in MBR										
1. Casting-belt	1.70	2.20	3.13	–	–	–		88.9	10.8	0.3
2. Extruded	1.45	1.72	2.38	–	–	–		92.0	7.7	0.3

* *All lots of UO_3 were unsulfated.*

** $\text{Ratio} = \dfrac{\text{Time required for hydrofluorination of sample to indicated per cent conversion.}}{\text{Time required for hydrofluorination of standard to indicated per cent conversion.}}$

† *Both samples of cubical pellets were prepared in the same manner as standard cubical pellets.*

†† *This run was made shortly before the HF cylinder emptied. The reaction was slowed by dilution of HF with water vapor. The indicated ratios are erroneously high.*

‡ *Casting-belt and standard pellets were rerun using a newly installed HF cylinder. The time ratios calculated used these new data for the standard.*

‡‡ *Rerun of the standard after a full HF cylinder was installed. The time ratios were calculated, using the data for the previous standard as the denominator. Data indicated that the new HF contained less water vapor.*

TABLE 10.2-3

LABORATORY HYDROFLUORINATION* OF EXPERIMENTAL AND FEED PELLETS (RUN 27)

SAMPLE**	HYDROFLUORINATION TIME RATIO† AT INDICATED CONVERSION LEVELS						DEHYDRATION WEIGHT LOSS (%)
	60%	70%	80%	90%	95%	97%	
A. UO_3 Lot 3E 16-704 (PE 99020) Dehydrated in Laboratory							
1. Milled clumps	1.16	1.24	1.39	1.74	2.22	2.52	6.82
2. Cubical	1.44	1.41	1.41	1.46	1.51	1.50	10.57
B. UO_3 Lot 3E 16-704 (PE 99020) Dehydrated in MBR							
1. Milled clumps	1.26	1.33	1.52	2.18	3.47	–	–
C. UO_2 Lot 3E 16-704 (PE 99020) Produced in MBR							
1. Milled clumps	2.43	3.18	4.93	–	–	–	–
D. UO_3 Lot 3E-16-706 (PE 99023) Dehydrated in Laboratory							
1. Extruded††	1.72	1.81	1.91	2.06	2.15	2.16	8.05
2. Cubical	1.38	1.33	1.27	1.22	1.18	1.13	10.42
E. UO_3 Lot 3E 16-706 (PE 99023) Dehydrated in MBR							
1. Extruded	2.10	2.20	2.37	2.78	–	–	–
F. UO_2 Lot 3E 16-706 (PE 99023) Produced in MBR							
1. Extruded	1.94	2.56	3.93	–	–	–	–

* *Analysis of the final hydrofluorination product was omitted as unnecessary, since calculated results based on weight changes were found to be in close agreement with analytical results.*

** $\text{Ratio} = \dfrac{\text{Time required for hydrofluorination of sample to indicated \% conversion}}{\text{Time required for hydrofluorination of standard to indicated \% conversion.}}$

† *All pellets were prepared from sulfated UO_3.*

†† *Extruded pellets were prepared with the addition of ammonium hydroxide to the water used for pelleting to slow setting. Ammonia addition was approximately 4% NH_3, based on the total weight of water added to the UO_3.*

4. The results indicate quite conclusively that a low water content in the pellets (measured as weight loss during dehydration) lowers the reactivity.

5. In general, the two major methods of pelleting (extrusion and casting onto a belt) yielded pellets of equal reactivity, provided that the water content of the finished pellets was about the same. However, it is possible to introduce more water into the pellets by the casting-belt technique and consequently these pellets show an enhanced reactivity.

6. Pellets prepared by the rotary-drum technique were reduced rapidly in the thermal balance but were hydrofluorinated very slowly. These dense pellets had to be dehydrated gradually to prevent them from exploding as the water vapor escaped. Their surprisingly rapid reduction reaction suggests that hydrogen is capable of penetrating the pellets rapidly.

7. In Runs 26 and 27, significantly larger losses in reactivity were associated with dehydration of the pellets in the MBR than with dehydration of the same pellets in the laboratory. This effect was not evident for the casting-belt pellets employed in MBR Run 25. To date, laboratory experiments have given no clue as to the cause of the reactivity loss. One factor that may be significant in causing this loss in reactivity is that the pellets prepared for Runs 26 and 27 were much lower in water content than were those prepared for Run 25.

8. The most serious loss of hydrofluorination reactivity was associated with samples of UO_2 that had been produced in the MBR.

9. Samples of essentially unreacted UO_2 pellets that had passed through the reduction reactor of the MBR in Run 25 reduced slowly in the laboratory, but hydrofluorinated as rapidly as samples of the original feed that had been dehydrated and reduced in the laboratory.

11.0 REDUCTION TO METAL PROCESS (URANIUM)

11.1 EVALUATION OF COMMERCIAL GRADE MAGNESIUM FOR THE REDUCTION OF UF_4 - S. L. Reese and S. O. Samoriga.

Two series of reductions were made in the Pilot Plant to determine:

(1) Reaction characteristics of primary grade (commercial) 99.8 per cent magnesium in depleted UF_4 reductions. (Commercial magnesium costs 9.5 cents per pound less than specially purified magnesium and has a wider source of supply.)

(2) The characteristics of magnesium shot with respect to handling, packing, and reaction.

Reductions Using Magnesium Machine Chips

Commercial-grade 99.8 per cent magnesium in the form of machine chips was used for the first series of reductions in 10-inch and 14-inch furnace pots. The machine chips or curls were approximately 1/32 inch thick by 3/16 inch wide and had a ½ to ¾-inch true length. Due to the configuration of the curled magnesium machine chips, the amount of UF_4 charged to the reduction pots was reduced approximately 15 per cent when they were used.

The magnesium chips were low in impurities, except for iron and manganese (Table 11.1-1). The iron analysis averaged 280 ppm, the manganese averaged 1030 ppm. It was calculated that uranium metal produced by using this magnesium would have its iron content increased by a maximum of 63 ppm and its manganese content by a maximum of 318 ppm (Table 11.1-2). (These values are not high enough to significantly affect the density or physical characteristics of depleted metal.) The impurities showed up as 150 ppm total iron and 286 ppm total manganese in the average top and bottom samples of five ingots cast from derby metal produced for this evaluation. There were no other characteristic differences (with regard to reaction time, slag-metal separation, or derby yield) between reductions using magnesium machine turnings and those using regular purified ground magnesium (-10 to +50 mesh).

Reductions Using Magnesium Shot

Possible advantages exist in the use of atomized or "shot" magnesium in the reduction of UF_4. The material has a higher pack density than regular ground magnesium and is free flowing. The particle configuration should give better control of reaction initiation than is possible with the odd-shaped chips of the ground magnesium presently in use. This should aid in eliminating premature reactions.

In this series of reductions, magnesium shot having different particle size specifications was used at various furnace control temperatures in 10-inch furnace pots. For control purposes, an equal number of reductions were made under the same conditions using regular ground magnesium. The blending of the magnesium shot and UF_4 was excellent. The shot did not increase the pack density of the charge, and its free-flowing characteristics made manual tamping of the charge somewhat more difficult.

TABLE 11.1-1
CHEMICAL ANALYSIS OF 99.8% PRIMARY MAGNESIUM

IMPURITY	AVERAGE ANALYSIS OF 5 LOTS (ppm)	MAX. ANALYSIS (ppm)	MAXIMUM IMPURITIES (Astm B92-52 Spec) (ppm)
B	<0.3	<0.3	-
Cd	<0.3	0.3	-
Fe	280	350	300
Mn	1030	1300	1500
Pb	3	5	-
Zn	73	225	-
		Total Impurities*	2000

* *Specification*

TABLE 11.1-2
ANALYSIS OF DERBIES PRODUCED FROM PRIMARY MAGNESIUM

IMPURITY	AVERAGE ANALYSIS (ppm)	MAX ANALYSIS (ppm)
Ag	<0.1	<0.1
Al	60	175
B	<0.2	0.3
Bi	<1	2
C	24	34
Cd	<0.2	<0.2
Co	<2	<2
Cr	2	3
Cu	10	25
Fe	80	130
Mg	31	80
Mn	131	200
Mo	<3	<3
N	12	52
Ni	21	80
Pb	2	4
SiO_2	<12	<12
Sn	<1	2
V	<10	22
Zn	<17	40

Magnesium shot of a more uniform particle size (-25 +60) was then used for a series of reductions. The length of time for reaction to occur was about the same with this shot as in the control reductions. There was no apparent benefit in using the (-25 +60) shot since firing time varied considerably and derby yields were not improved.

11.2 REDUCTION TO METAL OF SINTERED GREEN SALT (UF_4) AND GREEN SALT PRILL - S. L. Reese and H. A. Kraus.

Green salt prill was produced[7] with the objective of increasing charge density and thus throughput. The reduction of prill is evaluated in this report.

Normal prill and magnesium (4% excess) were charged into reduction pots. The packing density showed no improvement over that obtained using standard NLO green salt. The large size of the prill and magnesium particles (Table 11.2-1) inhibited the reduction reaction because of the small surface area presented.

TABLE 11.2-1

SIEVE DATA FOR REDUCTION MATERIAL *

Sieve No.	Normal Prill (%)	Pulv. Prill (%)	Mg (%)	Hydro-fluorinated UF_4(%)	UF_6-source UF_4(%)	Sintered UF_4 Drum 10 (%)	Sintered UF_4 Drum 14 (%)
-8 +12	53.27		13.47			0.07	0.07
-12 +20	39.70		58.92		0.73	3.24	3.07
20 +40	5.92	4.67	25.25	2.46	1.81	10.67	10.38
-40 +60	0.62	19.23	1.35	4.06	2.18	12.04	14.18
-60 +80	0.12	16.21	0.67	3.69	3.75	12.83	23.98
-80 +100	0.12	9.48		3.08	11.37		
-100 +200	0.25	16.76	0.34	9.24	73.52	36.77	42.76
-200 +325		16.62		73.52			
-325		17.03		3.95	6.64	24.37	5.56
Bulk Density	3.80	3.74	0.74	2.46	2.96	3.45	3.20
Tap Density	4.32	4.92	0.88	3.51	4.35	4.61	4.33

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[7] *Reese, S. L., and Kraus, H. A., Summary Tech. Rpt., pp. 72-74, NLCO-565, July 15, 1955.*

One-half of the prill was pulverized. The firing time was only slightly over normal when 10 per cent pulverized prill was substituted in the charge. With 50 per cent pulverized prill, the firing time was normal.

With a charge consisting of 50 per cent standard NLO hydrofluorinated green salt and 50 per cent pulverized prill, the charge weight was increased 8 per cent. With 100 per cent pulverized prill charge, the same increase in charge weight was obtained, as well as a 24 per cent increase in tap density of the green salt.

The cumulative weight per cent was plotted on a probability scale versus the log of the sieve size (Fig. 11.2-1). An ideal particle size distribution should make a straight line on the graph. This condition is most nearly met by a reduction charge of pulverized prill and 4 per cent excess magnesium. The poor particle size distribution of prilled green salt for maximum density is quite evident in the graph. Since it parallels the magnesium particle size quite closely, the blend of the two materials would have a poor size distribution.

Sintered green salt was pulverized and it and a control lot of green salt were reduced in the NLO Pilot Plant. (See Section 9.2 of this report for a description of the sintering process.) The UO_2F_2 content of the green salt was reduced from 1.14 to 0.35 during sintering, which is similar to the results obtained in prilling. The average yield for 12 reductions was 96.2 per cent, with a range of 90.5 to 99.2 per cent.

The data presented indicate that sintering or melting the green salt will increase the pack density. Pulverizing is desirable in any event, to provide intimate contact of the green salt with the magnesium reductant and to obtain the greatest charge weight increase. An effective method of densifying would be to melt the green salt, permit solidification, then crush and grind it.

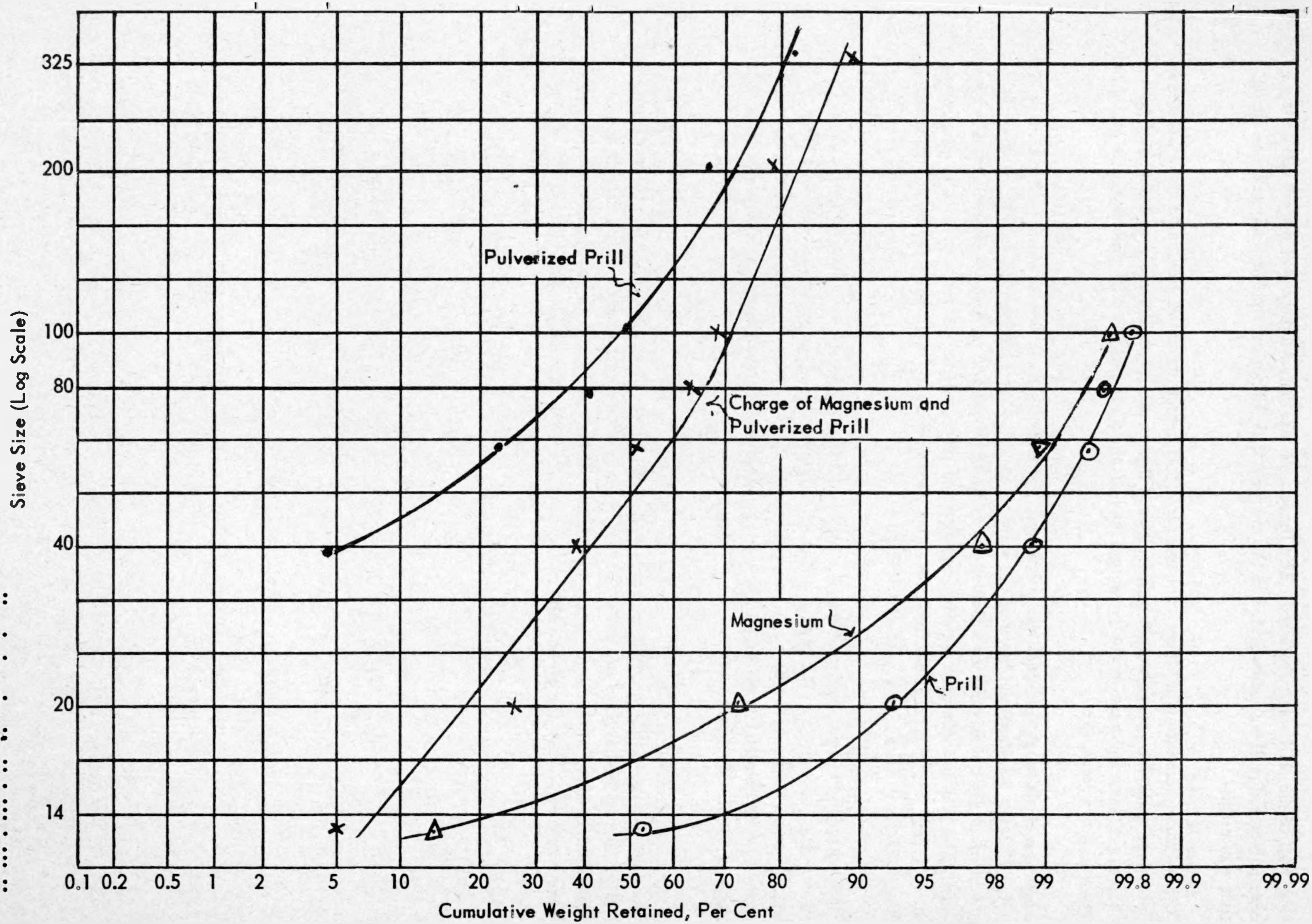

FIGURE 11.2-1 PARTICLE-SIZE DISTRIBUTION FOR GREEN SALT REDUCTION CHARGES

12.0 METAL CASTING PROCESS

12.1 INGOT SOUNDNESS EVALUATION - H. M. Eikenberry.

The purpose of the ingot soundness program was to determine:

1. The solidification patterns and the amount of secondary pipe in the seven-inch-diameter production ingots.
2. The effect on ingot soundness of insulating the seven-inch-diameter vertically split mold with a Fiberfrax blanket.
3. The effect on ingot soundness of insulating the seven-inch-diameter vertically split mold with an Alfrax insulator sleeve.
4. The effect on ingot soundness of casting an ingot on a thick graphite stool.
5. The effect on ingot soundness of casting a tapered ingot whose cross section has a maximum diameter of 7½ inches (rounded) and a minimum diameter (flat) of 5¾ inches at the ingot top and 5¼ inches at the ingot bottom.
6. The secondary pipe present in 4 inch by 11-inch rectangular ingots.

Seven-Inch Diameter, 45-Inch-Long Ingot

An ingot was cast with the following conditions:

1. 1250-pound charge (600 pounds of derbies, 250 pounds of briquettes, and 400 pounds of solid scrap)
2. A pour temperature of 2550°F (optical pyrometer reading).
3. One-inch pour hole
4. The top of the mold was ¼ inch or less below the bottom of the crucible.
5. The graphite stool was 8¾ inches high.
6. The mold assembly was on a water-cooled base.

Three minutes after pour, the temperature of the mold at the mold center clamp had increased from 380°F to 1230°F; two hours after pour, it had decreased to 380°F.

The ingot was sawed into 5-inch to 6-inch pieces and each piece was sawed vertically to expose the center of the ingot. Each piece was etched in concentrated hydrochloric acid for two minutes and then washed in concentrated nitric acid for approximately three seconds. A photomacrograph was taken of each piece. These were arranged in Figure 12.1-2 to show their original positions in the ingot.

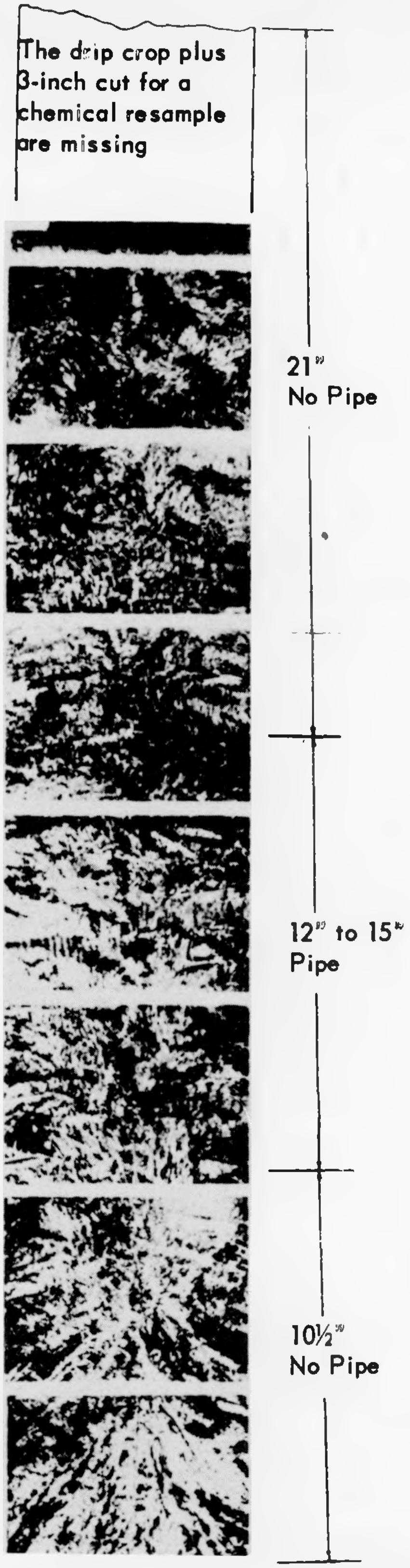

FIGURE 12.1-2 SEVEN-INCH DIAMETER, 45-INCH-LONG INGOT

As can be noted in Figure 12.1-2, the vertical dendrites extend nine to ten inches from the bottom of the ingot. Starting at the approximate intersection of the vertical and horizontal dendrites, the secondary pipe extended upward approximately 15 inches to the 24-inch level.

This method shows only that pipe exposed by the vertical cut. The only method of determining the total amount of pipe present in an ingot made by this procedure is to make a radiograph of the ingot with the betatron.

Seven-Inch-Diameter, 45-Inch-Long Ingot Cast Into A Fiberfrax-Blanket-Insulated Mold

The casting conditions were the same as those used to cast the previous ingot, except that the mold was insulated with a ½-inch-thick Fiberfrax blanket that extended 12 inches down from the furnace table (Fig. 12.1-3).

The ingot was sawed into vertical slices and etched. The location of the secondary pipe is shown in Figure 12.1-3. The vertical dendritic growth extended eight to nine inches from the bottom and the secondary pipe extended upward approximately twelve inches to about the 20-inch level, which was similar to the dendritic structure and pipe shown in the photomacrograph of the production ingot (Fig. 12.1-2). The secondary pipe did not seem to be as severe as in the 1st ingot.

Seven-Inch-Diameter, 45-Inch-Long Ingot Cast Into A Mold Insulated With Alfrax

The casting conditions were the same as those used to cast the production ingot, except that the mold was insulated with cast Alfrax. The Alfrax was contained in a sheet steel sleeve 14 inches long that slipped over the mold clamps. The top of the Alfrax insulator was ten inches below the bottom of the furnace table.

Figure 12.1-4 shows the mold heating and cooling curves. At the mold center clamp, the mold temperature was 340°F when the melt was poured; it increased to a maximum of 1210°F six minutes after pour. Ten minutes after 1210°F had been reached, the temperature had dropped only 60°F, compared to the 340°F drop obtained with the uninsulated mold (Fig. 12.1-1). This smaller temperature drop would indicate that the heat was retained in the mold long enough to allow for good directional solidification, but such was not the case. When the ingot was sectioned vertically and etched, the dendritic structure and secondary pipe were seen to be similar to that of the production ingot shown in Figure 12.1-2. The location of the secondary pipe is shown in Figure 12.1-5. Evidently, the heat capacity of the mold section that was insulated was great enough to absorb the latent heat of the liquid and most of the heat of fusion. As a result, the metal bridged across, thereby preventing the liquid from feeding down to the liquid-solid interface at the center of the ingot.

Seven-Inch-Diameter, 37-Inch-Long Ingot Cast Into An Uninsulated Mold With A Graphite Stool 17-Inches Thick

Another ingot was cast under the following conditions:

1. 1050-pound charge (600 pounds of derbies, 250 pounds of briquettes, and 200 pounds of solid scrap).

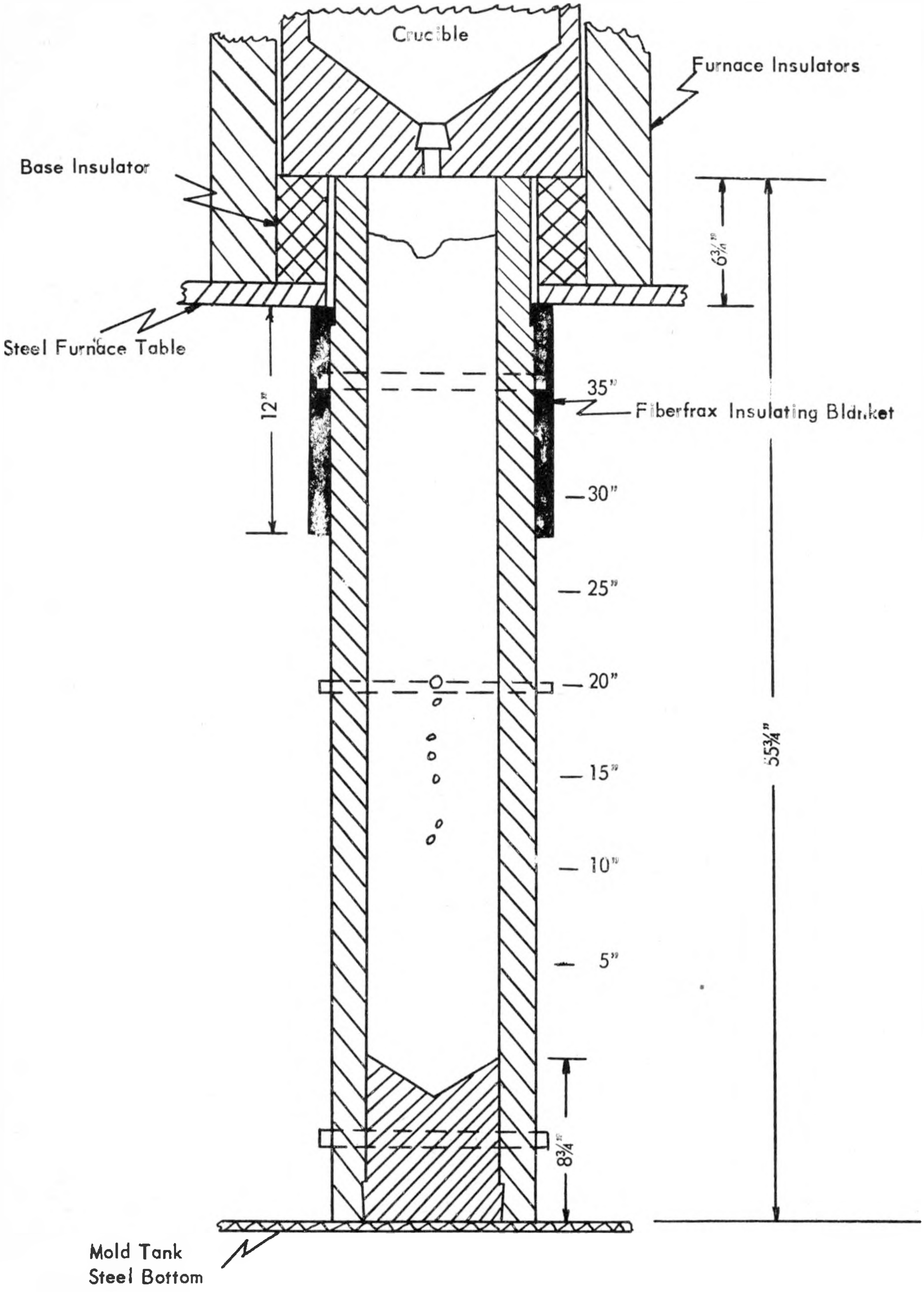

FIGURE 12.1-3 SEVEN-INCH-DIAMETER, 45-INCH-LONG INGOT CAST INTO A FIBERFRAX-BLANKET-INSULATED MOLD (INGOT 9543)

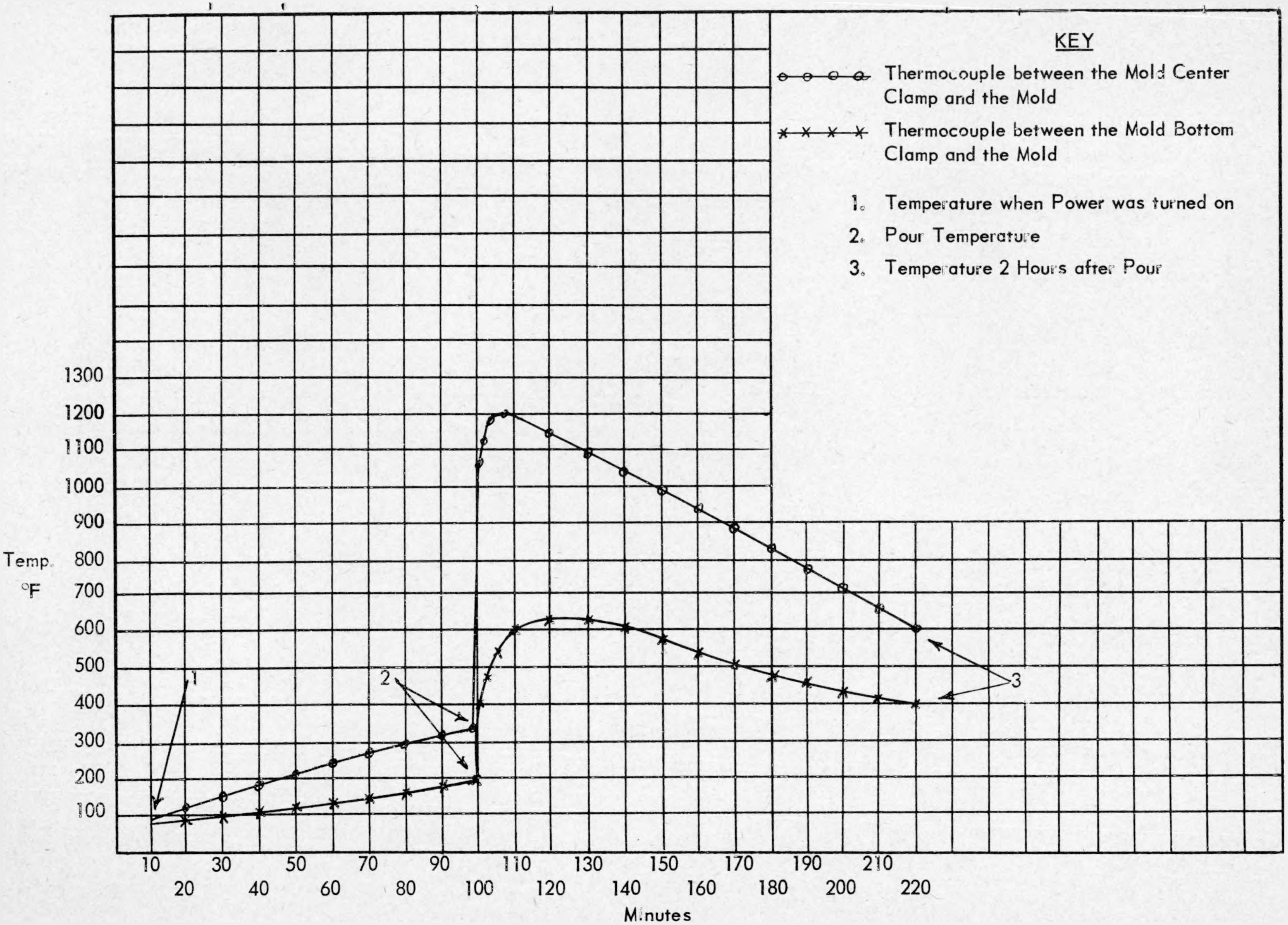

FIGURE 12.1-4 MOLD HEATING AND COOLING CURVES FOR THE MOLD INSULATED WITH AN ALFRAX INSULATOR

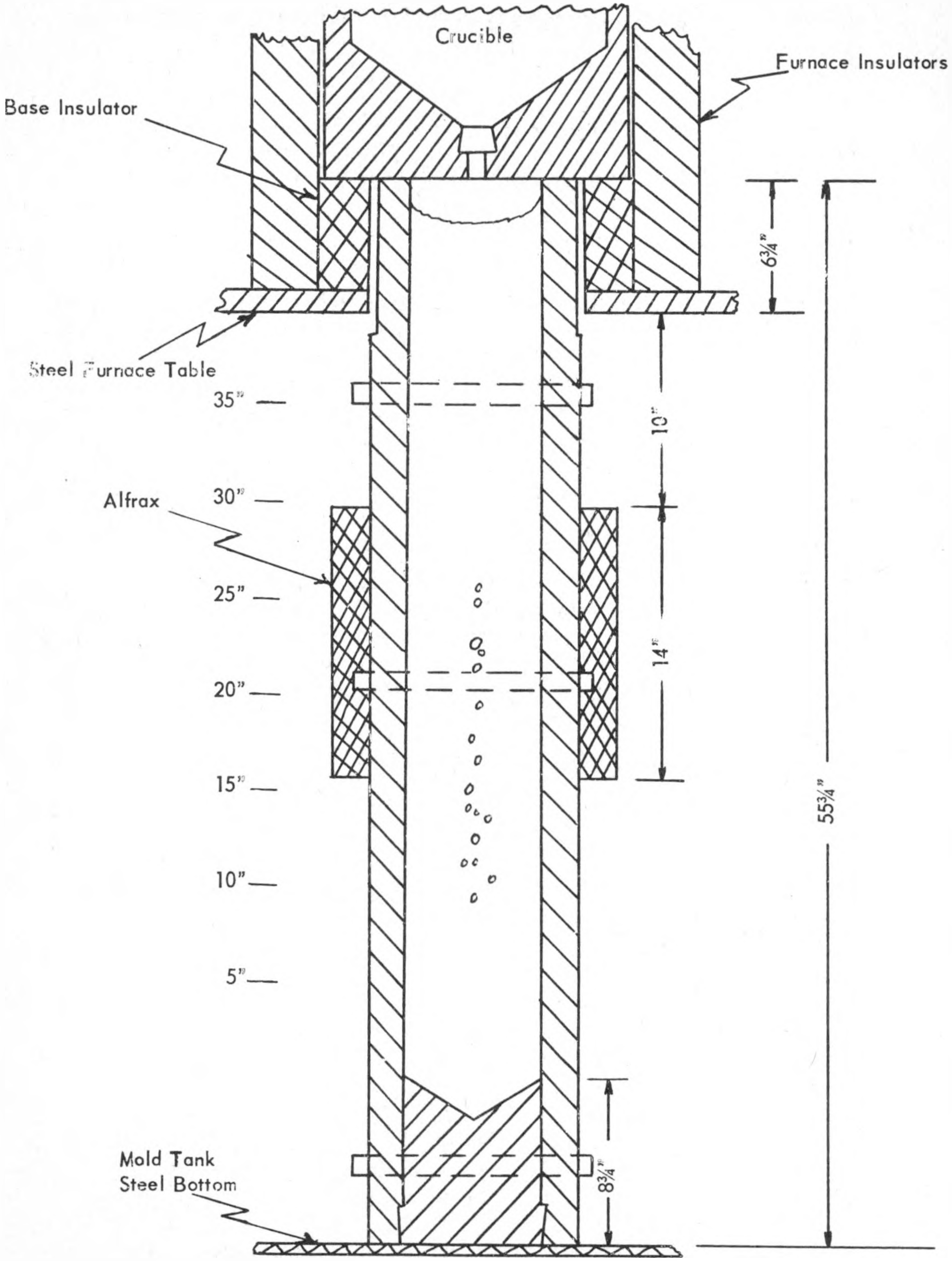

FIGURE 12.1-5 SEVEN-INCH-DIAMETER, 45-INCH-LONG INGOT: CAST INTO A MOLD INSULATED WITH AN ALFRAX INSULATOR (INGOT 9786)

2. 107-minute melting time to a pour temperature of 2550°F (optical pyrometer reading).
3. One-inch pour hole.
4. The top of the mold was ¼ inch or less below the bottom of the crucible.
5. The graphite stool was 17 inches thick.
6. The mold assembly was on a water-cooled base.

The ingot was sectioned vertically and etched. The vertical dendrites extended up eight to nine inches from the ingot bottom. From the approximate intersection of the vertical and horizontal dendrites, the secondary pipe extended upward for approximately seven to eight inches to the 18-inch level, as shown in Figure 12.1-6. Thus, the length of the secondary pipe decreased by the same amount as did the length of the ingot, namely, 8 inches. The width to height ratio for this ingot was 1:5 as compared to a width to height ratio of 1:6.4 for a 7-inch by 45-inch ingot.

Tapered Ingot (5¼-Inch to 5¾-Inch Flat By 7½-Inch Round) Cast Into An Uninsulated 11-Inch-OD Graphite Mold (Fig. 12.1-7)

The casting conditions were the same as those used to cast the 1st ingot, except that the graphite stool was four inches long instead of 8¾ inches long. The ingot was sectioned vertically and etched. The dendritic structure indicated that the vertical dendrites extended approximately five inches from the bottom, although the secondary pipe started at the eight-inch level. The secondary pipe extended for 20 inches to approximately the 28-inch level, as is shown in Figure 12.1-7.

Four-Inch by Eleven-Inch Rectangular Ingot, Forty Inches Long; Cast Into An Uninsulated 14-Inch-OD Graphite Mold

Two ingots were cast, one by each of two different casting procedures. The casting procedures were as follows:

1. Ingot 262D (cast in the Pilot Plant):
   a. 1150 pound charge of D-38 derbies.
   b. 320-minute melting time to a pour temperature of 2550°F (optical pyrometer reading).
   c. One-inch pour hole.
   d. The top of the mold was 10 inches below the bottom of the crucible.
2. Ingot 9803 (cast in the Metals Plant);
   a. 1150 pound charge (600 pounds of derbies, 250 pounds of briquettes, and 300 pounds of solid scrap).
   b. 110-minute melting time to a pour temperature of 2550°F (optical pyrometer reading).

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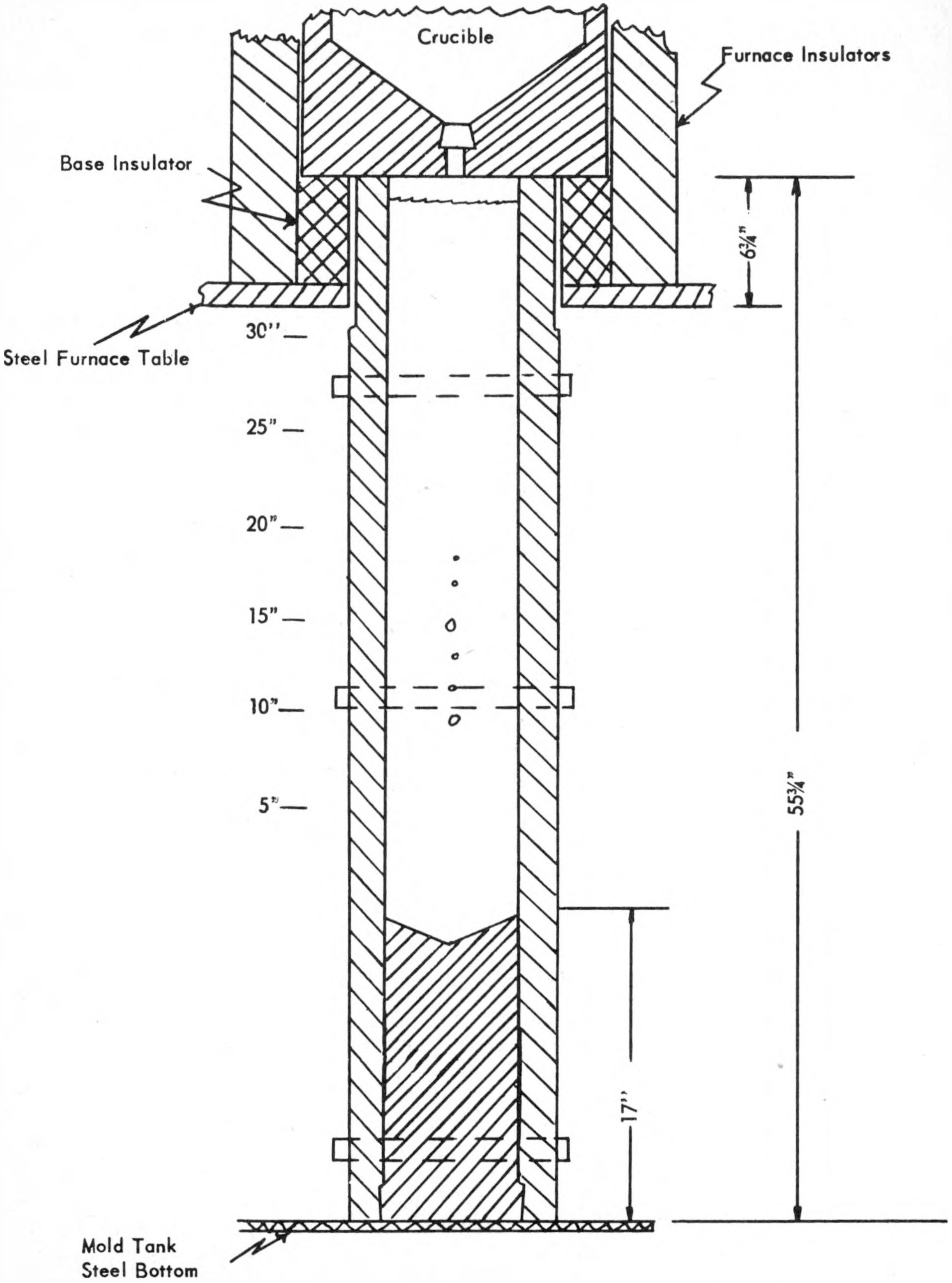

FIGURE 12 1-6 SEVEN-INCH-DIAMETER, 37-INCH-LONG INGOT CAST INTO AN UNINSULATED MOLD WITH A GRAPHITE STOOL 17 INCHES LONG (INGOT 9799)

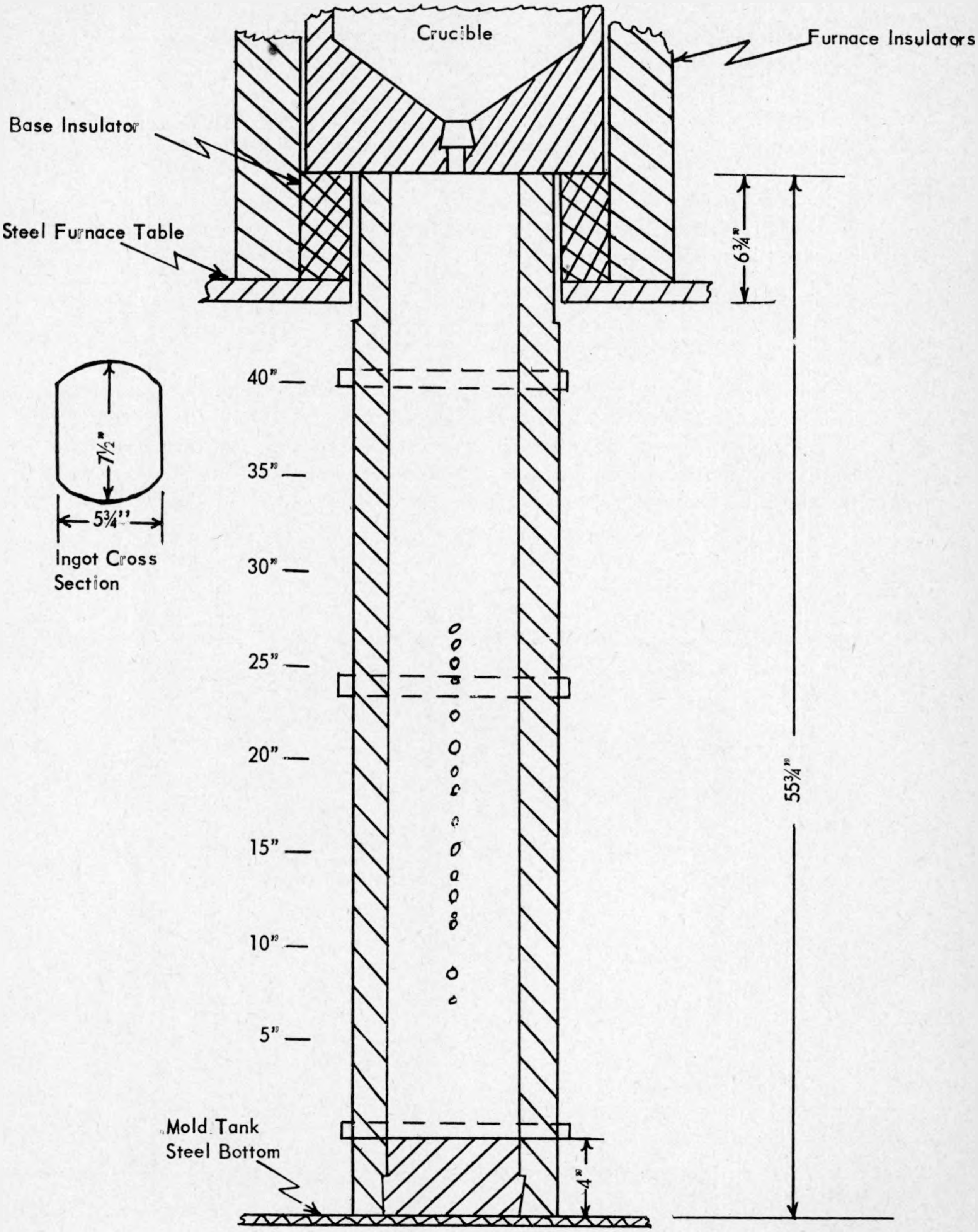

FIGURE 12.1-7

FLAT TAPERED FROM 5¼ TO 5¾ INCHES BY 7½ INCHES ROUND INGOT; CAST INTO AN UNINSULATED 11-INCH-OD GRAPHITE MOLD (INGOT 9803)

c. One-inch pour hole.

d. There was a graphite pour block between the crucible and the mold. The liquid level of the cast ingot was the same as that of Ingot 262D.

These two ingots were radiographed by the betatron at MCW. Except for a few random points, ingot 262D was essentially free of secondary pipe, as is indicated in Figure 12.1-8.

Ingot 9803 had considerably more pipe than Ingot 262D. As shown in Figure 12.1-9, the pipe was in a double band three inches in from each edge up to the 20-inch level. The pipe was in the middle five inches of the ingot between the 20-inch level and the 25-inch level.

Conclusions

The results indicate that there is approximately 15 inches of secondary pipe (extending from the 10 inch to the 25 inch level) in NLO 7-inch-diameter ingots. The 4 inch by 11 inch rectangular ingots cast in the Pilot Plant had fewer internal voids than did the rectangular ingots cast in the Production Plant. This may have been because of the longer melting time used in the Pilot Plant, which may have heated the top of the mold to a higher temperature.

Future Work

Work will continue on the design of a mold insulator (consisting of bulk Fiberfrax in a sheet steel container) that can be adapted to the vertical split mold.

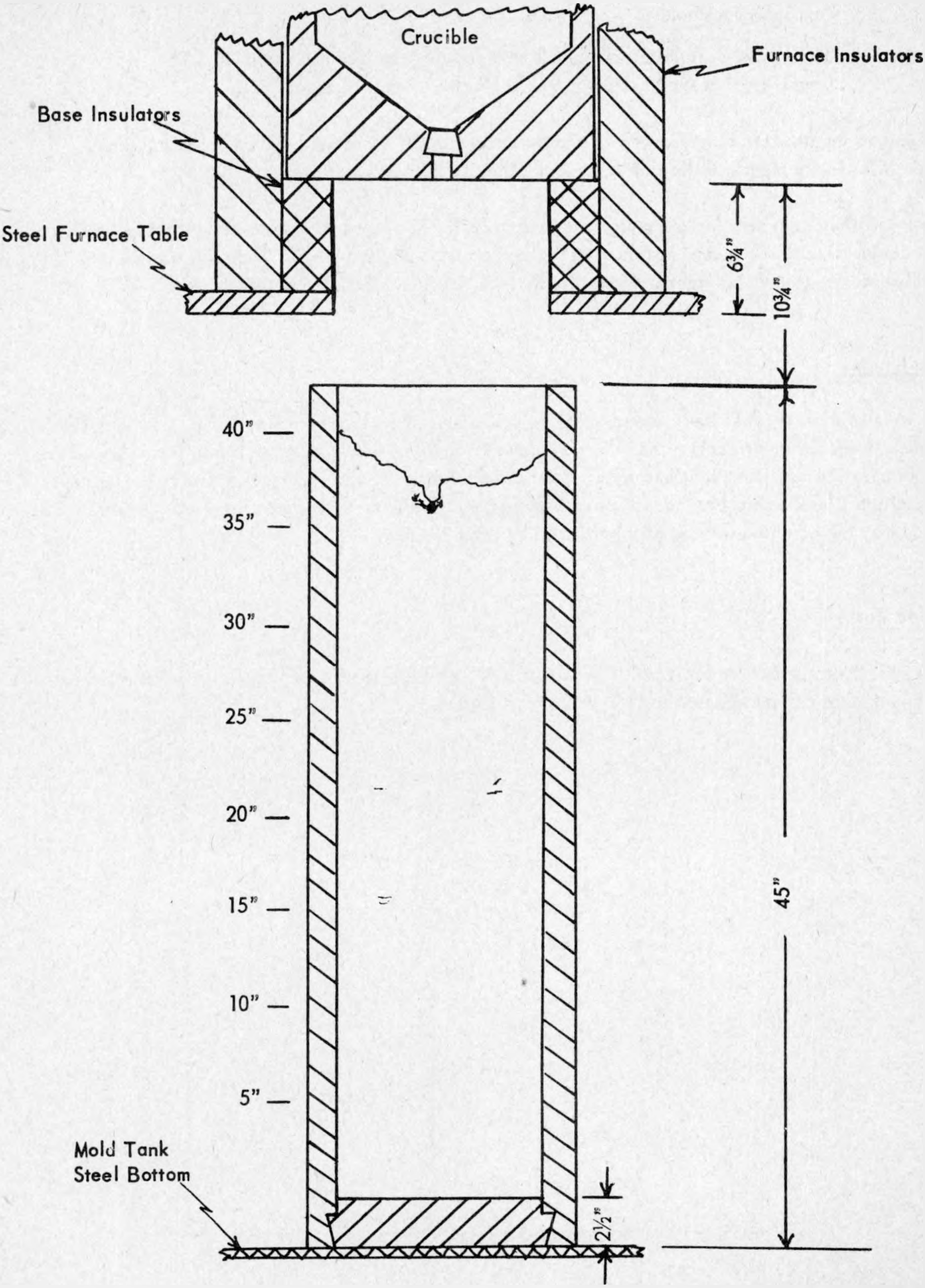

FIGURE 12.1-8 FOUR-INCH BY 11-INCH RECTANGULAR INGOT CAST INTO AN UNINSULATED 14-INCH-OD MOLD IN THE PILOT PLANT (INGOT 262D)

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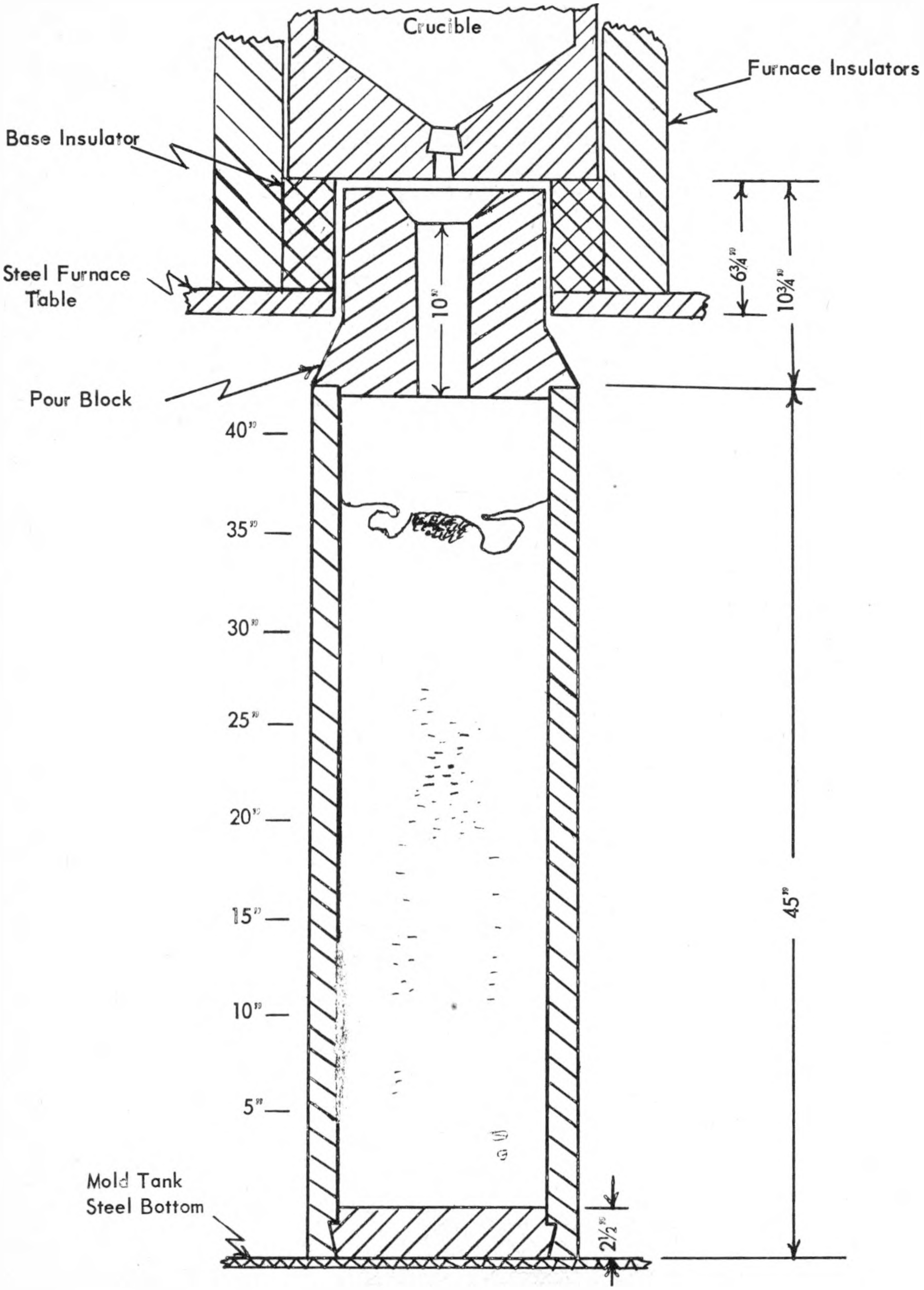

FIGURE 12.1-9 FOUR-INCH BY 11-INCH RECTANGULAR BY 40-INCH-LONG INGOT CAST INTO AN UNINSULATED 14-INCH-OD MOLD IN THE METALS PLANT (INGOT 9803)

13.0 RECOVERY OF URANIUM FROM SCRAP MATERIALS

13.1 RECOVERY OF URANIUM FROM SULFATED SLUDGES RESULTING FROM THE RECOVERY OF HF FROM MgF_2 REDUCTION BOMB SLAG - R. L. Doyle, E. O. Rutenkroger, T. F. Rupert, and E. R. Johnson.

During the production of uranium metal, considerable quantities of MgF_2 slag are generated as a by-product of the UF_4 reduction operation. In the past, this slag, along with the refractory bomb liner, has been processed for uranium recovery using a hydrochloric acid leach - ammonia precipitation technique. This process has served to produce a uranium concentrate suitable for refinery processing.

Recently, Mallinckrodt initiated the use of the by-product MgF_2 slag as a refractory liner for the reduction bombs. The reject slag (that slag produced in excess of the liner requirements) has been stockpiled for processing to recover the contained uranium values.

Since it is expected that other sites will convert to this process within the near future, consideration has been given to recovering HF from the slag. At a meeting held at Oak Ridge Operations Office, it was decided that samples of ground slag would be submitted to several HF manufacturers to determine how efficiently the MgF_2 responds to sulfuric acid treatment (see the following Section of this report). In addition, it was decided that NLO and MCW would conduct development studies designed to determine how the calcines resulting from the HF recovery could best be processed for the recovery of the contained uranium values.

The results of NLO studies using synthetic solutions have been reported previously.[1] Since that time, samples of H_2SO_4-MgF_2 slag calcines have been received from the Harshaw Chemical Company and the General Chemical Company for evaluation.

It was found that 97 to 98 per cent of the uranium in these sludges could be solubilized by a water leach in the presence of an oxidant. The resulting leach liquors contained less than 0.5 g/l fluoride. Recovery of uranium from the leach liquors was successfully effected by precipitation with NH_4OH as ammonium diuranate or by reducing with aluminum and precipitating with H_3PO_4 at a pH of 1.5 as uranous phosphate.

The ammonium diuranate cakes obtained by treatment of these sludge leach liquors assayed about 30 per cent uranium. The main contaminant was iron, whose concentration varied from 28 to 40 per cent of the product. The NLO Refinery tolerance limit for feed materials is 40 per cent iron on a uranium basis. Any product containing an appreciable excess of this would have to be blended prior to processing.

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[1] *Johnson, E. R., et al., Summary Tech. Rpt., pp. 119-120, NLCO-565, July 15, 1955.*

The phosphate precipitation process was successful in recovering uranium from sludge leach liquors in the form of a concentrate assaying 45 to 55 per cent uranium and 30 to 35 per cent phosphate. Subjecting this cake to alkaline hydrolysis produced a uranium concentrate assaying 67 per cent uranium and 4 per cent phosphate. The principal advantage of this process is that the iron present in the leach liquors does not separate with the uranium, as it does in the ammonia process. However, reagent concumption is higher, more equipment is required for processing, and the reactions are slower.

In both processes, the excess acidity present in the sludge samples required large quantities of reagents for pH adjustments.

13.2 THERMAL BALANCE STUDY OF THE REACTION BETWEEN MgF_2 SLAG AND SULFURIC ACID R. L. Doyle, E. O. Rutenkroger, and D. V. Huffman.

The AEC has expressed an interest in the possibility of recovering HF from the reject MgF_2 slag resulting from slag liner production. NLO has just completed a study of the recovery of uranium from the sulfated sludge resulting from the recovery of HF (preceding Section of this report). As an adjunct to this program, it was thought that the basic data obtained from an investigation of the reaction between MgF_2 slag and sulfuric acid would be valuable. For this purpose, use was made of the thermal balance.

The thermal balance consists essentially of an insulated closed reaction chamber with provision for heating and for the introduction of gases, and a reaction vessel (platinum basket or dish) suspended from the pan of an analytical balance. The balance provides a means of precise measurement of weight changes as a reaction proceeds.

Investigation was made of the effect of temperature, acid excess, and particle size on HF volatilization. Bed depth was held constant at one centimeter and, due to the physical limitations imposed by the thermal balance, all experiments were conducted in a static bed.

Data obtained from these studies indicated that a reaction temperature of 275° to 300°C, a 30 to 40 per cent excess of sulfuric acid, and a particle size distribution of at least 75 per cent less than 325 mesh were necessary, if a reasonable percentage of the contained HF values were to be volatilized in a three-hour retention time. Under such conditions, 55 per cent of the available HF was volatilized. It should be emphasized that these studies were carried out with a static bed and that higher yields would be expected in a stirred bed reactor.

13.3 PHOSPHATE SPECIFICATIONS FOR TVA HYDROCHLORIC ACID - A. B. Kreuzmann and D. V. Huffman.

During operation of the Metal Recovery Plant between March, 1955, and June, 1955, a steady decline was noted in the uranium assay of the final diuranate product. After various refinements in plant operation failed to effect a satisfactory improvement in product quality, attention was directed to possible chemical causes of the product adulteration.

Initial laboratory work indicated the possibility that phosphates, which were known to be present in the TVA acid being used, were coprecipitating with the uranium and thus contaminating the product. It was later discovered that the quantity of phosphate present in the TVA acid had increased considerably since it was first accepted for use. In view of this, a series of laboratory investigations was carried out to establish a phosphate tolerance level for plant use.

It was found that the phosphate tolerance in the acid is directly related to the uranium assay of the feed material. For an average feed value of 4.5 per cent uranium, a maximum tolerance of phosphate in the acid was found to be 7.5 g/1 phosphate. It was also found that the actual contaminant in the TVA acid was phosphite rather than phosphate. However, experiments showed that the valence state of the phosphorus made no difference in its effect on the final product.

13.4 AMMONIUM DIURANATE WASHING STUDIES - A. B. Kreuzmann.

A series of experiments was carried out to determine the possibility of fluoride removal by a water-washing technique from backlog ammonium diuranate. Samples of plant-produced diuranate cake were obtained at various periods of operation. The samples were divided into two portions, one of which was dried without further treatment, the other was slurried with water, filtered, and washed again on the filter. The dried cakes were then compared as to fluoride content. In no instance did the water wash result in a lowering of the fluoride content of the diuranate cake. On occasion, the fluoride showed an apparent increase, probably due to removal of other water-soluble constituents of the cake.

13.5 CORROSION STUDIES IN THE URANIUM SCRAP PROCESSING PLANT F. H. Meyer, N. N. Peters, and E. W. Torok

The evaluation of possible materials of construction for use in Scrap Plant digestion equipment has been continued during this quarter. Previous studies have been reported in past quarterlies.[1,2]

Evaluation of Materials of Construction For Scrap Plant Digestion Equipment

A series of materials of construction were evaluated in the Corrosion Laboratory, using synthetic digestion solutions. Individual tests were performed using 2000-ml reaction flasks fitted with reflux systems to maintain solution concentration. Temperatures were controlled using pyrometer controllers (a thermometer well in the flask contained the thermocouple).

Table 13.5-1 incorporates all significant data acquired since the last quarterly compilation. Synthetic solutions duplicated plant concentrations and tests were run at plant operating temperatures.

TABLE 13.5-1

CORROSION RATES OF VARIOUS ALLOYS IN SYNTHETIC DIGESTION SOLUTIONS

Solution Composition:

925 cc H_2O 77 cc HCl
75 g/1 $CaCl_2$
75 g/1 $MgCl_2$
1.5 g/1 MgF_2
1.6 g/1 $KClO_3$

Solution Temperatures: As indicated

MATERIAL	SOLUTION TEMP (°F)	EXPOSURE TIME (hr)	CORROSION RATE (MDD)*	CORROSION RATE (MPY)**	REMARKS
Polyvinyl chloride plastic	195	65	837 (gain)	1310 (gain)	Severely blistered, swollen
Teflon	195	96	None	None	Excellent
Tantalum	195	96	None	None	Excellent
Titanium 150 A	195	96	5293	1690	Very poor
Zirconium	195	96	628	121	Poor
Micarta plastic	150	120	98.7		Poor

*MDD - Weight loss in milligrams per square decimeter per day.

**MPY - Theoretical penetration rate in mils per year from the side of the process vessel wall that is exposed to the corrosive solution.

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[1] Meyer, F. H., Summary Tech Rpt. pp. 98-102, FMPC-540, April 15, 1955.

[2] Meyer, F. H., Summary Tech Rpt. pp. 121-122, NLCO-565, July 15, 1955.

Of the above materials, Teflon and tantalum showed the only really useful resistance to the test solution.

In addition to the above materials, a series of ten special formulations of plastics were submitted to us by the Eimco Corporation for test. All of the materials submitted showed poor to fair resistance to the test solution at 150°F.

14.0 THORIUM DEVELOPMENT AND OPERATIONS

14.1 PREPARATION OF THORIUM OXALATE PELLETS AND THORIUM CHLORIDE - S. L. Reese and C. C. Fogel.

The unit described in the previous quarterly[1] continued in operation at the Pilot Plant. The process consists of heating thorium oxalate pellets to 600°F in a helium stream, adding chlorine gas, heating, and adding carbon tetrachloride gas. A fairly constant supply of good quality thorium chloride was produced, which will be used in the "Metallex" program at ORNL.

At the same time, variations in the procedure were studied in an effort to gain greater completion of the reaction.

Making of Thorium Oxalate Pellets

The method of making pellets[2] has not been changed except that 1/8 to 3/16-inch pellets were made instead of 1/4 to 1/2-inch pellets. It is believed that the smaller pellets will react more completely, in that they have more surface area exposed for the solid-gaseous reaction.

Starch equivalent to two moles of carbon per mole of thorium was added to some of the pellets.

Chlorination

Chlorination is done in a graphite column reactor. Chlorine and carbon tetrachloride gases are fed into the bottom of the reactor and the off gases go to a caustic scrubber. Batch operation is used.

The maximum temperature used in the reactor is now 1250° to 1350°F, which is just below the sublimation temperature of thorium chloride (Table 14.1-1). This temperature appears to favor more complete reaction. Nevertheless, the completeness of reaction is not uniform throughout the bed. Apparently, there is local overheating, which causes sublimation of the thorium chloride formed. This thorium chloride then forms an impervious shell on some of the pellets before the reaction is completed. Evidence for this theory is the crystal-like appearance of the exterior and the amorphous appearance of the interior of reacted pellets.

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[1] *Reese, S. L. and Fogel, C. C., Summary Tech Rpt., pp. 131-133, NLCO-565, July 15, 1955.*

[2] *ibid.*

TABLE 14.1-1

CHLORINATION OF OXALATE PELLETS

Run No.	Feed Ratio Cl/Th	Feed Ratio CCl_4/Th	Temp At Start of Cl_2 Addition (°F)	Temp At Start of CCl_4 Addition (°F)	Maximum Temp (°F)	Run Time (hr)	$ThCl_4$ (Avg %)	SPECTROCHEMICAL ANALYSIS: Major Contaminants (ppm) Cu	Fe	Ni	SiO_2	REMARKS
7	6.4	2.16	560-570	830-890	1150	7.5	88.7	2	8	<4	<20	Start of Runs Measuring Bed Temperatures.
8	8.1	2.47	550-580	795-950	1100	7.25	81.8	8	15	300	<20	
9	7.0	2.00	410-530	740-1000	1150	7	75.6	8	6	200	<20	
10	8.8	2.04	470-560	910-950	1170	7.75	74.3	25	8	800	30	8-in. Heating Zone For Gases.
11	12.0	2.00	230-325	540-780	1205	8	75.0	8	8	10	<20	
12	9.5	2.40	470-580	765-960	1205	8.25	71.8	25	20	1000	<20	≈0.22 Mole Br/Mole Th
13	6.5	2.16	650-790	1050-1120	1365	8	56.8	25	10	8	30	Center Thermowell Couples 6 in. Apart.
14	6.6	2.04	620-670	785-895	1280	9.25	90.6	15	15	10	30	12-in. Heating Zone for Gases.
15	5.9	2.04	560-685	715-800	1170	9	70.6	4	30	700	120	120-minute Heat-up Time before Cl_2 Addition.
16	8.1	2.48	265-290	700-745	1130	9.5	87.8	30	15	60	120	Power Input Same as Run 14.
17	6.9	2.00	330-355	700-740	1090	9	78.1	10	<6	25	140	Wet Pellets Charged To Reactor. Dried in Reactor.
18	7.7	2.08	275-290	620-675	1080	9.5	77.5	4	8	100	180	Same Power Input as Run 14.
19	6.9	1.93	405-475	685-730	1080	12	81.8	10	<6	5	100	90-minute Heat-up Time Before Cl_2 Addition.
20	8.93	3.51	360-405	760-780	1095	12	78.5	20	6	4	200	Lower Starting Temperature for Cl_2 Addition.
21	5.73	1.93	450-535	885-910	1380	7	78.4	6	<6	<4	<20	Higher Maximum Temperature.
22	6.0	1.93	510-530	1030-1040	1365	7	44.4	50	<6	<4	140	High Maximum Temperature.
23	6.0	1.93	470-530	865-890	1325	7	68.1	40	<6	<4	<20	High Maximum Temperature.
24	6.5	2.17	665-720	905-1000	1300	7	68.1	4	25	4	<20	Starch Pellets 2 moles Carbon/mole Th.
25	6.6	2.17	480-685	845-1025	1290	8	65.0	4	<6	15	20	Pellets added in 5-pound increments Throughout Run
26	6.1	2.05	555-580	875-1105	1330	7	71.3	4	20	30	<20	Starch Pellets, 2 moles Carbon/mole Th.
27	5.5	1.93	575-585	900-945	1130	7	61.3	2	<6	5	20	Pellets Dried in Reactor For 9 hr at 500 - 600°F.

Another possible reason for incompleteness of the reaction is channeling of the reactant gases.

Starch-containing pellets were used in two runs so as to provide more heat (carbon being present as a reactant immediately when chlorine is introduced). The results of starch pellet runs, however, showed no improvement in the quality of thorium chloride produced (Table 14.1-1).

Bromine was used as an intermediate reactant in one run, but no improvement resulted.

Some preliminary work was done on producing thorium chloride from an aqueous solution. No conclusive results are available.

Results and Conclusions

All of the material was analyzed spectrochemically (Table 14.1-1). Analyses are quite similar, with copper, iron, nickel and silicon dioxide being the main contaminants.

To obtain high reaction efficiencies, a very close temperature control is necessary. Local overheating must be avoided because it sublimes the thorium chloride and makes the thorium dioxide inert.

Future Work

A vertically hinged tube-type resistance furnace is being installed. At the bottom of this furnace there is a gas preheat zone whose function it is to preheat the carbon tetrachloride to just below its cracking temperature. This will result in more heat being available for the reaction in the lower reaction zones. It is also hoped that more uniform temperatures will be produced over the entire length of the new reactor.

It is planned to use carbon monoxide gas in conjunction with chlorine and carbon tetrachloride. This should allow the reaction to proceed at a lower temperature, resulting in less inert thorium dioxide being produced and more thorium chloride. Then, as conversion nears completion, higher temperatures and cracked carbon tetrachloride will be used.

14.2 REMOVAL OF SULFATE FROM ThO_2 BY CALCINATION - J. H. Krekeler and R. C. Kispert.

A study was conducted to determine the feasibility of removing sulfate from ThO_2 by calcination at 670°C. Calcinations in air at bed depths ranging from 1/8 to 3/4 inch and for periods of from 30 to 240 minutes gave no effective change in sulfate concentration.

14.3 DEVELOPMENT OF METHODS OF ARC-MELTING THORIUM METAL - O. R. Magoteaux

In the process of manufacturing massive thorium metal, a melting and casting step is required in order to produce high-purity sound ingots which can be fabricated into fuel elements. During startup of the thorium semi-works at National Lead, virgin metal was induction-melted in stabilized zirconia crucibles. This was found to be unsatisfactory, because the metal was contaminated by crucible materials and because volatiles from the virgin thorium interfered with operation of the furnace.[1]

Consumable-electrode arc-melting was adopted as the most favorable method of improving metal quality[2] and preventing the interference of volatile materials in the casting practice. (Nonconsumable melting with a tungsten electrode introduces tungsten into the ingot.) This process change has led to better metal quality but required the development of methods of preparing electrode stock.

Equipment and Procedure

Two objectives of this process are: (1) to remove volatile impurities from the thorium and (2) to prepare a sound final ingot.

This process involves casting a primary ingot and a final (or secondary) ingot. Before the primary ingots may be cast, electrodes must be prepared by sawing, welding, and machining. In order to minimize pickup of oxygen, nitrogen, and hydrogen from the atmosphere, the electrode preparation and melting steps are conducted under a blanket of inert gas.

Sawing is necessary because the dezinced thorium derby is too large to be used directly as an electrode in the first casting step. A power hack saw is used to reduce the pieces to less than a three-inch-square cross section and to a six to eight-inch length (Fig. 14.3-1).

Welding of the sawed pieces is required in order to prepare sufficient metal for a practical production-size melt. Equipment for welding primary electrodes consist of a horizontal tank approximately three feet in diameter and three feet long, attached to which are two tanks nine inches in diameter and four feet long. One end of one of the small-diameter tanks has a door used for loading the electrode in the welding operation. A 200 cfm vacuum pump is connected to the other small-diameter tank. Welding is done with a hand operated electrode holder, which contains a 1/8-inch-diameter thoriated tungsten rod. Two hand holes are used in performing the welding operation.

The welding tank is first evacuated to 30 inches (gauge pressure) and then backfilled to atmospheric pressure with argon. A high-frequency electrical unit is used to start the arc to prevent direct contact of the tungsten electrode and the workpiece. A current of 180 to 200 amperes and a voltage of 20 to 25 are used.

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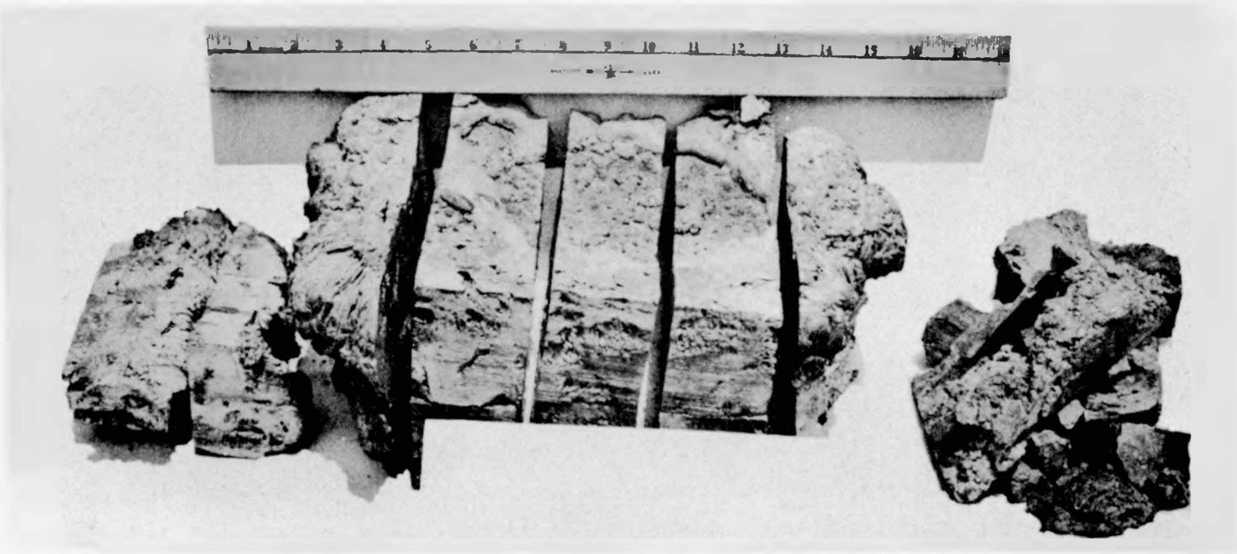
[1] *Clymer, W. B., Summary Tech. Rpt., pp. 144-152, FMPC-540, April 15, 1955.*

[2] *Magoteaux, O. R., ibid., pp. 153-156.*



SAWED DEZINC DERBY   DEZINCED THORIUM DERBY THAT HAS BEEN SAWED FOR WELDING INTO A PRIMARY ELECTRODE

DEZINCED DERBY ELECTRODE   WELDED ELECTRODE MADE FROM A DEZINCED THORIUM DERBY

FIGURE 14.3-1

The sawed pieces, which include a threaded section of derby called a stub, are butt-welded. (The stub serves as a means of attaching the electrode to the power leads of the casting furnace.) The weld, which penetrates about 1/8 inch into the workpiece, is made completely around each joint. Care is taken not to remove the electrode from the tank while hot so as to prevent reaction with the nitrogen and oxygen in the atmosphere.

The finished electrode weighs approximately 30 pounds and is stored until it can be melted into a segment of a primary ingot. Figure 14.3-1 shows a primary electrode made from a dezinced derby.

The furnaces used to arc-melt primary and final ingots are designed for simplicity of operation and with desirable safety features. The arc furnace consists of three parts:

(1) The upper tank, through which the furnace electrode (stringer) passes,

(2) The middle tank, which supports the upper and lower tanks and to which a surge tank is connected, and

(3) A lower section consisting of a water jacket into which the copper crucible is placed. (The ingot is cast in the copper crucible.)

The upper and middle sections are not water-cooled. Attached to each furnace is a vacuum line and vacuum gauge. The bottom section is clamped to the middle section, but the upper section is free to separate if an explosion occurs within the furnace. This reduces the possibility of restricting any explosive gases which may form during a water leak or burnout. The lid to the surge tank also can blow off in the event of a pressure buildup.

The power supply consists of 16 direct-current rectifiers having a capacity of 1200 amperes each and is located in a separate room through which filtered air is passed. Connected to the rectifiers are two main bus bars which lead to the furnace area.

The furnaces are operated from behind a protective shield at a panel board that controls the vacuum system, the purge system, the electrode drive, and the power. The operator views the furnace through high temperature-resistant glass. A master power-cut-off switch is located on the panel board for emergency conditions.

In casting a primary ingot, chips first are placed in a 5-inch-diameter copper crucible prior to evacuating the furnace. The arc furnace is evacuated to less than 500 microns pressure (Hg) and is maintained at a leak rate of less than 10 microns per minute. The furnace is then backfilled to 25 inches (absolute pressure) with argon. An arc is struck, and melting of the electrode is started at 2000 amperes and 25 to 30 volts. After 20 to 30 seconds, the amperage is raised to 3000 and is held at that level for the rest of the melt

Up to 12 consecutive melts have been used to form one primary ingot.

After the primary ingot is removed from the crucible, machining removes the volatiles that concentrate on the surface during melting. The top and bottom of the ingot are removed. Figure 14.3-2 shows a crude and a finished primary ingot.

A second tank, capable of handling an electrode up to 46 inches long and 10 inches in diameter, is used to weld stubs to the primary ingots for melting to final ingots. It is a water-cooled steel tank approximately 8 feet long, 2½ feet in diameter, and capable of being evacuated and purged. Connected to the welding tank are a 200-cfm vacuum pump and a 400-ampere direct current rectifier. Three water-cooled electrode-holders are spaced along the length of the tank to permit welding at various points. Tungsten electrodes of ½-inch diameter are used. The workpiece rests in two shafts that rotate it during welding. A hydraulic system moves the shafts horizontally and permits welding along the length of the workpiece.

Ingot chips are placed on the bottom of the crucible prior to evacuation of the furnace for casting of the secondary ingots. These ingots are cast into 7 or 7-3/8-inch-diameter water-cooled copper crucibles in equipment identical to that used for primary ingots. The furnace is evacuated and backfilled to the same conditions as for primary ingots, but the power input conditions are different. At the start of the melt, a current of 3200 amperes is used. Once the arc is struck and a pool is established, the power is increased to 6500 amperes and that level is maintained for the rest of the melt.

The ingots are removed from the crucible and the top and bottom ends are cropped. The top contains most of the impurities and the bottom consists of fused chips. The ingot surfaces are such that only about 1/8 inch of metal need be removed to prepare the ingot for fabrication. Since the fabrication facilities can utilize only a 6 1/8 inch diameter ingot, however, the 7-inch-diameter ingots are machined to that diameter. Figure 14.3-3 shows a crude and a conditioned final ingot.

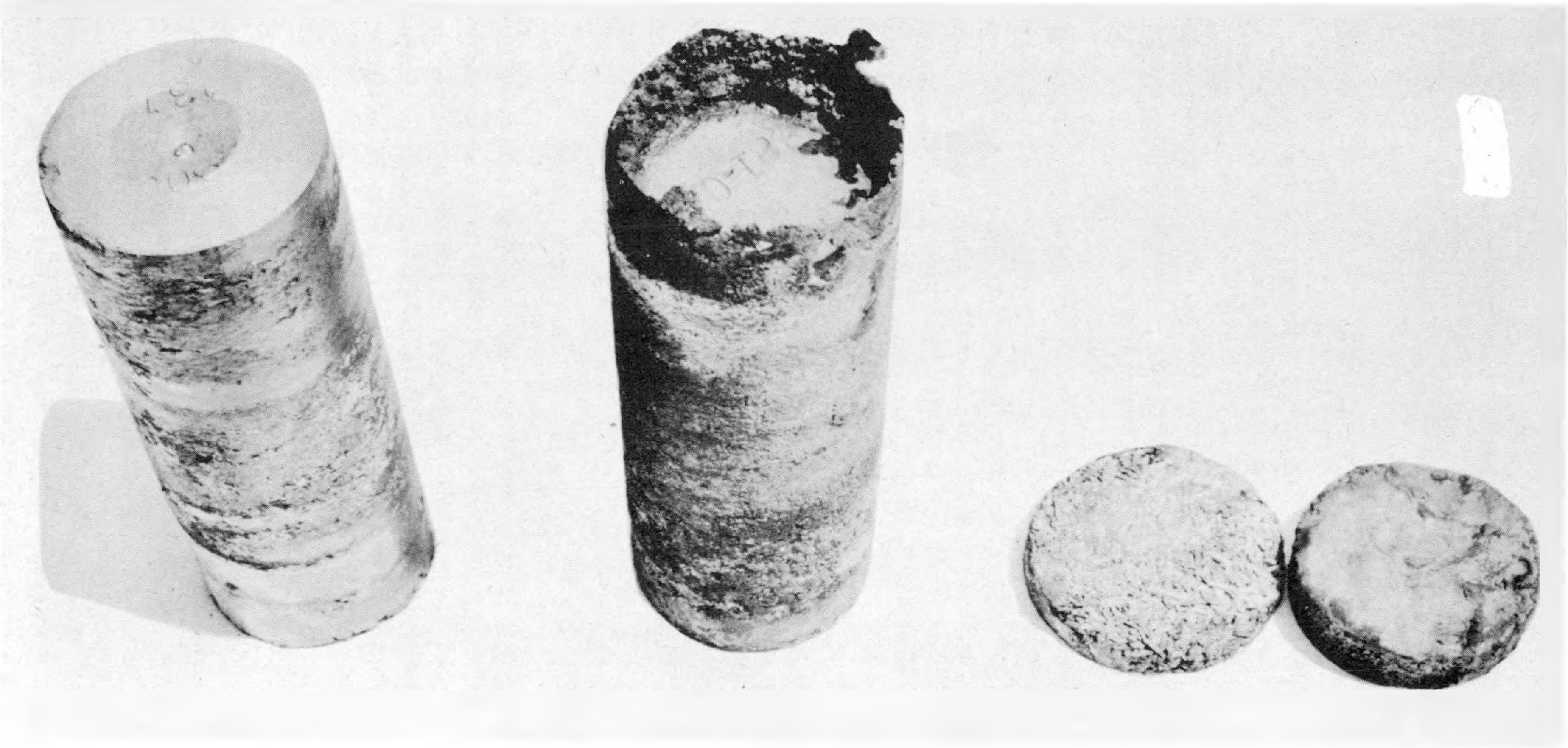
Conclusion

The operation of this equipment on a production scale has been satisfactory. Ingots prepared by this method have no visible defects and the surfaces of the ingots have been satisfactory. Chemical quality appears to be influenced most by the amount of impurities in the electrode stock and the operating conditions during melting and casting. Minor changes in equipment have permitted casting 10 inch-diameter final ingots with improved process efficiency and production rate.

Future Work

Development work has been started to improve the present process. (See Section 14.6 of this report.) The primary electrode step is undesirable since it is costly, piece-meal, and reduces the quality of the metal. Future development work will involve studying the effects of argon-helium mixtures, backfill pressures, vacuum, current input, and purity of inert gas on metal quality.

The problem of recycling metal scrap on a production scale is a most important field of development, since no suitable production method of recycling scrap metal has been established. Pressing the scrap into electrodes appears to be a promising method.

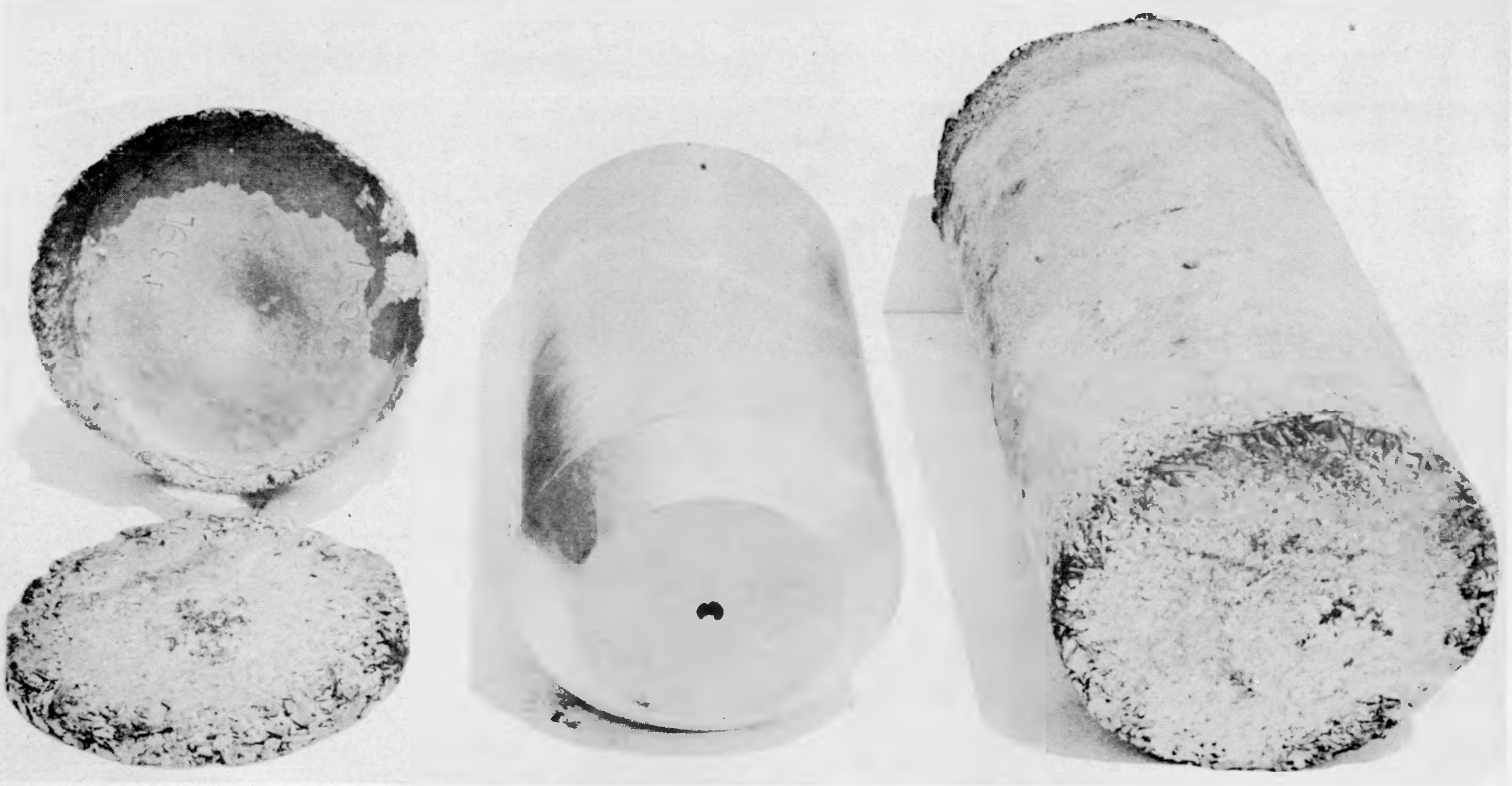


Primary Ingot
Finished 4½" Dia.

Primary Ingot
Crude 5" Dia.

Scrap

FIGURE 14 3 2 A CONDITIONED AND A CRUDE ARC MELTED VIRGIN THORIUM PRIMARY INGOT



Scrap

Secondary Ingot
Finished 6-1/8" Dia.

Secondary Ingot
Crude 7" Dia.

FIGURE 14.3-3 A CONDITIONED AND A CRUDE ARC-MELTED VIRGIN THORIUM FINAL INGOT

14.4 CHEMICAL REPROCESSING OF THORIUM METAL - W. C. Manser and J. H. Krekeler.

Laboratory studies are being conducted to determine the feasibility of reprocessing off-specification thorium metal by dissolution in HNO_3-NaF solution, followed by precipitation of thorium as the oxalate.

The effect of fluoride ion concentration in the 0.025M to 0.075M range on the dissolution rate of thorium metal in concentrated HNO_3 has been investigated. The results are presented graphically in Figure 14.4-1. Nitric acid consumption equal to approximately 20 per cent of the total charge has been encountered in all runs. A rather long (75-min) acid-addition time is required, due to vigorous reactions and foaming at the time of acid addition.

Preliminary studies of the decontamination achieved through oxalate precipitation indicate good decontamination from all metals except zirconium. However, the data presented in Table 14.4-1 are slightly erratic, especially with respect to copper, and additional studies are being made. It is thought that the zirconium contamination can be reduced to acceptable levels by blending dissolver solution with "zirconium-free" thorium nitrate prior to precipitation.

Laboratory corrosion studies will be conducted during the coming quarter.

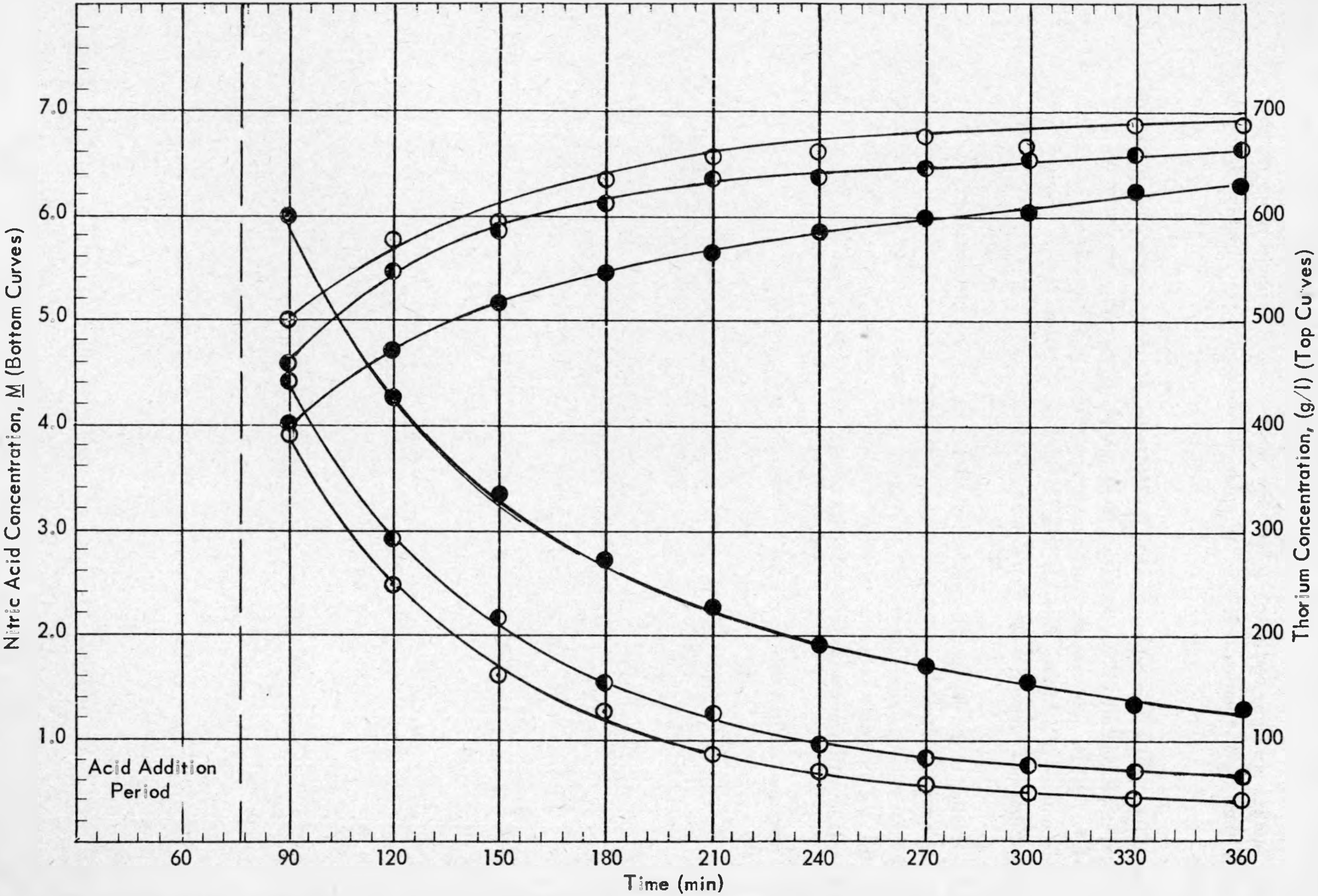


FIGURE 14.4-1 EFFECT OF F$^-$ CONCENTRATION ON THORIUM METAL DISSOLUTION.

Conditions: 15.8$\underline{N}$ HNO_3, 200% Excess Thorium Metal, 114°C

○ = 0.075$\underline{M}$ F$^-$
◐ = 0.050$\underline{M}$ F$^-$
= 0.025$\underline{M}$ F$^-$

TABLE 14.4-1

DECONTAMINATION RESULTING FROM THORIUM OXALATE PRECIPITATION*

	RUN 2			RUN 3			RUN 4		
	$Th(NO_3)_4$	$Th(C_2O_4)_2$	DF **	$Th(NO_3)_4$	$Th(C_2O_4)_2$	DF **	$Th(NO_3)_4$	$Th(C_2O_4)_2$	DF **
Al	>600	10	>60	>600	<10	>60	>600	<10	>60
B	2.5	<0.2	>13	7.0	<0.2	>35	3	<0.2	>15
Ba	–	–		–	–		<20	–	>20
Be	25	<1	>25	30	<1	>30	30	<1	>30
Bi	<2	<2	1	<2	<2	1	–	<2	–
Ca	200	<200	>1	<200	<200	1	<200	<200	1
Cd	<0.2	0.2	<1	<0.2	<0.2	1	<0.2	<0.2	1
Co	4	<1	>4	6	<1	>6	2	<1	>2
Cr	50	<4	>13	30	<4	>8	75	<4	>19
Cu	125	60	2	125	6	20	150	10	15
Fe	500	15	33	550	10	55	600	10	60
Mg	15	6	2.5	10	<4	>2.5	15	6	2.5
Mn	5	<1	>5	5	<1	>5	5	<1	>5
Mo	10	5	2	1	3	<1	<1	5	<1
Ni	>1000	50	>20	>1000	30	>33	600	30	20
P	<40	<40	1	<40	<40	1	<40	<40	1
Pb	20	20	1	20	10	2	15	15	1
SiO_2	30	<20	>1.5	20	<20	>1	<20	<20	1
Sn	2	2	1	2	<1	>2	1	<1	1
V	<10	<10	1	<10	<10	1	–	<10	–
Zn	<10	50	<1	<10	10	<1	<10	10	<1
Zr	5376	4615	1.16	5494	8494	<1	4070	6870	<1

* *All values expressed in ppm on Th basis.*

** *Decontamination factor (DF)* $= \dfrac{\text{Conc in } Th(NO_3)_4}{\text{Conc in } Th(C_2O_4)_2}$

– *Not determined.*

14.5 PRECIPITATION OF THORIUM FROM SUMP LIQUOR M. D. Snyder, J. H. Krekeler, and R. C. Kispert.

A laboratory study to determine the relative merits of hydrated lime, NaOH, and MgO as thorium sump precipitants was completed. These precipitants were compared on the basis of thorium removal efficiency, cost, slurry filtration rates, and resultant cake handling characteristics. In conjunction with this study, the use of barium as a carrier for the precipitation of thorium decay products from sump liquor was evaluated.

The data presented in Table 14.5-1 and Figure 14.5-1 indicate the following:

1. The efficiency of thorium removal from sump liquor was comparable for all three precipitants investigated.

2. Hydrated lime is the most economical (on a reagent cost basis) of the precipitants investigated.

3. The slurry neutralized with MgO has the highest filtration rate, as measured on a 0.1-sq ft filter test leaf.

TABLE 14.5-1

NEUTRALIZATION AND FILTRATION OF THORIUM-CONTAINING SUMP LIQUORS

PRECIPITANT	70% NaOH (FLAKE)	HYDRATED LIME	MgO (SEA WATER GRADE)
Pounds of precipitant required per gal of sump liquor *	0.234	0.227	0.177
Cost of precipitant **	\$90.40/ton†	\$18.65/ton	\$82.50/ton
Cost per gal sump liquor (cents)	1.06	0.35	1.22
Ratio of cost	3.03	1.00	3.49
Pounds of dry solids per gal of precipitant slurry	0.033	0.080	0.075
Thorium in filtrate (g/l)	<0.01	<0.01	<0.01

* *Neutralization to pH 7.5.*
** *Prices quoted by NLO Purchasing Department 6/8/55.*
† *Based on the quotation for 100 pounds.*

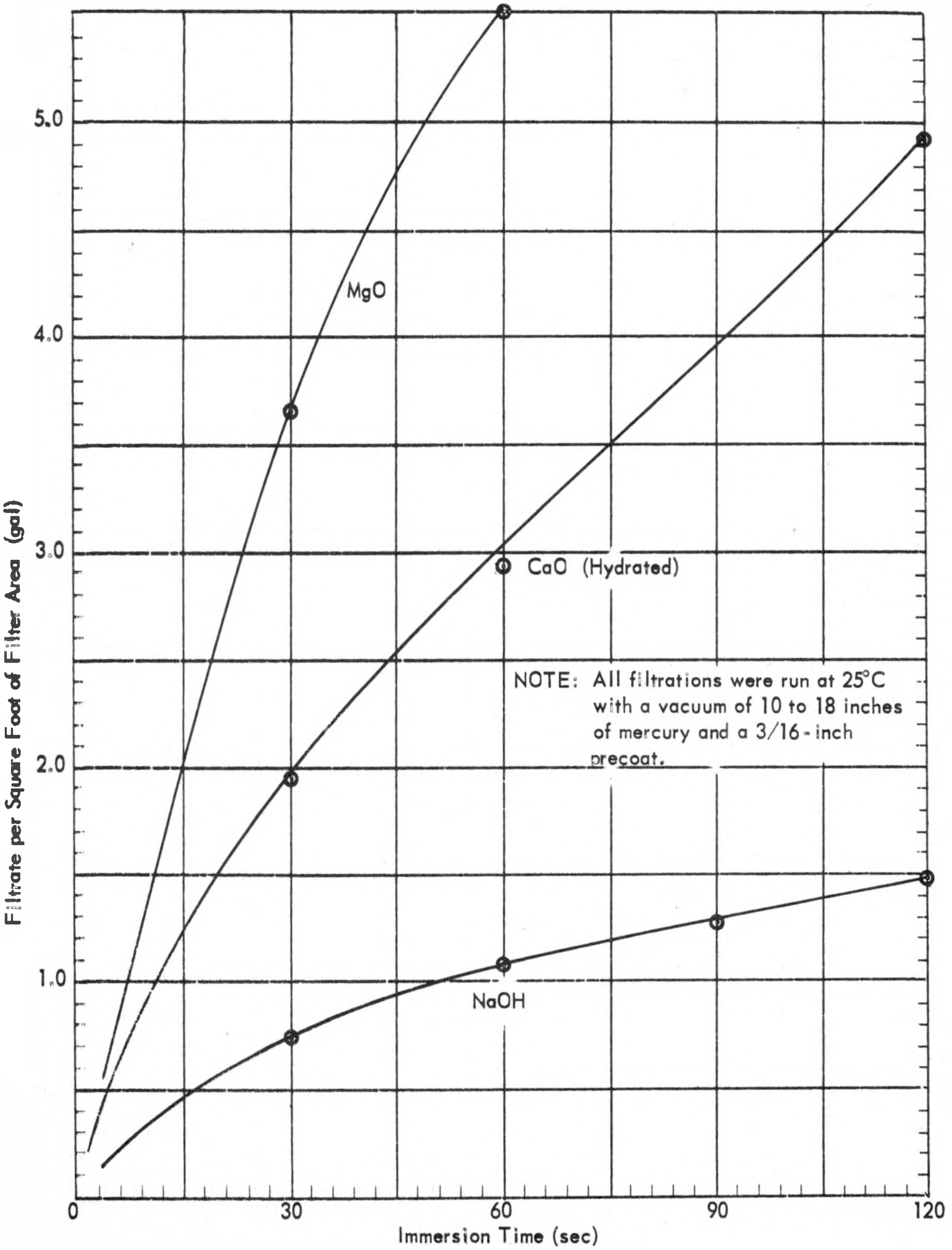


FIGURE 14.5-1 FILTRATION RATES OF NEUTRALIZED THORIUM SUMP LIQUORS

A comparison of the resultant cake handling characteristics indicates that the NaOH slurry had less solids content than the MgO and hydrated lime by a factor of two, but the cake was thixotropic in nature. The MgO and hydrated lime, while having more cake, were granular in nature.

A study of the use of barium as a carrier for the precipitation of the thorium-decay products in the sump liquor was carried out by Battelle Memorial Institute[1] for NLO.

They found that the use of barium as a carrier in the precipitation of thorium-decay products in sump liquor is no more effective than simple neutralization with NaOH. Results obtained here confirmed their data.

14.6 DEZINCING AND ARC-MELTING THORIUM METAL - H. H. Baker and O. Magoteaux.

In one step of the metallurgical phase of producing thorium metal, a thorium-zinc alloy (derby) is produced by the thermite reduction of ThF_4 and $ZnCl_2$ with calcium metal in a steel vessel protected by a tamped liner of dolomite. The resulting derby is approximately 9½ inches in diameter and 4 inches high. The derby is then heated in order to remove the zinc metal, and expands to approximately a 11-inch diameter and a 5-inch height.[2] The next step is to remelt the derby and cast the metal as an ingot. As is noted in Section 14.3 of this report, the shape of the dezinced derby has prevented its being arc melted directly. It has been necessary to saw the derby into small sections and weld the pieces together to form a rod before arc-melting, but this method has the following disadvantages:

1. It is wasteful of manpower and increases the cost of the product.
2. It requires saws and welding machines.
3. The metal is contaminated with tungsten as a result of welding rods breaking.
4. It is difficult to weld the pieces as a straight electrode and these often break during cooling.
5. Approximately 15 per cent scrap is generated in the sawing operation as there are small pieces produced that are unsuitable for welding.

This shows a definite need for producing a dezinced derby that has a shape suitable for arc-melting.

In an attempt to form a derby in the shape of a rod, a groove was formed in the liner along the length of the reduction pot. Upon firing, the pot was tilted to a horizontal position to allow the metal to flow into the groove. In the first attempt, the pot was turned to a horizontal position

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[1] *Calkins, G. D., Pobereskin, M., Gates, J. E., Blackmore, R. H., and Duffee, J. H., The Distribution of Thorium-Decay Products in the Thorium-Purification Process, p. 26, BMI-967, December 7, 1954.*

[2] *Clymer, W. B., Summary Tech. Rpt. pp. 135-141, FMPC-540. April 15, 1955.*

within five minutes after firing was indicated. However, solidification of the alloy had occurred before the pot was tilted. Since this technique would have required horizontal firing (not suitable to present equipment), this method was abandoned in favor of (1) the production of pigs and (2) crushing the thorium-zinc derby and using it as dezincing feed.

Production of Alloy Pigs

The three-pronged wooden mandrel shown in Figure 14.6-1 was substituted for the conventional steel mandrel in forming the reduction-pot liner. The resulting three-compartment liner is shown in Figure 14.6-2. No change in the standard operating procedure was necessary.

The initial tests resulted in cracked liners at the intersection of the side wall and the top surface of the compartment. However, further sanding of the mandrel, to give a greater radius at the intersection, eliminated the problem.

The amount of dolomite required to form this liner is 11 per cent greater than for the noncompartmented liner. The charge is reduced from 135 pounds of thorium tetrafluoride to 125 pounds, with corresponding reductions in the amount of zinc chloride and calcium used. Charging is accomplished as directed in the SOP except that the pot is filled at least 6 inches above the compartments before tamping, to eliminate the possibility of damage to the compartment walls.

Firing times were equivalent to those for conventional reductions. Breakout of these pots was considerably easier than when producing a derby because of the greater length to diameter ratio and the slight taper of the pigs. The pigs were 9 to 10 inches long and 3½ to 3¾ inches in diameter, and weighed 29 to 33 pounds each. Three typical pigs from one reduction are shown in Figure 14.6-3. Eleven reductions have been made with the following results:

REDUCTION NO.	TOTAL WEIGHT (lb)	YIELD (%)
2450	90.1	92.0
2472	94.6	97.0
2488	95.1	97.0
2490	94.2	97.0
2491	97.1	99.0
2502	94.1	95.5
2504	94.8	96.0
2550	95.5	97.5
2598	91.8	93.5
2625	88.1	91.0
2627	90.2	92.0

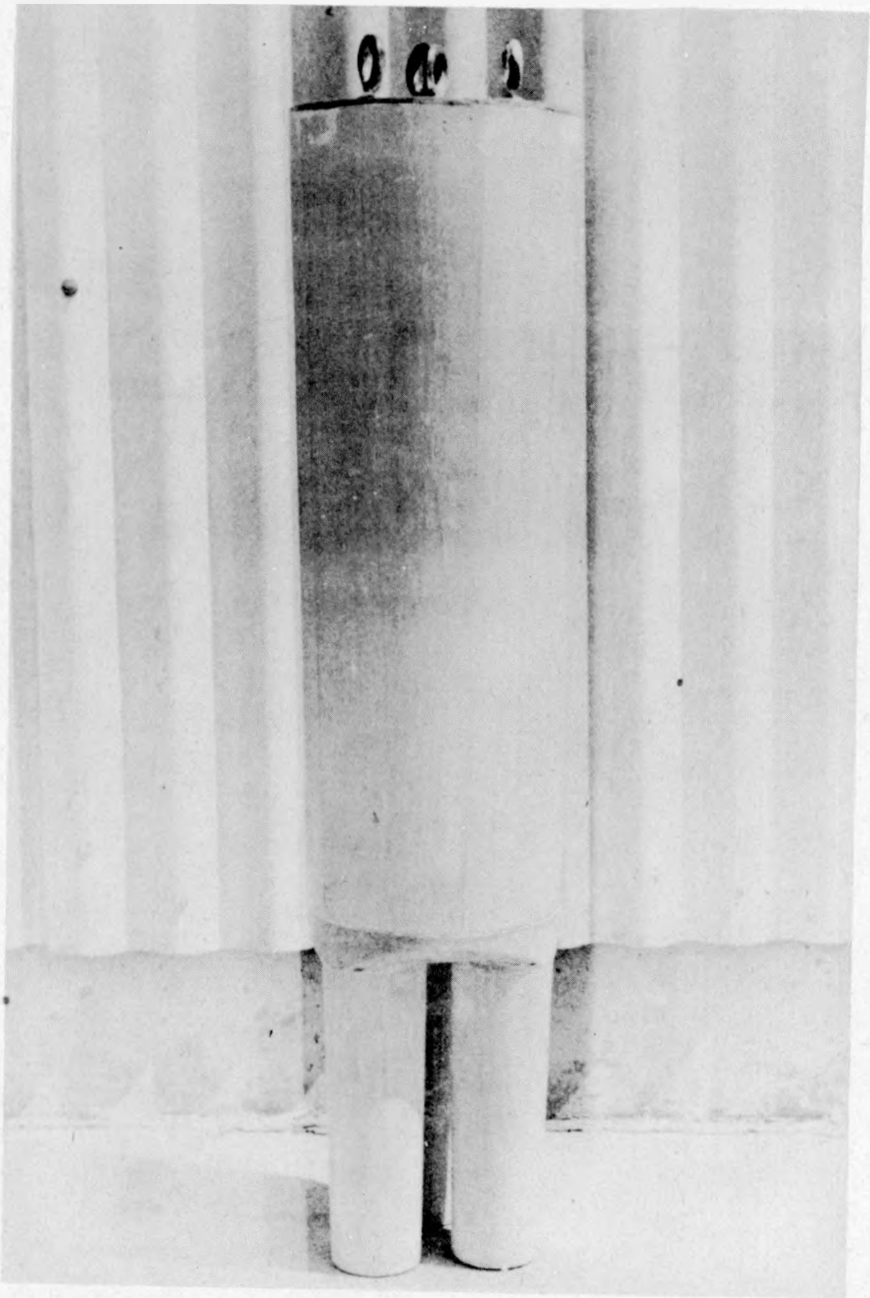


FIGURE 14.6-1 THREE-PRONGED WOODEN MANDREL

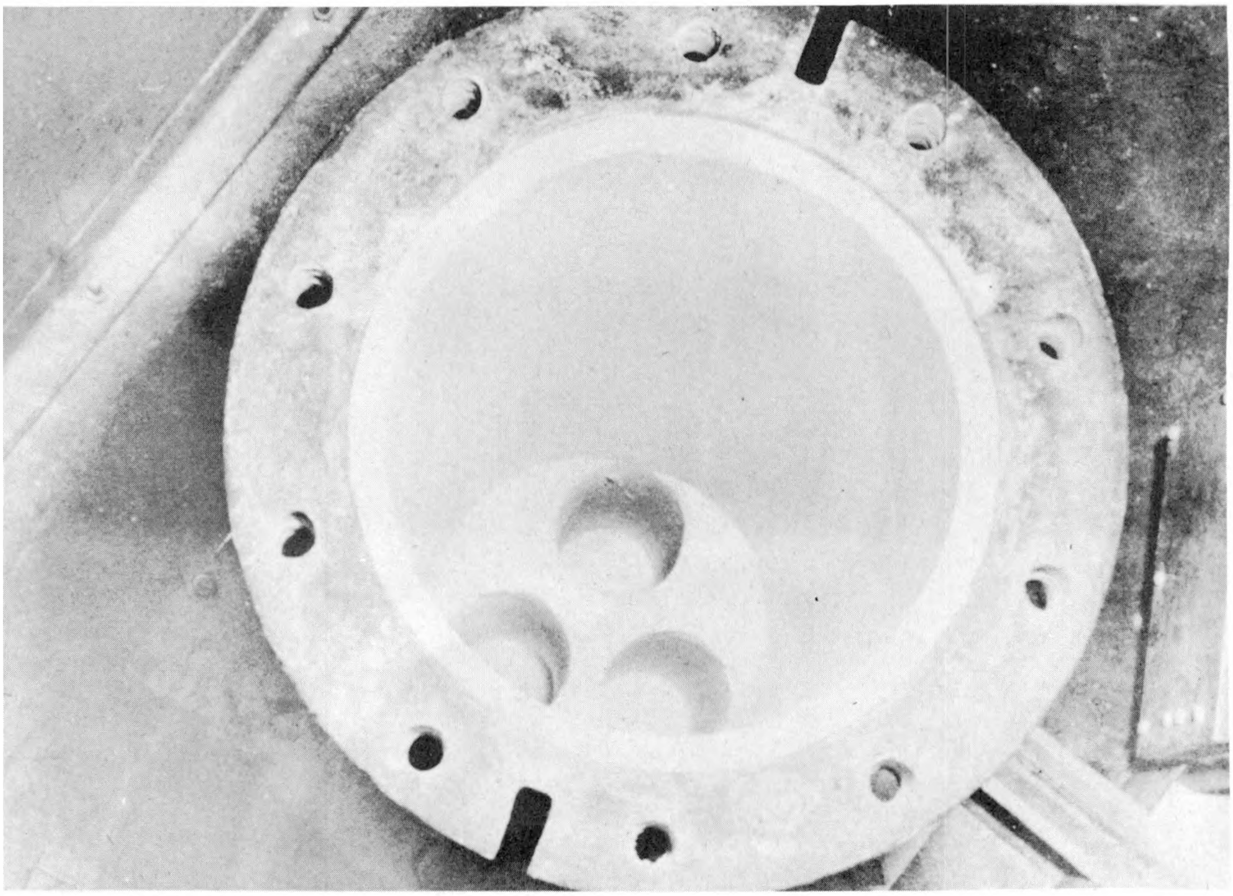


FIGURE 14.6-2 LINER FOR PIG REDUCTION

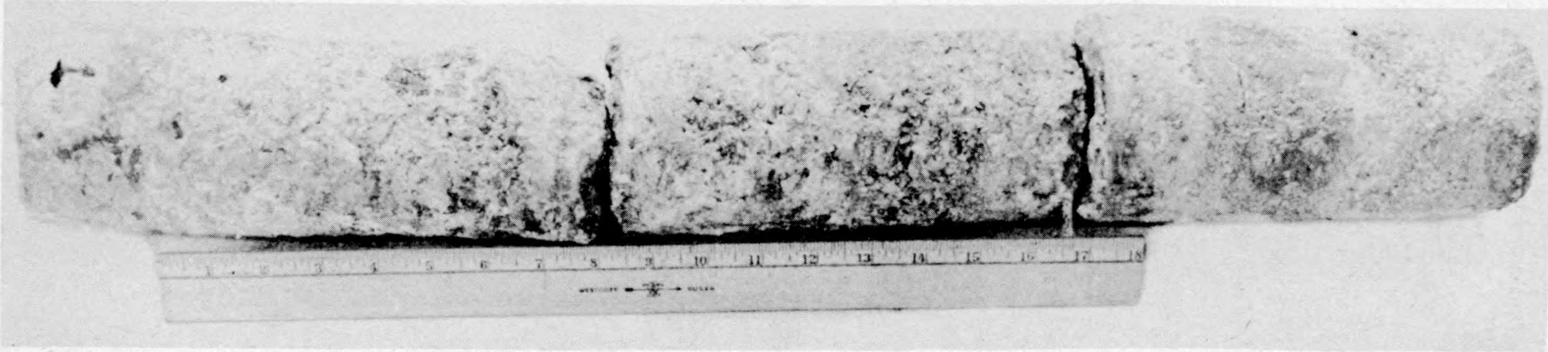


FIGURE 14.6-3   THREE PIGS (AS REDUCED)

Dezincing of the Pigs

Preliminary test showed that if these pigs are stacked vertically, they fuse during dezincing. The vertical-tube dezincing rack, shown in Figure 14 6 4, was designed to accommodate three pigs (which fuse to form an electrode) in each of six 4 inch ID stainless steel tubes. (Five tubes were located around the circumference and one in the center.) This would give a potential dezincing charge of 540 pounds.

The vertically split tubes were coated with magnesium zirconate (as directed in the SOP) before loading. Stainless steel bands were used to hold the tubes together during dezincing. Dezincing was not as complete as usual, as some zinc condensed on the lower surface of the tubes and was trapped by semi-plastic thorium-zinc alloy. This shortcoming may be eliminated in the future by providing vents around the bottom of the tubes to permit escape of these vapors.

In the first run, the appearance of the top of the electrode differed from that of the bottom 20 inches. However, in subsequent runs with Fiberfrax insulating rings around the top of the furnace, this zone was completely eliminated. This would indicate a definite temperature gradient at this point. The electrodes were cropped at the 20-inch level to give a smooth end for welding to the stub and to remove suspected high zinc-content metal. Analyses revealed, however, that the zinc content of the cropped metal was no greater than that of the bottom.

In some instances, erosion of the tube bottom plate was noted, indicating that a reaction had occurred between the stainless steel and the thorium zinc alloy. This has been noticed during normal operations and contributes to some extent to the Fe-Ni-Cr content of the metal. An analysis of a dezinced electrode is as follows:

ANALYSIS* OF DERBY ELECTRODE NO 2627

	TOP SAMPLE	BOTTOM SAMPLE
Al	30	40
B	0 4	0 2
Ca	200	4000
Cd	0 2	0 2
Cr	80	80
Cu	40	40
Fe	150	600
Mg	1500	1000
Mn	10	20
Ni	40	80
SiO_2	20	20
Zn	600	1000
C	307	233
N	128	78
P A I ** (ThO_2)	0 27%	0 11%

* *All values in ppm except where otherwise noted*

** *Perchloric acid insoluble*

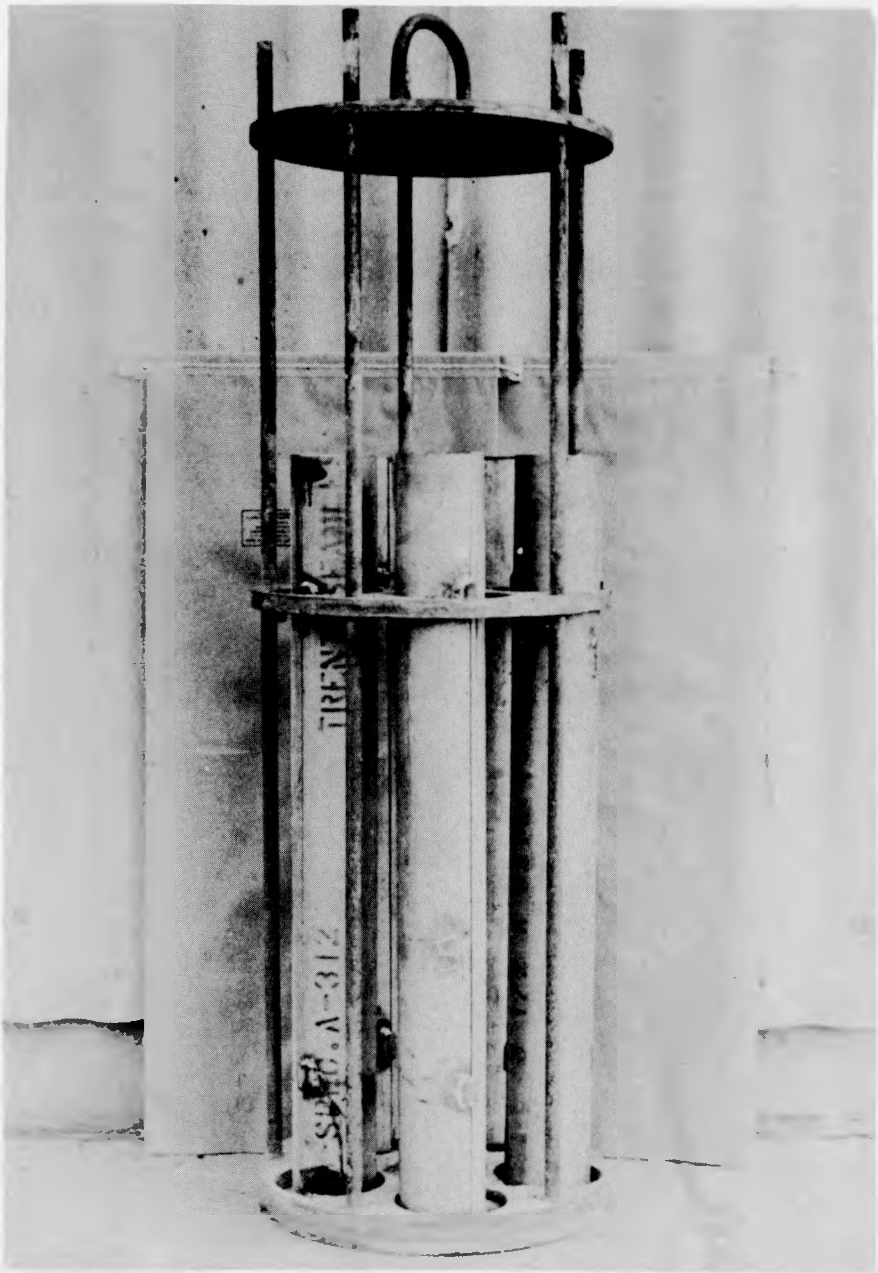


FIGURE 14.6-4 VERTICAL-TUBE DEZINCING RACK

The concentration of the more volatile Zn, Ca, and Mg can be reduced by subsequent melting and scalping.

Melting of Derby Electrodes

The first attempt to melt a derby electrode (Fig. 14.6-5) was made with an unscalped 4-inch electrode. A hole was burned in the 5½-inch-ID copper cup (mold) soon after an arc was struck, and further melting of 4-inch electrodes into 5-inch cups was abandoned. The electrode was then scalped to 3½ inches for melting into the 5-inch cup. The large metal loss obtained during that scalping indicated the need for melting the 4-inch electrode into a cup having an inside diameter of at least 6 inches. The welded electrode (shown in Fig. 14.6-6) was 34 inches long and weighed 132 pounds. This electrode was melted into a 7-inch copper cup and was sampled by the same procedure as is used for a secondary ingot. The analysis is as follows:

ANALYSIS* OF PRIMARY INGOT SP-1 (TOP SAMPLE)

Al	10
B	0.2
Ca	10
Cd	0.2
Cr	20
Cu	40
Fe	200
Mg	10
Mn	6
Ni	60
SiO_2	20
Zn	1000
Density (g/cc)	11.64
C	176
N	97
ThO_2(%)	1.76
U	15
Hardness (B.H.N.)	52

* ***All values are ppm except where otherwise indicated.***

This primary ingot met all of the specifications for secondary ingots except that for zinc. It is thought that changes in the dezincing step, such as providing holes in the tubes and/or using crushed dezincing feed, will reduce the zinc content to within the allowable limits. The use of crushed material in dezincing is discussed below.

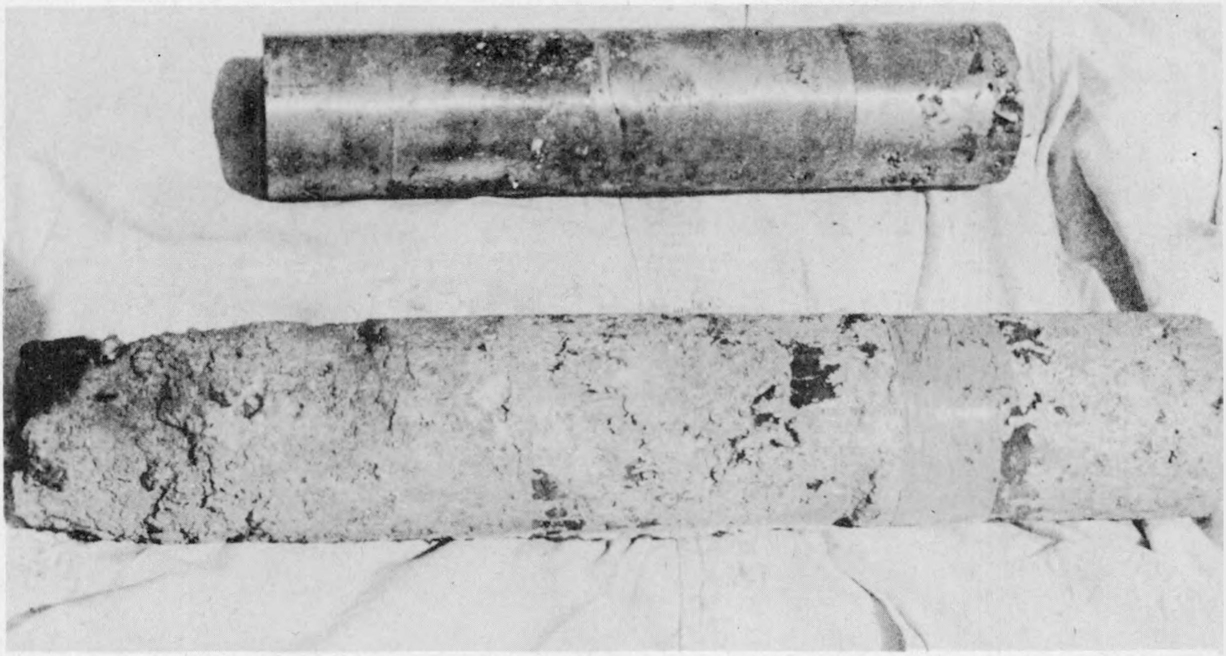
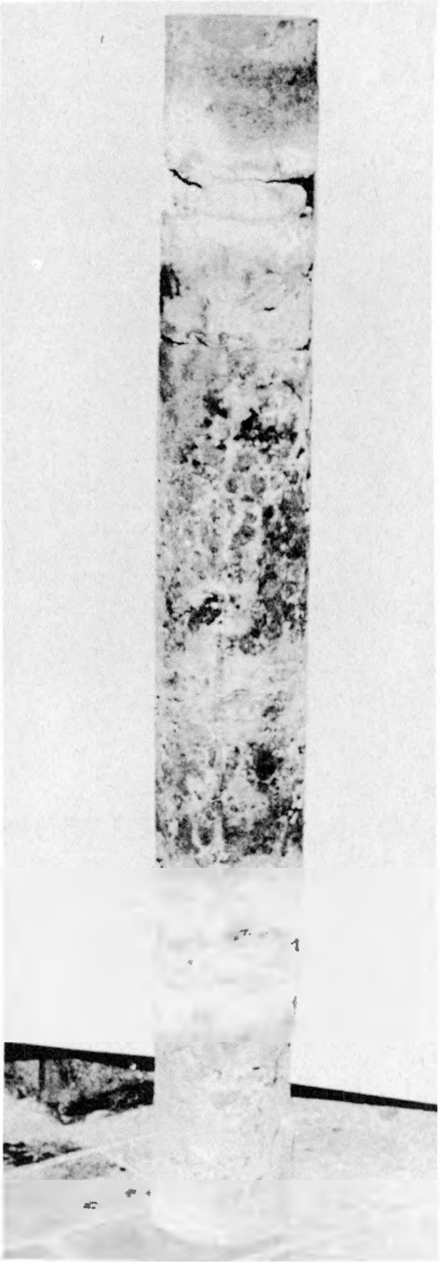


FIGURE 14.6-5 DEZINCED DERBY ELECTRODE BEFORE AND AFTER SCALPING



<u>FIGURE 14.6-6</u> DERBY ELECTRODE (WITH WELDED STUB AT TOP)

Dezincing and Melting of Crushed Alloy-Scrap Mixtures

The reprocessing of dezinced saw scrap (pieces having a cross section less than that required for welding) would greatly increase the yield through the Thorium Plant. After successful fusion of thorium alloy pigs was accomplished, it was thought that a crushed alloy-scrap mixture could be fused. Earlier work by W. B. Clymer using crushed alloy feed had been unsuccessful due to a lack of sufficient pressure on the pieces during dezincing. It was thought that adequate pressure could be applied and subsequent stub-welding eliminated by placing a stub of sufficient weight in the tube above the crushed material.

A 3-inch-OD stub weighing 25 pounds was placed in the 4-inch-ID tube on top of 50 pounds of crushed alloy-scrap mixture. The dezinced electrode that was formed (Fig. 14.6-7 and 14.6-8) had ample strength to permit melting without sawing or welding. The stub and the crushed mixture fused well enough to resist breakage during routine handling.

This 4-inch electrode was melted into a 7-inch cup at 4000 amperes and held a steady arc throughout the melt. The resultant ingot was sectioned to determine whether particles had fallen into the pool without melting. No evidence that this had occurred was found. This ingot was quite sound and showed good solidification characteristics. On the basis of these results, it is thought that at least 50 per cent of the scrap-alloy mixture in the dezincing tube may be scrap without affecting the strength of the electrode.

Conclusions

Although sufficient work has not yet been done to sustain conclusions, the potential of this method is apparent. Both a great saving in manpower through the elimination of sawing and welding operations, and an increase in plant production capacity through a reduction in the amount of scrap generated are quite possible.

Future Work

Future work will be aimed at developing the following studies:

1. Determination of metal quality by means of slug evaluation of dectrode (derby-electrode) material.
2. Determination of the optimum tube diameters and lengths.
3. Use of crushed alloy metal as dezincing feed and the possibility of single-melting this material through more complete zinc removal.
4. Blending of crushed scrap with crushed alloy metal prior to dezincing and its effect on metal quality.

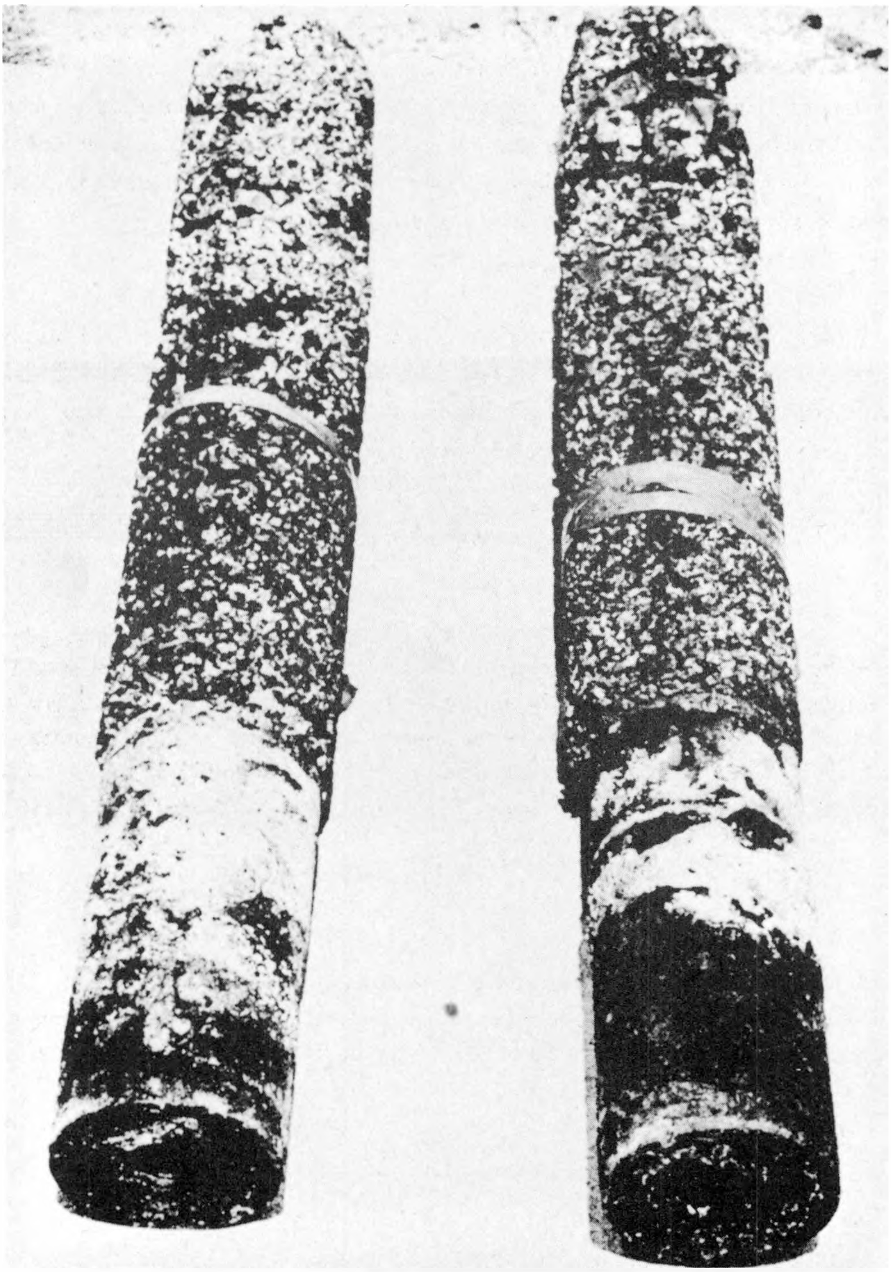


FIGURE 14.6-7 SINTERED ELECTRODES (WITH FUSED STUB)

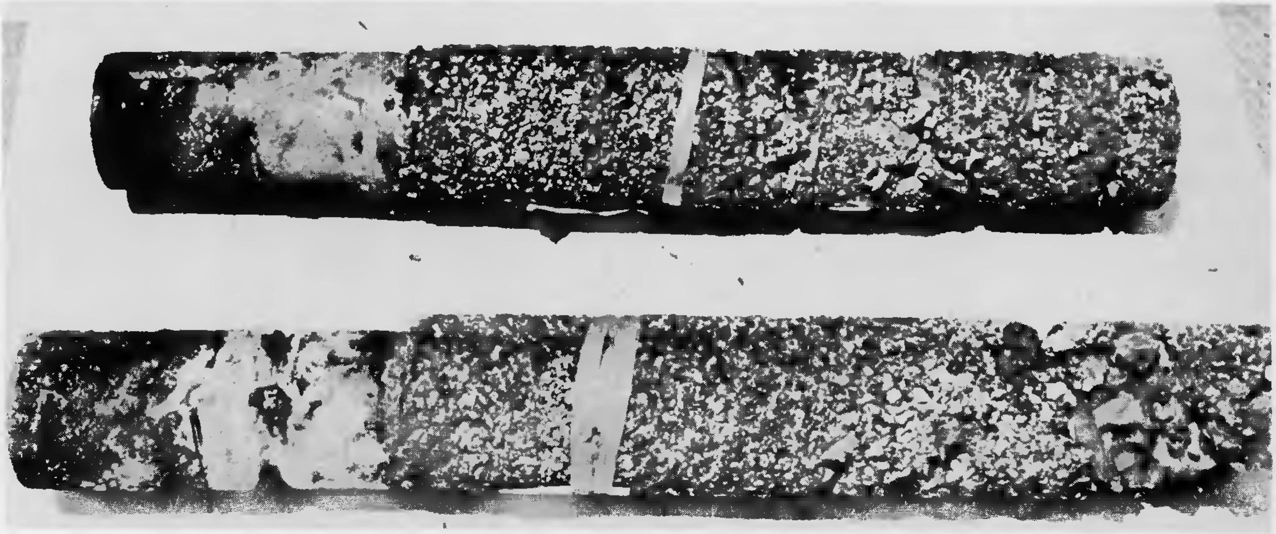


FIGURE 14.6-8 SINTERED ELECTRODES (WITH FUSED STUB)

5. Determination of the optimum conditions for the processing of derby electrodes or sintered electrodes.

6. Comparison of the cost of using the crushed electrode (with its greater efficiency) and the derby electrode (with its high production rate).

15.0 NEW PROCESSES AND SPECIAL PROJECTS

15.1 PREPARATION OF URANIUM SHOT - S. L. Reese and H. A. Kraus.

There has been considerable interest in uranium shot for the preparation of "matrix" fuel elements. Since green salt prill had been made here successfully,[7] we were encouraged to investigate preparation of uranium shot by the same method used in making prill, i.e., by pouring molten metal through small holes at the top of a 22-foot-high prill tube. Heat transfer calculations indicated that removal of heat from the uranium metal shot should be no more difficult than heat removal from green salt shot.

This investigation was instituted and met with some success.

Equipment and Procedure

The metal charges are melted by induction heating in a 13½-inch ID graphite crucible which has a plug in the bottom containing two holes. At about 2200°F, the molten metal pours, falling free for 22 feet at atmospheric pressure through a countercurrent flow of helium. The helium cools and thus solidifies the molten metal.

The problems encountered were as follows:

1. Choice of a wetting agent which would allow the use of small size holes.

2. Choice of hole size and design.

3. Choice of heat input level and helium flow rate.

It was observed that the molten uranium would not pour through holes which had diameters of less than 1/8 inch unless a wetting agent was used to enable the molten uranium to wet the graphite. This was attributed to the known high surface tension of high-melting-point metals. (The surface tension of metals melting near 1000°C is approximately 1000 dynes/cm, while that of water is 81.) To wet the graphite, two ounces of barium chloride was placed in the cup of the pour plate. This appeared to wet the graphite plate satisfactorily although barium chloride fuses and pours at about 1775°F, which is 400°F below the uranium pour temperature.

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[7] *Reese, S. L. and Kraus, H. A., Summary Tech. Rpt., pp. 72-74, NLCO–565, July 15, 1955.*

TABLE 15.1-1

PREPARATION OF URANIUM SHOT

RUN NO.	NO. OF POUR PLUG HOLES	SIZE (IN.) AND DESIGN OF HOLES	POUR TEMP (°F)	HELIUM FLOW RATE	WAS $BaCl_2$ USED?	REMARKS
1	2	1/32	Did not pour	None	No	Uranium did not enter the pour holes.
2	3	1/32, 1/16, 3/32	2200	None	Yes	The 1/16 in. and 3/32 in. holes poured 50 lb.
3	1	1/16-in.-ID tube	Did not pour	Back-filled to 10 in. Hg	No	Graphite tubes extended 1/8 in. inside and outside of pour plug.
4	2	1/32	Did not pour	None	Yes	A Carbocell plate was used below the crucible for more insulation.
5	2	1/16 tapered	Did not pour	None	No	Pour plug holes were tapered from 3/16 in. to 1/8 in. to 1/16 in.
6	2	1/16 tapered	2200	Back-filled to 10 in. Hg	Yes	58.5 lb poured, with some metal clinging to the tube wall. Some shot was formed.
7	2	1/16	2285	To 15 in. Hg	Yes	Intermittent pour for a total of 4 minutes. Some shot was formed.
8	2	1/16 tapered	2210	To 15 in. Hg and to 0 in. at end.	Yes	All 200 lb of metal poured in 9 minutes. Short (1/16 in. deep) hole eroded to 1/8 in. About 5 or 6 lb of shot formed.
9	2	3/64, 1/32	2250	75 cfh to 28 in. Hg; 25 cfh to 25 in. Hg	Yes	One stream poured for about 10 minutes. No shot evident. Product looked like sponge.
10	2	3/64	2210	75 cfh to 20 in. Hg	Yes	Poured for 12 minutes. Short lengths of wire formed and a small amount of fine shot.
11	2	3/64	Did not pour		Yes	A 10-inch crucible was placed inside the regular crucible.
12	2	3/64	2075	See Remarks	Yes	The 10-inch crucible split and poured through the crack. The helium was turned on and let flow at 150 cfh. The power was turned off but it still poured for 8 minutes. Two or three lb of shot was produced.

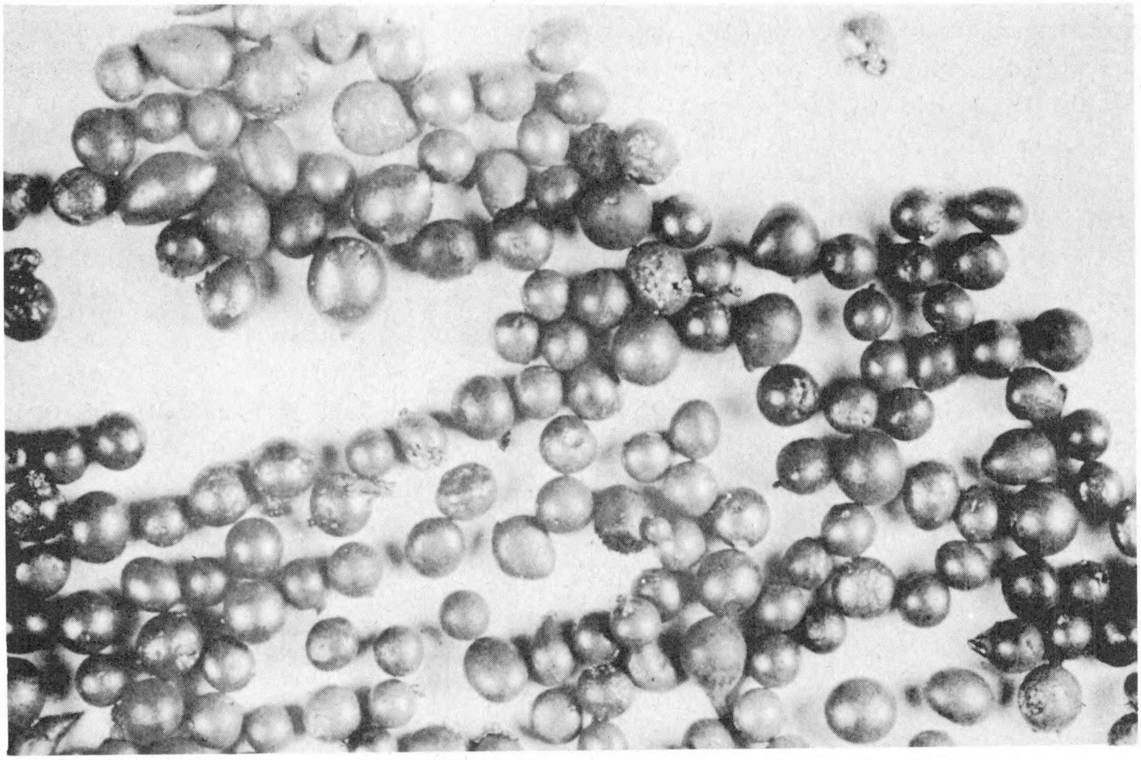

FIGURE 15.1-1 SCREENED SHOT

The size of the pour plug holes was varied. It was found impossible to make a pour when the hole size was less than 3/64 inch, even with the use of barium chloride. With a hole 1/8 inch or larger, the uranium poured readily (approximately 10 lb/min); however, this size stream is too large to produce satisfactory shot. Holes of 3/64 inch and 1/16 inch diameter were used for most runs, the former resulting in the best pours (Table 15.1-1). The pour holes eroded somewhat during the pour.

It was found to be very difficult to so balance heat input with helium flow that a flow of barely molten metal would drop through the pour slug holes. In one run, this relationship was such that short lengths of 1/32 inch uranium wire were produced. In most instances, the pour stream wavered and as a result was difficult to direct to the center of the shot tube.

The material that poured was screened with the use of a vibrating tray. Shot and nearly spherical pieces weighing eight pounds were obtained (Fig. 15.1-1).

In future work, other salts whose melting temperatures are near that of uranium will be evaluated as wetting agents, a special pour block will be used, and other methods of chilling the molten shot will be tried.

15.2 TIME FOR BETA TRANSFORMATION OF URANIUM AT 685°C, 695°C AND 715°C - R. L. Griffith.

At the present time, 735°C is used as the beta transformation temperature in the heat treating of uranium in salt baths. It has been suggested that different beta-transformation temperatures should be investigated in an effort to obtain a more uniform, less stressed, and randomly oriented heat-treated structure. It was thought that a less stressed structure could be obtained if the bath temperature were lowered to approximately 700°C, as there would then be less thermal shock associated with the quench.

In this study, the minimum time for transformation was determined at 695 ±5°C, although on a production basis the operating range of the beta heat-treating furnace would be 705 ±5°C. This safety factor should allow for temperature fluctuations and temperature gradients in the production salt bath. In addition, salt bath temperatures that represent greater variations than are normally encountered were investigated to determine their effect on the time required for beta transformation.

Method

Fifty 1.430-inch diameter rods, 8.5 inches long, were available for the determination of the beta transformation time at 700°C. A ½-inch metallographic sample was cut off each rod for the determination of the original structure of the rod.

A small Rockwell electric resistance furnace was used to heat a cast-iron pot containing approximately 70 pounds of carbonate salt of the eutectic composition, 46 w/o Li_2CO_3:54 w/o K_2CO_3. A platinum, platinum-13 per cent rhodium thermocouple in a stainless steel protection tube was immersed in the salt bath to check the temperature of the salt. The uranium rods were held in steel clamps during heat treating and were treated while in a vertical position. This installation is shown in Figure 15.2-1.

After heat treatment, the rods were quenched in approximately 30 gallons of still water, which was maintained at a temperature of 40° ±5°C. The transfer time from the salt bath to the quench was maintained at 20±3 seconds, with the rod being held over the salt bath for approximately 10 seconds of this time.

Following the heat treatment, a 1¼-inch discard was cut from each end of the rod to eliminate the "end effect" and to minimize any effect the heat-treating clamp might have had upon the final structure of the rod. A ½-inch metallographic sample was then cut from the rod and submitted for analysis. The metallographic samples were given a bright field etch and photographed at 8X, which gave sections that included the edge and the center of the samples.

After the time for beta transformation was determined at 695°C, the time for beta transformation was determined at 675°C and 715°C. At each temperature, ten rods were heat treated for 1 to 10 minutes in one-minute increments.

Results

The times for transformation to the beta phase were: 4 minutes at 715°C, 6 minutes at 695°C, and more than 10 minutes at 675°C. Since the time for transformation at 675°C was so long, 10 additional rods were treated at 685°C. The time for transformation at this temperature was determined to be 7 minutes.

Since only one sample was heat treated at each time to obtain the above results, six additional samples were heat treated at 685°C, 695°C, and 715°C for time periods close to the transformation times. The structures resulting from these heat treatments are shown in Figures 15.2-2, 15.2-3, and 15.2-4. They establish the times for the transformation at 4 minutes at 715°C, 5 minutes at 695°C, and 7 minutes at 685°C.

Summary and Conclusions

The minimum times for uranium to transform to the beta phase are as follows:

TEMPERATURE (°C)	TIME (min)
715	4
695	5
685	7

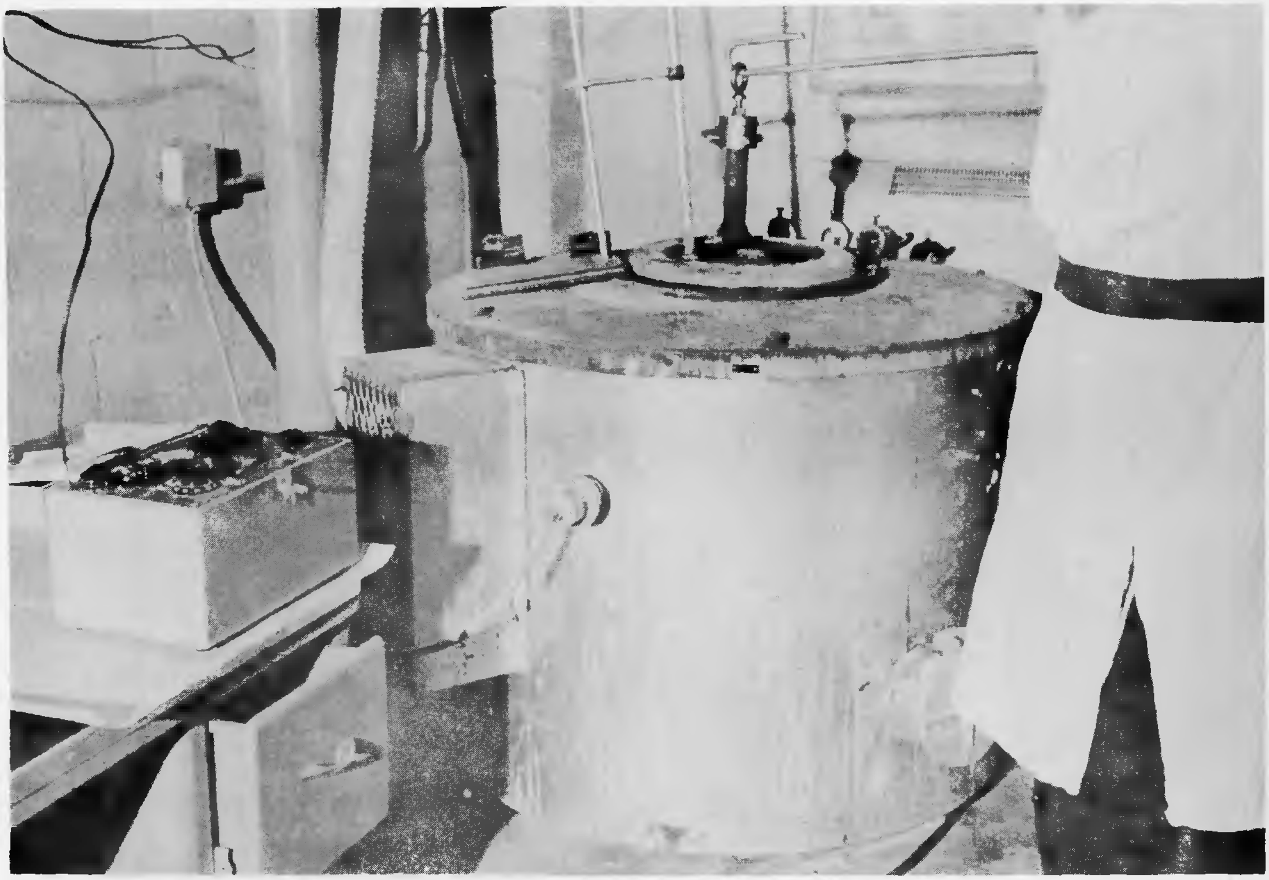

FIGURE 15.2-1 LABORATORY HEAT-TREATING FURNACE

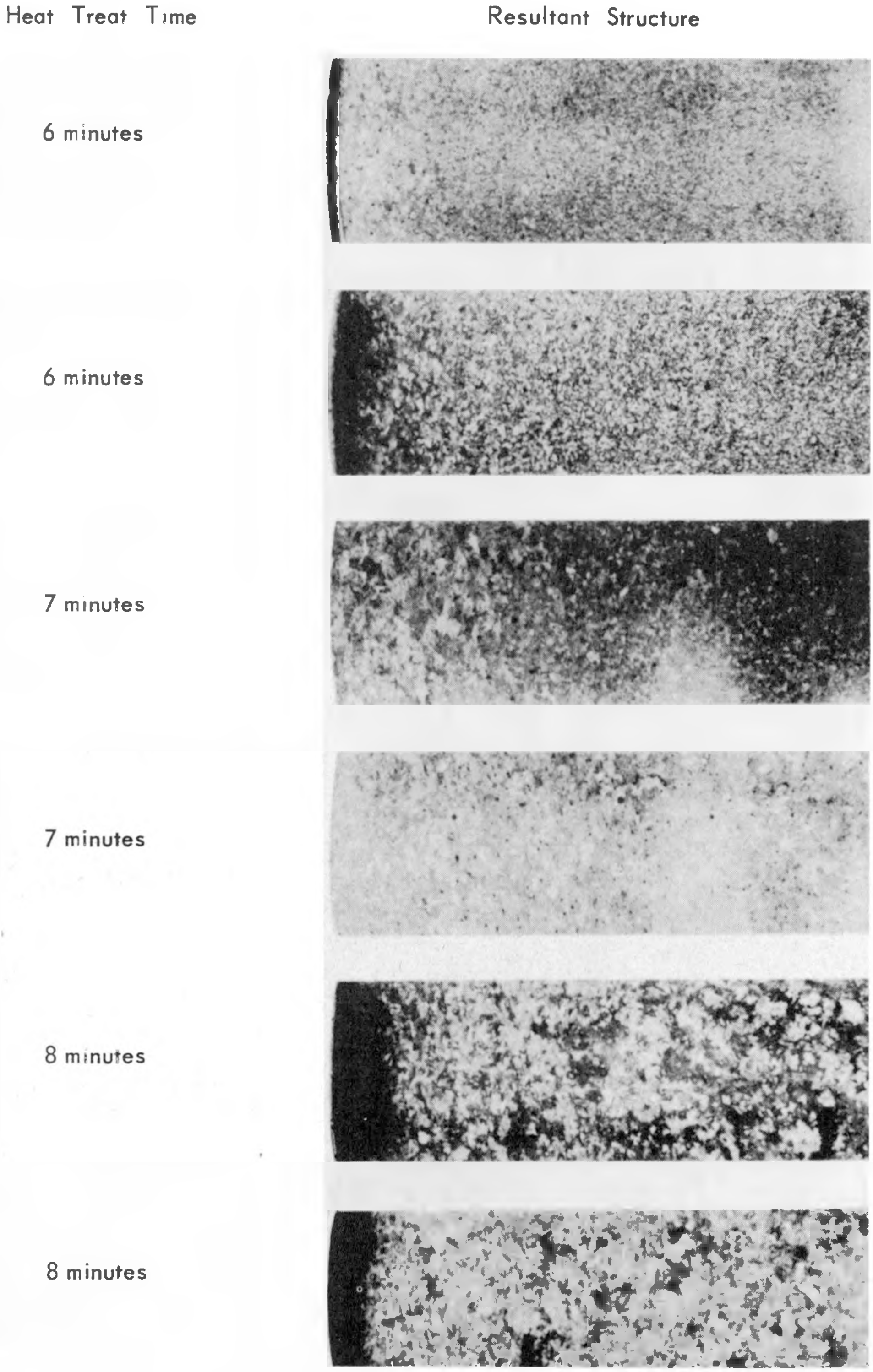

FIGURE 15.2-2 TIME FOR BETA TRANSFORMATION AT 685°C

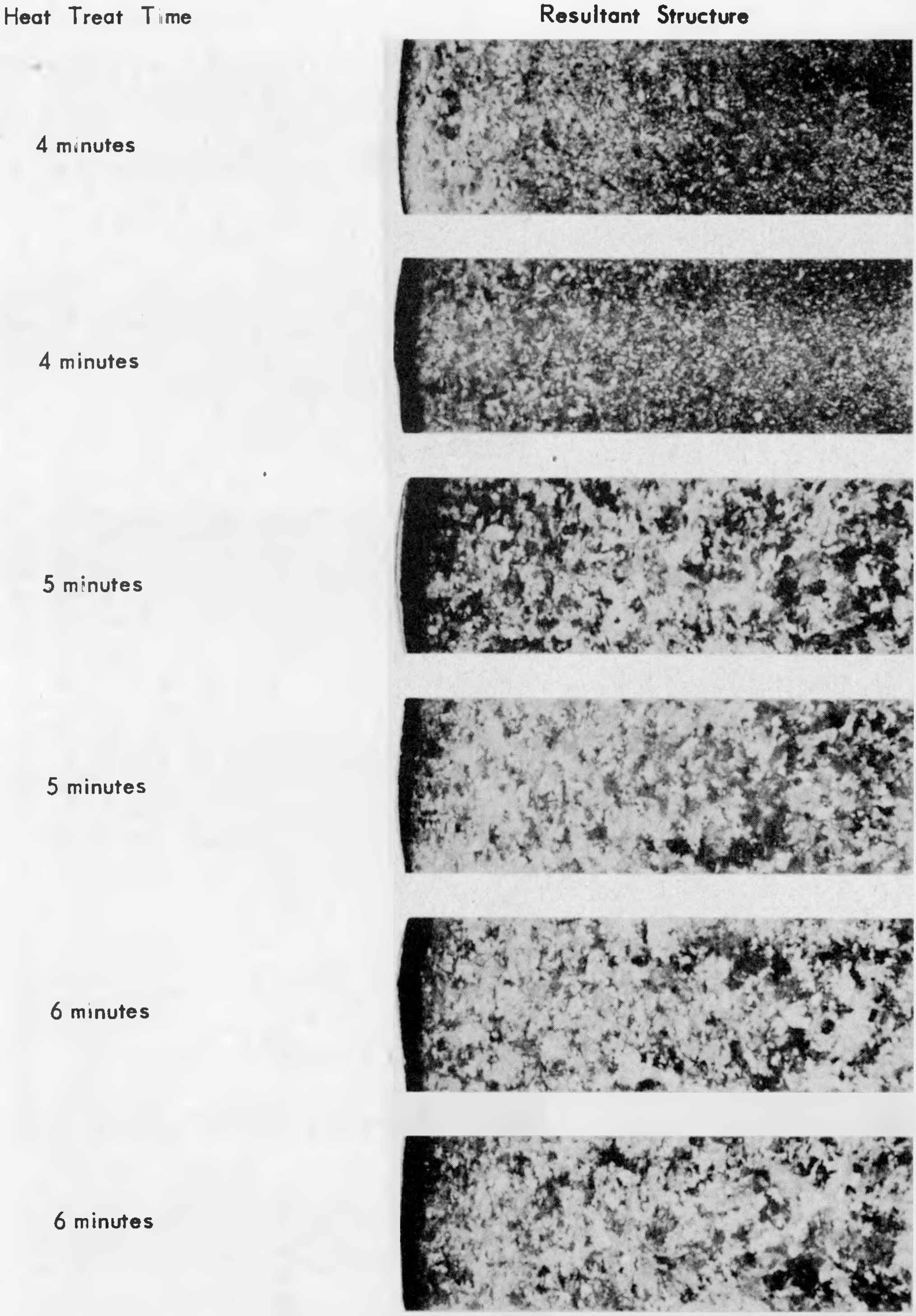

FIGURE 15.2-3 TIME FOR BETA TRANSFORMATION AT 695°C

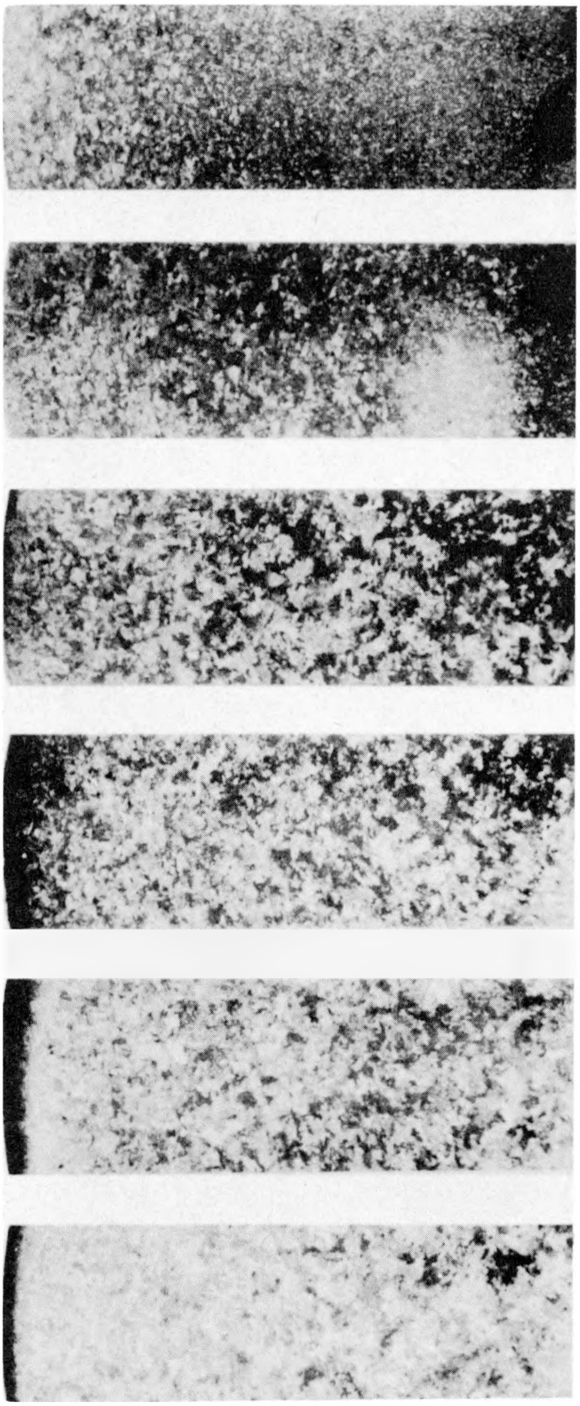

FIGURE 15.2-4 TIME FOR BETA TRANSFORMATION AT 715°C

Future Work

Work will be done to determine the effect of various heat-treating temperatures on the rate of hydrogen pickup in the heat-treated rods. The effect on the final structure of different quenching rates and quenching mediums will also be determined.

15.3 GRAIN SIZE OF BETA HEAT-TREATED URANIUM - A. E. Guay.

When alpha fabricated uranium is heat-treated in the beta temperature range, the resultant structure shows grains that are coarse, very ragged in appearance, and irregularly shaped and also shows "subgrains" and "ghost" grains. Accurate notation of a true grain is therefore very difficult. Measurement of the grain size of beta-treated uranium is required for the following reasons:

1. The measured grain size can be used in controlling the operation of the heat-treating process.

2. The grain size is thought to be directly related to the magnitude of the "bumping" that forms on the surface of the metal during irradiation.

Grain size is of prime importance to the companies represented on the Metallography Subcommittee of the Metal Quality Working Committee (on uranium). These include not only the companies that produce the metal and the bare fuel elements (Mallinckrodt Chemical Works and National Lead Company of Ohio) but also the pile operators (General Electric, Hanford, and E. I. duPont, Savannah River). Also participating in this work is Battelle Memorial Institute.

A cooperative program of investigation has been started. Preliminary consideration by the Subcommittee resulted in the decision to attempt to correlate the beta-transformed structures with the structures that result from annealing in the high-alpha temperature range (instead of employing direct measurements on the beta-transformed structure). This correlation was attempted because the alpha annealing causes a refinement in the beta-transformed grains such that small, uniform, equiaxed grains result. Though the mechanism of this refinement is not positively known, it is assumed to be polygonization rather than recrystallization. To motivate the refinement, residual stress, which results from the water quench that follows the beta soak, must exist; structures that have been air-cooled do not refine upon annealing.

The work covered by this report was aimed at correlating the apparent grain size of beta-transformed samples with the grain size of those same samples after they were annealed.

Procedure

Approximately 150 samples were cut from an equal number of bare fuel elements, which had been machined from rods which had been alpha-rolled and air-cooled and then beta-heat-treated and water-quenched. The samples were approximately ½ inch long in the direction of rolling and were split in half along a central longitudinal plane. This central longitudinal plane was rough-ground on water cooled rotating silicon carbide laps down to 400-grit size. Then they were given a final polish with 6 micron diamond paste on a cotton toweling covered rotating lap. To delineate the grain structure, the samples were electro-etched for three minutes at 27 volts dc in a solution of chromic and acetic acids

The samples had a flat, polished face approximately 1.35 inches in diameter and were photographed at 8X to show their structure from the edge to the center of the sample. Having been photographed, the samples were annealed for 20 minutes at 640°C in a 45:55 weight per cent eutectic salt mixture of Li_2CO_3:K_2CO_3. To insure a uniform heating period, the samples were removed from the salt bath, held in air for 15 seconds, and quenched in water held at 40°C.

Samples in the annealed condition also were polished and photographed by the method described above.

Results

The photomacrographs of the beta-treated samples were arranged in order of decreasing apparent grain size. This was reasonably easy to do because of the following factors:

1. Magnification at 8X effectively suppressed the effect of the "subgrains". The large irregular grains were easily viewed. The rating of grain size was thought to be not only reasonably accurate from sample to sample but very precise for the extremes of the range.

2. The use of a bright field etch lessened the effect of ghost grains, which are prevalent in micro studies when a polarized etch is used.

The corresponding photomacrographs of the structures after alpha annealing were placed beside the photomacrographs of the beta-treated samples. Two observations were made:

1. There was no relation between the apparent grain size of the beta-treated specimens and the structures resulting from an anneal for 20 minutes at 640°C.

2. Not all of the heat-treated samples responded to the anneal to the same degree. Some of the structures were very uniform in grain size from the edge to the center of the specimen; others showed patches of new grains that were equiaxed and other patches that were quite ragged. Yet other samples showed equiaxed grains at both the edge and center but a large variation in grain size from edge to center.

Conclusions

1. It is apparent that the grain size of beta-treated material cannot be related to the grain size of that metal after it has been given an anneal at 640°C for 20 minutes.

2. If it is true that residual stess is required to effect the "polygonization"[r] mechanism, all samples that were used did not contain the same amount of stress. Possibly, if the residual stresses had been the same, the structures would have been correlated.

Future Work

Future work will be aimed at determining the reproducibility of grain size determinations on beta-treated samples. Whereas previous work has involved mainly techniques at 100X magnification with polarized etches, future work will be at lower magnifications and bright field etches will be used.

Much of the planning that has been done and will be done is to be credited to the Subcommittee as a whole.

15.4 HYDROGEN IN BARE FUEL ELEMENTS - A. E. Guay.

A bilateral program, which is aimed at relating the hydrogen content of bare fuel elements to their canning behavior, is being carried on by the General Electric Company (Hanford) and the National Lead Company of Ohio (Fernald). This program is one of the main sources of data for the Hydrogen Subcommittee of the Metal Quality Working Committee (uranium).

Essentially, this program has the following aims:

1. Improvement of existing vacuum hot-extraction methods for determining the total hydrogen content of metal samples.
2. Improvement of sampling techniques.
3. Examination of the variables in the manufacturing of bare fuel elements with a view to lowering the hydrogen content of the fuel elements.

5. Development of an analytical method that will give a measurement of the gas content of a bare fuel element that is related to its canning performance.

It is thought that objectives (1) and (2) above need no explanation, but that the investigations leading to the latter three objectives should be described: A preliminary survey was made[1] whose objective was to establish the level of hydrogen in the various metallic intermediate products (ingot, billet, rod) and in fuel elements. Its results showed that a fuel element machined from an alpha rolled rod had a lower hydrogen content than an equivalent fuel element derived from a rod that had been heat-treated. This work confirmed the work of Gardner,[2] who had shown that the hydrogen content of metallic uranium varies with the heat treating technique. Thus, the heat-treating operation was suspect, but the cause and nature of the hydrogen absorption remained to be proved.

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[1] *Guay, A. E., Summary Tech. Rpt., pp. 173-181, FMPC-540, April 15, 1955.*

[2] *Gardner, H. R., An Investigation of Specific Processes which Influence the Hydrogen Content of Uranium, p. 14, HW-33725, January 7, 1955.*

Study of Production Operations

Though there was an urgent need to examine the variables of the production heat-treating operation in order to learn the nature of the hydrogen absorption mechanism, there was an even more urgent need to avoid the production of a non-cannable product. Since the mechanism was in doubt, no corrective measures were applied immediately and the work was undertaken as described below:

1. The production operation was observed and the values of all variables were recorded.

2. As the data indicated the source of trouble, the most feasible remedial treatments were adopted.

3. As production data were obtained, laboratory experiments were set up to shed some light on the problem.

Beginning on April 18, 1955, samples were taken from:

1. The salt from the beta heat-treating furnace. Dip samples of the molten salt (45:55 Li_2CO_3:K_2CO_3) were allowed to freeze on a steel rod inserted in the bath. These samples were analyzed[7] to determine their alkalinity.

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[3] *Guay, A. E., Hardt, H. A., Kattner, W. T., and Ruehle, A. E., Quart. Rpt. of the Working Committee on Metal Quality and Fabrication, pp. 20-26, MCW-1375, March, 1955.*

[4] *Kattner, W. T., A Compendium of Recent HAPO data on Hydrogen in Uranium, HW-33876, November 23, 1954.*

[5] *Guay, A. E., Hart, H. A., Kattner, W. T., and Ruehle, A. E., loc. cit.*

[6] *Jenkins, F. E. and Hall, C. F., Summary Tech. Rpt., pp. 172-174, NLCO-565, July 15, 1955.*

[7] *Gessiness, B., Gerhardt, E., and Tieman, E., Summary Quart. Rpt., p. 205 FMPC-505, January 15, 1955.*

2. A heat treated rod from the allotment for HAPO (one fuel element daily). From this element, two 1-inch long samples were cut; a 5-minute hot extraction was made at 600°C on both of the samples and afterward the temperature on one of the samples was raised to 820°C and the total hydrogen content measured.

In Figure 15.4-1, it can be seen that by the end of the third week in June, a complete cycle had occurred, from increased alkalinity of the salt bath through decreased alkalinity. From hydrogen data then available, it was apparent that the curves for hydrogen content after 5-minute hot extraction and after total hot extraction were parallel to the alkalinity curve. Not yet shown, however, was the mechanism between the hydrolysis of the salt bath and the hydrogen content of the metal. This could be determined if:

1. The source of water vapor could be found (though the absolute humidity was suspected) and
2. The complementary mechanism that resulted in the production of hydrogen could be demonstrated.

It now seemed reasonable to attempt a first remedial treatment. Prior laboratory experiments had indicated that the alkalinity of the salt bath could be reduced by the addition of CO_2 gas:

$$2LiOH + CO_2 \longrightarrow Li_2CO_3 + H_2O$$

It was thought probable that sparging the salt bath with CO_2 would also remove the water that resulted from the above reaction.

To determine the relationship between humidity and CO_2 gas additions, the amount of CO_2 gas bubbled through the salt bath was gradually increased and the absolute humidity readings were recorded daily. (Fifty pounds of CO_2 gas had been added each day in order to reduce the alkalinity of the bath and to increase the life of the electrodes.)

Reference should be made to Figure 15.4-2, which shows a plot of the absolute humidity, the rate of CO_2 introduction, and the observed OH ion concentration of the salt bath. It may be seen that for the period, April 18 through June 17, the alkalinity of the bath varied directly with the absolute himidity. For the period beginning with June 6, the CO_2 additions to the bath were constantly increased and as the relative humidity rose, the OH ion concentration rose. However, during the second week of July, when approximately 100 pounds of CO_2 was being added each day, the hydrolysis reaction was reversed and the alkalinity decreased rapidly until the second week in August.

Simultaneous examination of Figures 15.4-1 and 15 4-2 indicates that the hydrolysis of the salt bath varies directly with the absolute humidity. The hydrogen content of the uranium metal may then increase with increasing moisture in the salt bath by the reaction,

$$U + 4H_2O \longrightarrow U(OH)_4 + 2H_2.$$

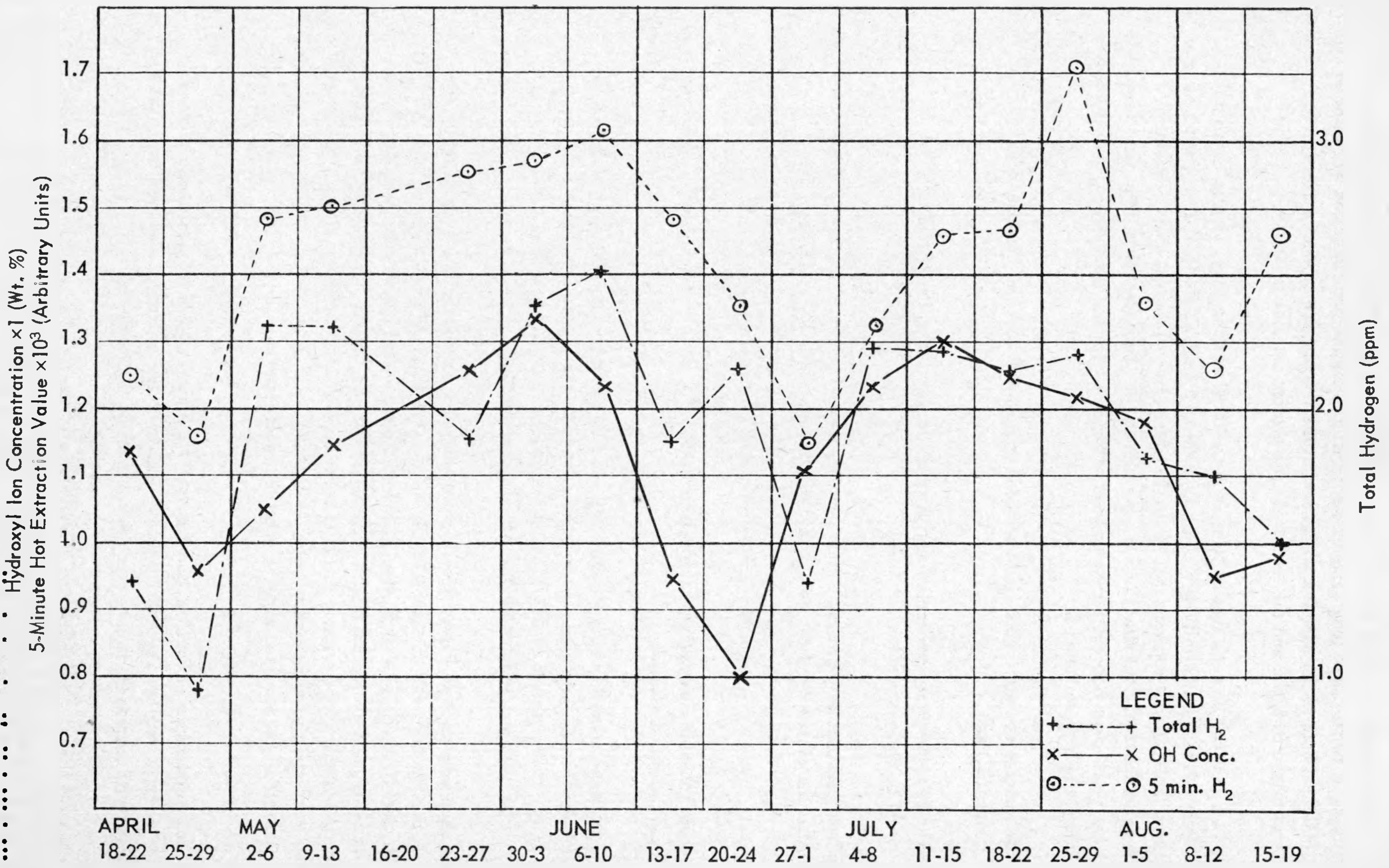

FIGURE 15.4-1 A RUNNING PLOT OF WEEKLY AVERAGES OF SALT BATH ALKALINITY AND HYDROGEN CONTENT OF FUEL ELEMENTS

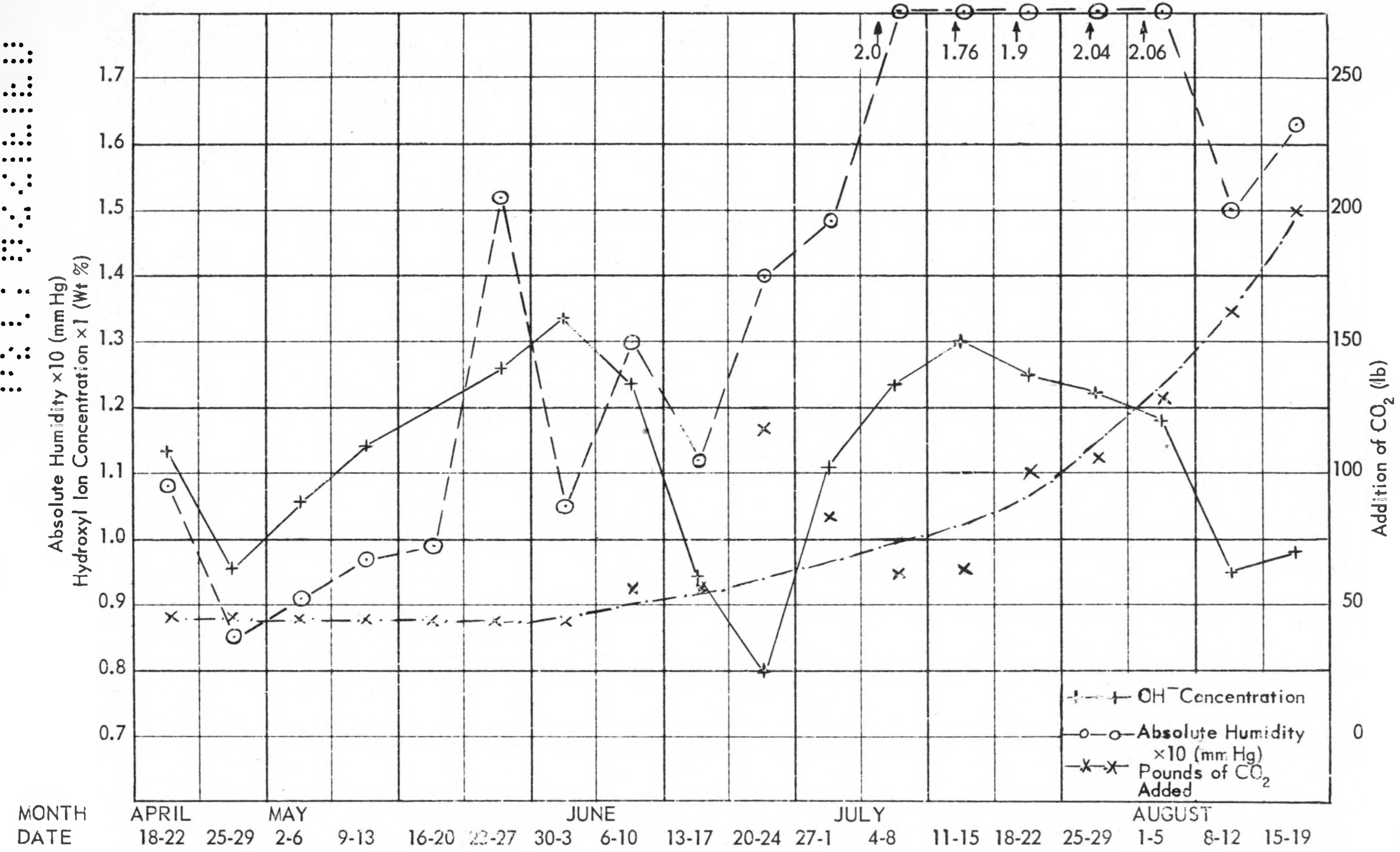

FIGURE 15.4-2 A RUNNING PLOT OF WEEKLY AVERAGES OF SALT BATH ALKILINITY, ABSOLUTE HUMIDITY, AND CO_2 ADDITIONS

Admittedly, there is a limited amount of data here, but high humidity is considered to be the condition necessary for a high hydrogen content of fuel elements that are processed without the benefit of CO_2 gas additions to the salt bath. This hypothesis is further substantiated by the data in 1954, when no CO_2 additions were made. During the humid summer and fall months of 1954, the metal was high in hydrogen and HAPO suffered severe canning rejection rates.

Laboratory Experiments

To investigate the roles of relative humidity and the sparging of the salt bath with the gas, preliminary laboratory work was done. Using a small muffle furnace holding 70 pounds of the molten salt mixture, the relative humidity over the bath was raised by sealing the room and boiling water in the room. This produced a high OH ion concentration in the bath, but difficulty with analytical techniques has prevented accurate determination of water content.

Lacking water vapor analyses to support the theory, it has been shown that CO_2 gas (whether added as a blanket over the bath or bubbled through the bath) will effectively lower the OH ion concentration by the reaction,

$$2LiOH + CO_2 \longrightarrow Li_2CO_3 + H_2O.$$

When reliable analytical methods are developed for measuring the water content of the salt bath, an attempt will be made to determine how CO_2 gas additions lower the OH concentration. The chemical reaction given in the previous paragraph will be compared with the mechanism of CO_2 gas going into the salt bath dry and coming out laden with moisture.

Summary and Conclusions

Based on observations of the variables, (the hydrogen content of the metal and the alkalinity of the salt bath) a hypothesis is presented that relates the hydrogen content of the heat-treated metal to the absolute humidity. It has been shown that the hydrolysis of the salt bath varies directly with the absolute humidity, and that the water vapor that is necessary for this hydrolysis may be eliminated by either bubbling CO_2 through the bath (mechanical combination) or by blanketing the bath with the CO_2 gas.

Admittedly, a small percentage of the fuel elements were sampled and there is urgent need to develop a short-duration hot-extraction test that will allow a greater number of samples to be analyzed. At the same time, workers at HAPO recognize that they require a nondestructive test that will evaluate the exact amount of porosity encountered in the bonding layer of the canned assemblies, so that a direct correlation of the porosity with the gas content can be made.

Future Work

Recording of routine data of the production operation will be continued during ensuing quarters. It is thought that if the yearly cycle of the humidity follows the patters of 1954, addition of CO_2 gas to the production salt bath will prevent a great many fuel elements from having a hydrogen content that would be detrimental to the yields of the canning operation at HAPO.

The Analytical Department now believes that they have developed an analytical technique that will yield precise values of the water vapor content of the salt samples. This will allow resumption of laboratory investigations of the mechanisms that interrelate humidity, hydrogen content, and CO_2 gas additions.

15.5 DEVELOPMENT OF TECHNIQUES FOR THE CENTRIFUGAL CASTING OF SLUGS - E. B. Blasch, G. E. Wuller, J. C. Straub, V. G. Minutolo, and J. W. Natwick.

A series of twelve heats involving dilute zirconium, silicon, and molybdenum alloys of uranium were centrifugally cast during the past quarter. Previous reports[1,2,3,4] on this project describe the equipment and the operational methods used. A variety of casting conditions were examined. Pour temperatures as high as 2800°F were used for some of these alloys. Vacuums of 10^{-3} to 10^{-2} mm Hg were maintained, and very satisfactory operation of the mold rotation equipment was achieved.

Considerable attention has been given to obtaining optimum vacuum pumping capacity and minimum mechanical in-leaking. Difficulty had been encountered in maintaining a vacuum seal on the rotary casting table shaft, but this was eliminated by incorporating a liquid-well seal at the point where the shaft enters the furnace.

Thermal cycling at the higher temperatures has caused cracking of the coil insulating refractories and subsequent heat loss. Thermal dissociation has resulted in lowering of vacuum at high operating temperatures.

The castings produced have exhibited remarkable internal soundness. It has been found that proper control of mold filling can impart a high degree of surface smoothness and prevent cold shutting during solidification. An attempt has been made to obtain essentially gravity filling conditions and then to impart maximum centrifugal force during solidification within the mold. Speeds of 500 to 600 rpm have commonly been used in this operation, though higher speeds may be obtained at a later date.

A typical cycle for this series of runs is:

TIME	METAL TEMPERATURE (°F)	VACUUM (μHg)	LEAK RATE (μHg/min)	REMARKS
1200	80	10	25	Power on.
1240	2000	15	- -	Power at 15 kw; melted.
1250	2300	15	- -	Power at 25 kw; bubbling.
1300	2500	10	- -	Pour

Approximately 32 pounds of homogeneous vacuum-melted alloy stock is charged for each heat. Fourteen slugs result and a recovery of 98 per cent is obtained in crude castings. An average cropping loss of 20 per cent that is presently being experienced is associated with pouring on a cold graphite distributing block. Although the cropped ends are remeltable scrap, this factor should be improved upon. A possible solution may be the use of a pour block that is better insulated.

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[1] *Stapf, A. J. and Natwick, J. W., Summary Tech. Rpt., pp. 120-122, FMPC-475, October 15, 1954.*
[2] *Stapf, A. J. and Natwick, J. W., Summary Tech. Rpt., pp. 191-200, FMPC-505, January 15, 1955.*
[3] *Stapf, A. J., and Natwick, J. W., Summary Tech. Rpt., pp. 164-172, FMPC-540, April 15, 1955.*
[4] *Stapf, A. J., Summary Tech. Rpt., pp. 148-164, NLCO-565, July 15, 1955.*

16.0 ANALYTICAL DEPARTMENT – "WET CHEMICAL" DEVELOPMENT

16.1 RAPID DENSITY DETERMINATION OF HIGHLY CONCENTRATED URANYL NITRATE SOLUTIONS - J. Werdmann and E. A. Brown.

It was necessary to make density determinations on "boildown solutions" of uranyl nitrate. This type of solution solidifies at a temperature range of 200° to 250°F. Densities may vary between 2.2 and 2.6 g/cc.

A rapid procedure was established in which a balance and a stainless steel plummet were utilized in making the tests by the displacement principle.

16.2 STUDY OF THE METHOD FOR DETERMINING HCl-INSOLUBLE IN ORANGE OXIDE - M. Jursik and E. A. Brown.

A study was initiated to determine the effect of certain variables on the results of the "HCl-insoluble" test. The test is, of course, empirical and must be standardized. The method that is used at NLO is summarized as follows:

1. A 10-gram sample of orange oxide is added to 40 ml of 1:3 hydrochloric acid and stirred until the major portion is dissolved.
2. The solution is warmed on a steam bath to complete dissolution of material other than that which appears to be contaminants.
3. The solution is cooled to room temperature and filtered through a sintered-glass crucible.
4. The residue is dried at 110°C and weighed.

Tests that were conducted to determine the effect of varying acidity revealed that HCl/water ratios of 1:2, 1:3, 1:5 and 1:7 caused no significant change in results. However, additional tests in which digestion time was varied yielded the results that are given in Table 16.2-1.

A visual examination of the residues showed that the orange oxide was completely dissolved in all samples within the five-minute period. Further digestion caused the dissolution of black oxide and other foreign material. A five-minute digestion time was adopted as the standard procedure

TABLE 16.2-1

VARIATION OF DIGESTION TIME IN THE DETERMINATION* OF HCl - INSOLUBLE

SAMPLE NO.	DIGESTION TIME (min)			
	1**	5	15	30
1	0.55	0.39	0.19	0.03
2	0.34	0.24	0.09	0.01
3	2.86	1.22	0.92	0.57
4	0.50	0.26	0.11	0.06

* *Values given are per cent insoluble.*

** *A small amount of yellow residue was observed.*

16.3 DETERMINATION OF ZIRCONIUM IN URANIUM-NIOBIUM-ZIRCONIUM ALLOY -

F. E. Jenkins and M. Jursik

Zirconium in ternary niobium-uranium alloy is now being determined by a volumetric method that is a modification of the versene - bismuth method described by Fritz and Johnson.[1] This method replaces the conventional gravimetric-phenylarsonic acid method, which is a time-consuming operation. The procedure is summarized as follows:

The samples of alloy are most conveniently dissolved by (1) conversion of the metal to oxides, (2) fusion of the oxides with potassium pyrosulfate, and (3) dissolution of the melt with nitric acid. An aliquot of the nitric acid solution is stripped of excess uranium with tributyl phosphate Shell Dispersol (30% TBP), and the aqueous phase is evaporated to fumes of SO_3. An excess of standard sodium dihydrogen versenate solution is added, and the excess is titrated with standard bismuth solution to a yellow thiourea end point. A pH of 2 should be maintained during the titrations.

A series of standard samples which simulated the composition of the 2 per cent niobium, 5 per cent zirconium, 93 per cent uranium alloy were analyzed. The results are shown in Table 16.3-1.

The volumetric method described above is quite satisfactory. It is a rapid method that affords acceptable precision and accuracy.

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[1] *Fritz, J. F. and Johnson, M., Volumetric Determination of Zirconium, ISC-571, February 1, 1955.*

TABLE 16.3-1

DETERMINATION OF ZIRCONIUM IN A ZIRCONIUM-NIOBIUM-URANIUM STANDARD (THE MODIFIED VERSENE-BISMUTH VOLUMETRIC METHOD)

Zr PRESENT (mg)	Zr FOUND (mg)	Zr FOUND IN A 1-GRAM SAMPLE (%)	DEVIATION FROM THEORETICAL 5.14% Zr (%)	RELATIVE DEVIATION (%)
12.85	13.06	5.22	+0.08	+1.6
12.85	12.34	4.94	- 0.20	-3.9
12.85	12.81	5.12	- 0.02	-0.4
12.85	12.93	5.17	+0 03	+0.6

16.4 ESTIMATION OF MOLYBDENUM IN URANIUM-ZIRCONIUM-NIOBIUM-MOLYBDENUM ALLOY - P. Hallbach, H. Werner, and F. E. Jenkins

The conventional thiocyanate and butyl acetate extraction method for the determination of molybdenum in the presence of uranium[1] was investigated for possible interference from zirconium and niobium. Standard curves were prepared from uranium solutions containing (1) molybdenum (2) molybdenum and zirconium (3) molybdenum and niobium and (4) molybdenum, niobium, and zirconium. The results are shown in Table 16.4-1.

TABLE 16.4-1

EFFECT OF NIOBIUM AND ZIRCONIUM ON THE COLORIMETRIC ESTIMATION OF MOLYBDENUM IN QUATERNARY URANIUM ALLOYS

γ Molybdenum in 25 ml of Butyl Acetate after Extraction	Per cent Transmission at 740 μ of Molybdenum-Thiocyanate Complex in Butyl Acetate Extraction of Aqueous Solutions of the Following Compositions:			
	9300 γ/100 ml U.	9300 γ/100 ml U, 40 γ/100 ml Zr	9300 γ/100 ml U; 20 γ/100 ml Nb	9300 γ/100 ml U; 20 γ/100 ml Nb; 40 γ/100 ml Zr
0	100.0	100.0	100.0	100.0
20	70.0	71.0	68.0	71.5
40	47.5	48.0	47.0	50.5
60	32.8	34.5	33.5	36.5
80	23.0	24.0	23.5	26.0
100	16.0	17.5	16.0	19.0

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[1] *Rodden, C. J., "Analytical Chemistry of the Manhattan Project," NNES-VIII-1, pp. 450-5, McGraw-Hill, New York, 1950.*

Variations of ±0 05 per cent molybdenum are within specifications Therefore, the interference from niobium and zirconium is not significant, as the maximum variation in per cent transmission is equivalent to a variation of 0.016 per cent molybdenum.

The butyl acetate extraction – thiocyanate colorimetric method appears to be suitable for the estimation of molybdenum in this quaternary uranium alloy.

16.5 ASSAY OF HYDROUS HYDROFLUORIC ACID - F. E. Jenkins and A. E. Carter

It has been standard procedure to analyze hydrous hydrofluoric acid samples after their temperature has been reduced to slightly above dry ice temperature. This is a safety precaution – at the lower temperature, evolution of hydrofluoric acid fumes is minimized.

The assay of samples stored in dry ice has been consistently higher than the assay at room temperature. This has been shown when a rush analysis was needed and samples were assayed without cooling. Check assays, made after the sample had been stored in dry ice, were significantly higher. The average difference between assays was 0.88 per cent hydrofluoric acid, and the cold sample was positively biased.

Further investigation indicated that hydrated molecules of hydrofluoric acid crystallized on the sides and bottoms of the containers at the low storage temperature, resulting in nonrepresentative sampling.

16.6 ASSAY OF VIRGINIA-CAROLINA GREEN SALT - D. Valent and B. Gessiness

A sample of Virginia-Carolina green salt was received for the first time by the NLO Ores Laboratory for a uranium assay. This material was reported to be high in phosphate, because of possible phosphate interference, it was necessary to obtain the phosphate value and an estimate of the uranium content before an accurate uranium assay could be undertaken. It had been verified in the NLO Ores Laboratory that no difficulty in the routine assay procedure would be encountered if the ratio of uranium to phosphate was at least 1.8 to 1. (This ratio agreed with that given by Rodden.)[1]

The material was found to contain 15.7 per cent phosphate A fluorimetric estimation showed the uranium content to be about 20 per cent. In order to adjust the uranium-to-phosphate ratio to a convenient working range, 0.16 gram of uranium was added to approximately 0.5 gram of Virginia-Carolina green salt. The uranium-to-phosphate ratio then became 3.2 to 1. Duplicate portions of standard uranium solution (containing no Virginia-Carolina green salt) were titrated, along with duplicate spiked samples. Results of the analyses are shown in Table 16.6-1.

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[1] *Rodden, C. J., "Analytical Chemistry of the Manhattan Project" p. 56, McGraw-Hill, New York, 1950.*

TABLE 16.6-1

DETERMINATION OF URANIUM IN VIRGINIA-CAROLINA GREEN SALT CONTAINING 15.7 PER CENT PHOSPHATE

Material	Dichromate Titer (ml)	Dichromate Value (mg U/ml $K_2Cr_2O_7$)	Total U (g)	Total U in Standard Soln (g)	U in Sample (%)
25 ml Standard Soln	50.24 50.22 Avg 50.23	0.003180	0.15973	——	——
25 ml Standard Soln +0.5076 (g) sample	79.59	0.003187	0.25365	0.09392	18.50
25 ml Standard Soln +0.5054 (g) sample	79.39	0.003187	0.25302	0.09329	18.46

16.7 ASSAY OF ELDORADO ORANGE OXIDE PRODUCED AT PORT HOPE - D. Valent, W. Steigerwalt, E. Ross, and B. Gessiness

One of the principal assignments of the NLO Ores Laboratory during the past quarter was the analysis of the first lot of orange oxide produced at Port Hope. The lot consisted of 100 drums of material, composited as 10 samples that represented 10 drums each. One group of official blender samples was received from Port Hope; two additional groups of the same material, representing blender and dried materials, were received from the NLO Sampling Plant. These three series of samples for the same lot of material were analyzed in duplicate by three different analysts. Their results are shown in Tables 16.7-1, 16.7-2, and 16.7-3.

The precision obtained by the analysts has been determined by the NLO Quality Control Department and is indicated in Table 16.7-4.

The data obtained for the samples from the first shipment indicate that consistently good precision can be obtained by using a volumetric procedure for the assay of the uranium content. Samples from the second and third shipments of orange oxide from Port Hope are not being analyzed.

TABLE 16.7-1

ASSAY OF PORT HOPE ORANGE OXIDE
(Official Port Hope Sample)

Analyst A

Lab No	As-Received Uranium (%)		Loss at 110°C (%)	Calculated Uranium Content after Drying (%)	
14-1764	81.74	81.68	0.14	81.85	81.79
14-1765	81.91	81.83	0.07	81.97	81.89
14-1766	82.63	82.69	0.08	82.70	82.76
14-1767	82.46	82.58	0.11	82.55	82.67
14-1768	82.44	82.48	0.34	82.72	82.76
14-1769	81.86	81.87	0.09	81.93	81.94
14-1770	82.38	82.42	0.14	82.50	82.54
14-1771	81.91	82.01	0.22	82.09	82.19
14-1772	82.19	82.14	0.07	82.25	82.20
14-1773	82.23	82.19	0.09	82.30	82.26

TABLE 16.7-2

ASSAY OF PORT HOPE ORANGE OXIDE
(Blender Sample from NLO Sampling Plant)

Analyst B

Lab. No.	As-Received Uranium (%)		Loss at 110°C (%)	Calculated Uranium Content after Drying (%)	
1-8486	81.17	81.12	0.19	81.32	81.27
1-8487	82.35	82.49	0.09	82.42	82.56
1-8488	82.72	82.53	0.08	82.79	82.60
1-8489	82.57	82.69	0.09	82.64	82.76
1-8490	82.42	82.50	0.14	82.54	82.62
1-8491	81.86	81.95	0.10	81.94	82.03
1-8492	82.43	82.34	0.14	82.55	82.46
1-8493	82.16	82.22	0.13	82.27	82.33
1-8494	82.28	82.28	0.10	82.36	82.36
1-8495	82.46	82.37	0.11	82.55	82.46

TABLE 16.7-3

ASSAY OF PORT HOPE ORANGE OXIDE
(After drying in Plant 1)

Analyst C

Lab. No.	"Dried" Uranium (%)		Loss* at 110°C	Calculated Uranium After Laboratory Drying (%)	
1-8566	81.04	80.97	0.17	81.18	81.11
1-8567	82.38	82.37	0.10	82.46	82.45
1-8568	82.55	82.62	0.11	82.64	82.71
1-8569	82.53	82.55	0.11	82.62	82.64
1-8570	82.41	82.43	0.12	82.51	82.53
1-8571	82.03	81.97	0.05	82.07	82.01
1-8572	82.43	82.48	0.07	82.49	82.54
1-8573	82.30	82.37	0.07	82.36	82.43
1-8574	82.28	82.24	0.09	82.35	82.31
1-8575	82.43	82.35	0.08	82.50	82.42

* *The losses obtained upon heating to 110° C were comparable to the 110° C losses obtained for the blender samples. This indicates that the original drying was ineffective.*

TABLE 16.7-4

PRECISION OF ANALYSTS FOR THE ASSAY OF ORANGE OXIDE *

	ANALYST		
	A	B	C
Average difference between duplicates	0.054	0.079	0.044
Standard deviation for duplicate determinations	0.031	0.049	0.026
Standard deviation for single determination	0.044	0.069	0.037
95% of the time, differences between duplicates should not exceed:	0.11	0.17	0.09
99% of the time, differences between duplicates should not exceed:	0.14	0.22	0.12
Average Assay Value	82.39	82.34	82.32
Average Moisture Value	0.14	0.12	0.10

* *All results given in per cent.*

16.8 DETERMINATION OF SULFATE IN ORANGE OXIDE - E. Gerhardt and B. Gessiness

An intensive study has been made, seeking the optimum conditions for the determination of sulfate in orange oxide in concentrations of 100 to 1000 ppm. A procedure has been developed that appears to give consistently reliable results. The sample of orange oxide is dissolved in 3N nitric acid; the uranium is extracted by a 1:1 TBP-CCl_4 solution. Nitrate ion is then removed from the aqueous phase by several fumings with HCl; sodium ion is added to retain the sulfate. The pH of the solution is then adjusted to 2.0 and 2.4 and the sulfate is determined turbidimetrically by measurement of the opacity at 375 mu, using 5-cm cells and a spectrophotometer. Results obtained on duplicate samples indicate the precision to be within 10 per cent. Recovery of sulfate appears to be good.

Additional studies are being made to determine the feasibility of sulfate analysis in orange oxide without prior removal of the uranium. Preliminary results indicate interference of the yellow uranium color with the measurement of the turbidity. Absorption curves have been prepared at various wave lengths, comparing the effect of the colored uranium ion upon the measurement of the turbidity. Other pertinent conditions are being studied systematically and will be summarized in a later report.

16.9 DETERMINATION OF MOLYBDENUM IN ORES - R. Scheer, E. Tieman, and B. Gessiness

A colorimetric procedure has been adapted for the determination of molybdenum in ores, using thiocyanate as the chromogenic reagent. The molybdenum-thiocyanate complex is extracted with butyl acetate and the absorbency is measured at 470 mu, using 10-cm cells and a spectrophotometer. Samples of South African concentrate and Colorado black oxide were analyzed; duplicates agreed within ±0.003 per cent. Samples spiked with 50 ppm molybdenum were analyzed; 48 ppm was consistently recovered.

16.10 DETERMINATION OF BORON IN THORIUM NITRATE - E. Frank and B. Gessiness

A study was undertaken to determine the boron content of a thorium nitrate (TNT) standard used by the NLO Spectrographic Laboratory. The standard was subjected to direct distillation of the nitrate without prior conversion to the oxide. An aliquot, containing 0.5 gram of thorium, was taken from a TNT solution that contained 2.7 micrograms of boron per gram of thorium. The aliquot was neutralized with calcium oxide (which also acted as a retainer for the water that was present), and then was distilled. The conventional colorimetric procedure followed. The following results were obtained: 2.84, 2.40, and 2.10 micrograms of boron, compared with the spectrographic value of 2.7. These results are sufficiently encouraging to warrant study of additional spiked samples.

17.0 ANALYTICAL DEPARTMENT – SPECTROCHEMICAL DEVELOPMENT

– G. L. Stukenbroeker

The development studies in the Spectrographic Group centered about (1) the refinement of methods associated with the impurity analysis of thorium materials and (2) the development of analyses for determining impurities in auxiliary materials required in the production of thorium metal. Studies reported here include rare earth separations from thorium and uranium materials and the method for alkali analysis of calcium metal.

A paper has been prepared for presentation at the Sixth Annual Analytical and Physical Testing Symposium, Seyreville, New Jersey. The paper is titled: "Analysis for Individual Rare Earth Elements in Thorium Materials" by M. G. Atwell, C. E. Pepper, and G. L. Stukenbroeker.

The combined effort of the group is best illustrated by Table 18-3, which shows 144,886 determinations reported for 9,394 samples.

17.1 CHEMICAL SEPARATION OF RARE EARTHS IN THORIUM MATERIALS - M. G. Atwell

Previous quarterly reports[1,2,3,4,5] have presented the method used at NLO for the chemical separation of the rare earth elements in thorium materials. Further refinement of the method of rare earth separation was undertaken this quarter.

As reported in the last quarterly report,[6] the efficiency of extraction of the rare earth elements from thorium materials, utilizing the method used at NLO, is approximately 75 per cent. Therefore, tests were designed to locate the most important points where rare earth elements were being lost in the separation procedure. The pentaether-nitric acid extraction step, the hydrogen peroxide precipitation step, and the 8-hydroxyquinoline-chloroform step were investigated.

It was found that the 8-hydroxyquinoline-chloroform step was responsible for a considerable amount of the loss. Further investigation showed that the pH of the aqueous phase during the extraction was very important. At a pH greater than 4.0, losses of several elements (Gd, Nd, Pr, Sm, Y, and Yb) became quite severe. Table 17.1-1 lists typical data showing this selective loss of several of the rare earths with varying pH.

It is possible that other organic compounds will be found whose use does not result in rare earth losses such as those indicated in Table 17.1-1. In the near future, these losses will be the subject of a further investigation in which radioactive tracers will be used.

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[1] *Stukenbroeker, G. L., Summary Tech. Rpt., pp. 123-125, FMPC-405, April 15, 1954.*

[2] *Stukenbroeker, G. L., Summary Tech. Rpt., pp. 127-129, FMPC-437, July 15, 1954.*

[3] *Stukenbroeker, G. L., Summary Tech. Rpt., pp. 135-138, FMPC-475, October 15, 1954.*

[4] *Stukenbroeker, G. L., Summary Tech. Rpt., pp. 215-218, FMPC-505, January 15, 1955.*

[5] *Atwell, M. G. and Haberle, C., Summary Tech. Rpt., pp. 179-181, NLCO-565, July 15, 1955.*

[6] *Ibid.*

TABLE 17.1-1

RARE EARTH CONTENT *

	(X)**	SAMPLE 1 (pH 3.5)	SAMPLE 2 (pH 3.8)	SAMPLE 3 (pH 4.0)	SAMPLE 4 (pH 4.2)	SAMPLE 5 (pH 4.4)	SAMPLE 6 (pH 4.6)
Dy	1	0.4	0.4	0.5	0.4	0.4	0.4
Er	1.5	1	0.8	1	0.7	0.7	0.7
Eu	0.8	0.8	0.7	0.8	0.4	0.3	0.3
Gd	1	0.8	0.5	0.7	0.6	0.6	0.5
Ho	1.5	1	0.8	1	0.8	0.8	0.8
Lu	2	1.5	0.8	1	0.7	0.6	0.6
Nd	1.5	0.8	0.5	0.6	0.4	0.3	0.2
Pr	1.5	0.8	0.7	0.8	0.4	0.3	0.2
Sm	1	0.7	0.5	0.6	0.4	0.3	0.2
Tb	1.5	1	1	1	0.8	0.8	0.8
Y	6	0.8	0.7	0.8	0.5	0.6	0.7
Yb	2	0.9	0.8	0.8	0.3	0.3	0.3

* *Values in ppm based on thorium metal.*

** *Amount of rare earth added before extraction.*

17.2 ANALYSIS OF RARE EARTHS IN URANIUM MATERIALS - M. G. Atwell and C. E. Pepper.

A procedure has been developed for the chemical separation and spectrographic analysis of rare earth elements from uranium materials at NLO. This procedure is based on one used at Oak Ridge for this purpose.[1]

The Oak Ridge procedure did not require any separation of common impurity elements from the rare earths. In order to obtain a sufficient amount of rare earth oxides for spectrographic analysis, however, it was necessary to increase the size of the original sample taken from one gram to twenty grams. With a one-gram sample the quantity of common impurity elements was not sufficient to cause trouble, but with a twenty-gram sample provisions had to be made for their removal. This removal was accomplished by introducing an 8-hydroxyquinoline-chloroform extraction step following the extraction of the uranium from the original sample. The rare earth elements were then precipitated as quinolates after the addition of a lanthanum carrier, and ignited to the oxides. The residues were then analyzed spectrographically by a method similar to that used for thorium rare earth residues.[2,3]

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[1] *McIlhenny, R. C., Procedures for Uranium Spectrography, Y-B41-543, p. 37, July 31, 1952.*

[2] *Stukenbroeker, G. L., Summary Tech. Rpt., pp. 135-138, FMPC-475, October 15, 1954.*

[3] *McIlhenny, R. C., Procedures for Uranium Spectrography, Y-B41-543, p. 44, July 31, 1952.*

17 3 CHEMICAL SEPARATION OF RARE EARTHS FROM Q-11 ORE - M. G. Atwell

A method for the chemical separation of the rare earth elements from Q-11 ore has been developed for routine use at NLO This procedure is based on the method for the analysis of uranium ores given in "Analytical Chemistry of the Manhattan Project"[1] and on the method in use at NLO for the separation of rare earths from thorium

The procedure is as follows The sample of Q-11 ore weighing approximately one-half gram, is treated with a 5 milliliter portion of 48 per cent HF and evaporated to dryness over a steam bath for the removal of silicon. This treatment is repeated once. Nitric acid is added, and the solution is evaporated to dryness to remove the fluoride ions After dilution, the solution is filtered and the insoluble residue is fused with Na_2CO_3 The melt is then dissolved, diluted, and made alkaline with NH_4OH This melt solution is filtered, and the precipitate is dissolved with nitric acid and added to the main solution

The sample is next evaporated to a volume of approximately 10 milliliters, 20 micrograms of thulium is added as a monitoring element, and the solution is first extracted with pentaether-HNO_3 solution to remove uranium and then evaporated to dryness. This residue is next treated with a few drops of nitric acid, diluted to 50 milliliters, and treated with 12 milliliters 48 per cent HF to remove some extraneous interferring cations. After standing, the sample is filtered and the filtrate is discarded The filter paper is ignited and the residue is treated with several milliliters of concentrated sulfuric acid and is evaporated to dryness to again remove fluoride ions.

The sample residue is again dissolved with 20 milliliters of 1:9 HCl and diluted to 60 milliliters. After the addition of 12 milliliters of 8-hydroxyquinoline acetic acid to the solution, the pH is adjusted to 4.0 ±0.1 with NH_4OH This solution is then extracted with three 10-milliliter portions of 8-hydroxyquinoline-chloroform to remove remaining impurities The sample is extracted with 20 milliliters of chloroform, 1 milligram of lanthanum is added as a coprecipitant, and then the pH is adjusted to 8.5 ±0.2 with NH_4OH Finally, the precipitate is filtered, washed, and ignited to RE_2O_3 This residue may be redissolved with a little HCl, reprecipitated, filtered, and again ignited

This procedure yields an excellent residue of rare earths very free of uranium and impurities that cause spectral interference.

17.4 ANALYSIS OF K, Li, AND Na IN CALCIUM METAL - C. A. Haberle and C. E. Pepper

The presence of small quantities of the alkali metals as impurities in stored calcium metal affords a potential fire hazard To detect the elements, potassium, lithium, and sodium, to a low limit of 5 ppm, standards were prepared and a spectrochemical procedure was developed.

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[1] *Rodden C. J., "Analytical Chemistry of the Manhattan Project", NNES-VIII-1, p. 506, McGraw-Hill, New York, 1950.*

Standards were prepared by adding an aqueous solution containing potassium, lithium, and sodium to $Ca(OH)_2$. The calcium hydroxide was prepared by adding enough water to CaO to produce a thin paste-like suspension. The $Ca(OH)_2$ containing the alkali metals was dried overnight in an oven at approximately 120°C and ground for one hour to insure complete mixing.

Early attempts to prepare standards had involved the adding of alkali metal solutions to a calcium acetate solution, evaporating to dryness, and converting to the oxide over Fisher burners. This method of preparing standards proved unsatisfactory, since alkali metals, especially potassium, are lost at this ignition temperature. Later attempts to convert $Ca(OH)_2$ to CaO at 800°C in a muffle also showed a similar but smaller loss. Tests showed conversion may be made from the hydroxide to the oxide form at 600°C without loss of potassium, lithium, and sodium, but this oxide appears to have no advantage over the hydroxide in spectral burning characteristics.

Samples to be analyzed are prepared by reacting the calcium metal with water and then drying the $Ca(OH)_2$ produced in an oven at approximately 120°C. The $Ca(OH)_2$ is ground for several minutes to insure homogeneity.

A 25-mg charge is excited at 15 amperes d.c. in a ¼-inch graphite electrode with cavity dimensions of 5/32 inch by 5/32 inch. The charge must be carefully vented after a very firm tamping. For sodium and lithium, exposure of 30 seconds on Eastman II-F(3) plates with a slit width of 20 microns is required, whereas only 20 seconds is required for potassium on Eastman I-N plates at a slit width of 30 microns on a Jarrell-Ash 21-foot Wadsworth Mount spectrograph. A Corning glass filter No. 3480 is used to filter out second-order spectral interferences.

The analysis of calcium metal by this method will permit determination of the impurities, potassium, lithium and sodium, to a low limit of 5 ppm or less.

18.0 ANALYTICAL DEPARTMENT - PROCESS CONTROL

E. A. Brown, F. E. Jenkins, and G. L. Stukenbroeker

Table 18.0-1 shows the number of samples that have been analyzed each quarter during the past eighteen months.

TABLE 18.0-1
COMPARISON OF SAMPLE LOAD FOR THE PAST 18 MONTHS

PERIOD	NO. OF SAMPLES ANALYZED
March 15 - June 15, 1954	44,854
June 15 - September 15, 1954	47,754
September 15 - December 15, 1954	57,771
December 15, 1954 - March 15, 1955	61,652
March 15 - June 15, 1955	58,494
June 15 - September 15, 1955	61,045

TABLE 18.0-2

SUMMARY OF WET CHEMICAL SAMPLE LOAD

	Source	No. of Samples Received	No. of Samples Reported	No. of Determinations Made on Reported Samples
1	Sampling Plant	1,982	1,837	7,348
2	Ore Refinery	15,721	15,806	60,197
3	Nitrate Plant	4,507	4,533	18,132
4	Green Salt	6,117	6,091	28,730
5	Metal Production	5,262	5,328	21,396
6	Metal Fabrication	637	658	1,566
7	New Processing	3,493	3,497	7,064
8	Scrap Plant	2,842	2,855	11,420
9	Thorium Plant	4,650	4,556	17,225
10	Service Products	430	439	1,756
11	Metallurgy Development	642	669	268
12	Chemical Development	2,033	1,898	7,799
13E	Pilot Plant Extraction	2,332	2,427	9,678
13G	Pilot Plant Green Salt	394	377	1,508
13M	Pilot Plant Metal	299	315	1,260
13T	Pilot Plant Thorium	71	89	356
14	Co-op (Non-FMPC Samples)	236	276	1,104
	TOTALS	51,648	51,651	199,220

TABLE 18.0.3

SUMMARY OF SPECTROCHEMICAL SAMPLE LOAD

Source	No. of Samples Received	No. of Samples Reported	No. of Determinations Made on Reported Samples
Sampling Plant	142	109	1,716
Ore Refinery	817	808	6,717
Nitrate Plant	380	383	7,489
Green Salt Plant	1,036	1,035	5,955
Metal Production	4,513	4,461	84,922
Metal Fabrication	5	3	60
New Processing	198	195	3,012
Scrap Plant	1	1	20
Thorium Plant	1,211	1,198	20,073
Service Products	408	373	502
Metallurgy Development	45	45	900
Chemical Development	130	132	2,480
Pilot Plant	341	337	6,713
Non-Fernald	228	314	4,327
TOTALS	9,455	9,394	144,886