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SUMMARY TECHNICAL REPORT

For The Period

January 1, 1963 to March 31, 1963

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FEED MATERIALS PRODUCTION CENTER
NATIONAL LEAD COMPANY OF OHIO

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SUMMARY TECHNICAL REPORT
FOR THE PERIOD
JANUARY 1, 1963 TO MARCH 31, 1963

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CONTENTS

	Page No.
1. Conversion of Low-Grade Uranium Residues to Winlo Feed	7
Residue Processing by Semicontinuous Ion Exchange	8
A semicontinuous ion exchange column was used for the pilot-scale production of purified uranyl chloride solutions from scrap leach liquor.	
Residue Processing in a Mixer-Settler System by an Aliquat-336 Extraction .	20
Continuous, laboratory, box mixer-settler tests demonstrated that an Aliquat-336 -- Solvesso 100 system will satisfactorily extract uranium from scrap leach liquor.	
2. Cleaning Derbies with an Airless Blaster Using Uranium Shot	33
An airless shot blaster is being used to clean slag from derbies using uranium shot as the blasting medium.	
3. Installation and Initial Operation of Plasma-Spraying Equipment	49
Plasma-spraying equipment was installed for coating graphite crucibles and molds with refractory materials.	
4. Consumable-Electrode Arc-Melting of Uranium	55
Production-size uranium ingots having fine, evenly dispersed inclusions were produced by consumable-electrode arc melting under vacuum.	
5. The Effect of Rolling Mill Variables on Uranium Fuel Core Structure and Texture. .	69
Variations in uranium billet temperatures prior to rolling were found to affect the amount of recrystallization and the texture coefficients in the alpha-rolled rods.	
6. Texture Gradients in Water-Quenched HAPO I and E Fuel Cores	77
Four HAPO I and E fuel cores that had been beta heat treated and water quenched were examined for texture gradients. G_2 , G_3 , and J data are tabulated.	
7. Electron Microprobe Examination of Phosphides in Uranium	83
Uranium phosphide inclusions were identified in production-grade derby metal of high phosphorous content.	

1. CONVERSION OF LOW-GRADE URANIUM RESIDUES TO WINLO FEED

N. R. Leist

Abstract

Both ion-exchange and solvent extraction systems were investigated as means for producing feed for the Winlo process from low-grade uranium residues.

A Higgins semicontinuous ion-exchange column was used for the production of pure uranyl chloride solutions from scrap leach liquors. Operating conditions for an ion-exchange process were developed in this pilot-scale contactor. Product samples from pilot-scale ion-exchange tests were converted into metal-grade UF_4 in laboratory Winlo precipitation tests.

Continuous laboratory box mixer-settler runs demonstrated that a 20 w/o Aliquat 336 — 80 w/o Solvesso 100 system will satisfactorily extract uranium from a hydrochloric acid leach liquor made by the digestion of low grade residues. The desired uranium purification was achieved by following the extraction with a 2.0M HCl scrubbing operation. The use of sulfurous acid as a re-extraction agent was found to produce a 150 g/l aqueous uranium solution, but the poor phase disengagement of the re-extraction step would require the use of a centrifugal contactor.

Introduction

The concentration and purification of uranium from magnesium fluoride slag (normal or enriched) and other low-grade residues by the HCl leach — UAP precipitation process in the Scrap Recovery Plant at the National Lead Company of Ohio consists of several unit operations. The residues are calcined, ground, and dissolved in hydrochloric acid containing MnO_2 as an oxidant. The acid slurry is filtered, the filtrate is reduced with sodium thiosulfate to retard iron precipitation, and the uranium content of the filtrate is precipitated as $UO_2NH_4PO_4$ (UAP) by the addition of ammonia and

phosphoric acid. The UAP cake is then filtered and calcined to remove ammonia and fluoride.

Recently a large-scale uranium tetrafluoride aqueous precipitation production unit (Winlo¹) was put on stream in the Scrap Recovery Plant. The unit is used in alternate campaigns of normal and slightly enriched materials. Feeds for the enriched campaigns consist of black oxide, metal dissolver product, and calcined UAP. Laboratory investigation and plant operating experience have shown that the UAP process should be replaced as a means of producing enriched feed to the Winlo process for the following reasons:

1. The UAP process, which was originally developed to prepare a phosphate-containing concentrate for processing with thorium-bearing concentrates in the Refinery, is outmoded in that too many operations (including recycling as previously mentioned) must be performed to prepare a purified, concentrated, uranyl chloride feed solution for Winlo. A more direct route specifically designed to produce feed for Winlo would reduce feed preparation costs.

2. Some of the low-grade enriched residues to be processed cannot be converted to UAP of sufficient purity for Winlo feed; and the UAP product from these residues must be recycled through the system, thereby increasing costs and reducing the total throughput of the UAP system.

3. Recent plant experience has revealed that the green salt produced from calcined UAP by the Winlo process contains 100 to 300 ppm phosphorus which carries through to the metal. Since the effect of this amount of phosphorus on metal quality is unknown, it would be best to eliminate this contaminant.

Objectives

To develop either a semicontinuous ion-exchange process or a solvent extraction flowsheet

capable of purifying and concentrating the uranium values in hydrochloric acid leach liquors sufficiently for subsequent aqueous precipitation of metal-grade UF_4 by the Winlo process. A major consideration in the development of either of such processes would be to obtain a minimum operating cost for the recovery of uranium from all types of low-grade residues.

RESIDUE PROCESSING BY SEMICONTINUOUS ION EXCHANGE

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Introduction

Ion-exchange processes have long been in common use for the recovery of uranium from naturally occurring ores. The majority of these processes consist of batch contacts between uranium dissolved in a suitable acid and an ion-exchange resin. More recently the Japanese government utilized a Higgins semicontinuous ion-exchange contactor for processing uranium concentrates in a hydrochloric acid system.^{2,3} At about the same time, a semicontinuous ion-exchange process was applied to the recovery of uranium on a tonnage scale from metal reduction residues and other solid salvage materials at the Y-12 plant of the Union Carbide Nuclear Company.⁴

The accomplishments of the Union Carbide and Japanese personnel indicated that a semicontinuous ion-exchange process could be utilized to recover uranium dissolved in a hydrochloric acid system. Such a process showed promise of substantially reducing scrap recovery costs.

Summary of Results

1. Dowex 21K anion exchange resin has been utilized in a pilot-scale Higgins semicontinuous ion-exchange contactor for the extraction of uranium from plant leach liquors. Metal-grade UF_4 has been precipitated from the ion-exchange aqueous

product in a laboratory-scale Winlo precipitation process.

2. Higgins contactor operating variables associated with uranium adsorption, resin scrubbing, and uranium elution have been studied to determine the best operating conditions for a large scale semicontinuous ion-exchange process. Data required for the design of a large-scale contactor have also been obtained.

3. The capability of the semicontinuous ion-exchange process to reduce metallic impurities has been investigated when using plant leach liquors as the uranium feed solutions. Decontamination of alkali and alkaline earth metals was good.

Experimental Equipment and Procedures

Both laboratory ion-exchange equipment and a Higgins pilot scale semicontinuous ion-exchange contactor were used in this development work. The pilot scale semicontinuous contactor, which is described below, was the primary tool used in the development effort. However, a laboratory static-bed ion-exchange column and batch ion-exchange contacting equipment were used extensively to augment test data from the semicontinuous contactor.

Laboratory Equipment

A 1-inch-diameter glass column was utilized for static-bed ion-exchange tests. The column, which was 4 feet high, was employed for both uranium adsorption and elution testing. Glass beads and glass wool packing were used to support a resin bed (generally 24 inches high) in the column. In adsorption tests, the solution to be tested was fed to the column from the top at a controlled rate. Liquid was withdrawn from the bottom of the column at a variable rate so as to maintain a given volume of liquid (one void resin volume) above the packed bed. The withdrawal rate from the column varied with the volume change of the solution being tested. Elution tests were conducted in a sim-

ilar manner. Water and/or other stripping agents were fed to a 24-inch resin bed (loaded with uranyl chloride) from the top and at a controlled rate. Again, the column discharge rate was adjusted to maintain a liquid level of one void resin volume above the resin. The column effluent stream was sampled and analyzed at specific time intervals during the adsorption and elution tests.

Batch resin-aqueous equilibrium contacts were employed to determine rates of uranium transfer and final uranium distribution coefficients. Glass distilling flasks with three necks were used for the batch contacts. The sealed flasks were agitated through the center opening of the flask with a flat bladed glass and plastic stirrer. Heating and temperature control were obtained through powerstat controlled electric heating mantles. A thermometer was inserted through the seal of one flask neck while a sample pipet was placed in position in the other flask neck. Known quantities of resin and various aqueous solutions were mixed together in the flasks until equilibrium conditions were obtained. Initial tests indicated that as the uranium adsorption progressed, the rate of uranium transfer decreased and that true uranium equilibrium was not obtained for many hours. Figure 1.1 illustrates the transfer of uranium in one such equilibrium test. These scoping tests indicated

FIGURE 1.1 Batch Uranium Adsorption Test

that at resin uranium loadings of less than 100 g/l (wet resin basis) approximately 24 hours were required to reach ~ 99% of an equilibrium condition. Consequently, these contacts were limited to 24-hour periods, and after this time the aqueous and resin phases were considered to be at equilibrium with respect to uranium for developmental purposes.

Semicontinuous Ion-Exchange Contactor

A 2-inch glass Higgins ion-exchange contactor was purchased from the Chemical Separations Corporation, Oak Ridge, Tennessee, for the development of an ion-exchange flowsheet. This contactor which is pictured in Figure 1.2, is constructed of

1318-1

FIGURE 1.2 Ion-Exchange Column

DWG. 46-63

FIGURE 1.3 Higgins Two-Inch Ion Exchange Contactor

2-inch diameter pipe sections formed into a U shape. The total height of the column itself is approximately 14 feet. Three air-actuated ball valves sectionalize the column as illustrated in Figure 1.3. Two valves separate the adsorption, scrub and strip portions of the column from the resin classification and resin reservoir sections. The third valve in the system is used to direct the resin movement clockwise around the column.

The movement of the resin is controlled by sequence timers which simultaneously shut off all solution pumps. These sequence timers also actuate air-controlled ball valves in feed lines to the column and the three main column valves. During the pulse cycle (Figure 1.4) the resin is moved hydraulically with plant water (~50 psig) in a clockwise direction around the column. Column operation at a resin rate of 5 inches per minute has been satisfactory. The pulse cycle time re-

quired to move the resin 5 inches was found to be approximately 6 seconds.

The second distinct cycle associated with the contactor is the solution pumping cycle or the production cycle (Figure 1.4). During this cycle, the resin bed is stationary; and the feed, scrub,

FIGURE 1.4 Operating Cycles of the Pilot-Scale Higgins Contactor

and strip water streams are introduced into the column. The product is withdrawn from the column at a constant rate during this period. An electrical conductivity measurement of the product stream is used to control a portion of the strip water feed to the column. The main portion of strip water is fed to the column at a constant rate. Since operation of the column is cyclic, the dual strip water system is desirable to prevent large surges of water to the column which could pack the resin and make resin pulsing difficult.

Pulse water from the resin pulse operation and raffinate are alternately withdrawn from the column during the production cycle. Pulse water is removed from the column during the first part of this cycle until a conductivity cell, located in the column midway between the pulse water and raffinate take-off points, detects the presence of acid. At this time the pulse water valve closes, and the raffinate take-off valve opens for the remainder of the cycle.

Backwash water is introduced to the column through the pulse water line during the solution pumping cycle. As the resin which was pulsed out of the stripping section during the last pulse cycle returns to the resin reservoir, it is roughly classified by this constant volume backwash stream. The continuous removal of particles smaller than 50 mesh insures smooth resin movement during the pulse cycle. Particles larger than 50 mesh are caught and returned to the contactor system.

The major auxiliary equipment used with the two-inch contactor includes three Model T6S Sigmamotor pumps, two graphite tube heat exchangers wrapped with heating tape, one Eastern Model 2J-34 centrifugal pump, and a small Research Controls air-activated diaphragm control valve. Air-operated $\frac{1}{2}$ -inch Chemtrol valves are used for positive shut-off of the process streams. Rotameters and glass calibration tubes are used for process stream control. Two Eagle Signal Company timers (Models HP54A6 and HP50A6) and

a sequence controller (Time delay DA2102-001; Haydon Division, General Time Co.) are used to control operating cycle times and pump operation. The strip water control system (based upon the conductivity of the product stream) utilizes a 60-cycle wheatstone-bridge input transducer. The 60-cycle output from the bridge circuit is demodulated and filtered to a d-c signal which is fed into a Foxboro emf-to-current converter. A conventional Foxboro Model 64 flow controller is used to actuate a current-to-pneumatic transducer. The output from this transducer controls the strip water input to the column.

The Higgins column is constructed of Kimax glass pipe sections (12-inches long) which are flanged together for rapid disassembly. During the initial column tests, 7 feet of column length were used for adsorption while the elution and scrubbing sections were 5 and 3 feet long, respectively. During later tests, it proved desirable to alter the lengths of each of the three sections. Consequently, the length of column used for adsorption, scrub, and elution has varied between 5 to 9, 3 to 5 and 5 to 7 feet, respectively.

Discussion and Data

Resin Selection

Static-bed adsorption and elution tests were used to evaluate many different types and sizes of strongly basic anion exchange resins. Uranium loading capacities, uranium transfer rates, and fluid flow characteristics of the system were determined in the adsorption or loading tests. Uranium elution rates were determined in the latter tests.

The adsorption tests were conducted at a constant temperature (76°F) and at a given volumetric throughput of 280 gal/hr/sq ft (gsfh), resin-void volume basis. The feed solution for these loading tests was a pure UO_2Cl_2 solution (25 g/l U) which contained 7M HCl. The effluent from the static-bed tests was monitored periodically for uranium

content. The elution tests were also conducted at a constant temperature, but these tests were conducted at a slower volumetric throughput rate (140 gsfh, resin-void volume basis). Various anion resins loaded to a full uranium capacity constituted the packed bed in these tests.

Anion exchange resins having particle size ranges of 10 to 20, 10 to 50, 20 to 50, and 50 to 100 mesh were tested in static-bed tests. Although higher uranium transfer rates were achieved with 50 to 100 mesh resin, excessive column pressure drops were created as the resin adsorbed uranium. As uranium loads on the resin, the resin beads swell and produce a very tight bed packing. Consequently, tests with 50 to 100 mesh resins were discontinued since semicontinuous operation would be difficult with a tightly packed resin bed. Generally the 10 to 20 mesh resins adsorbed uranium relatively slowly; hence further testing of these resins was discontinued. Uranium extraction characteristics of 10 to 50 and 20 to 50 mesh resins

were generally satisfactory, and static-bed flow characteristics during these tests were good.

The uranium adsorption characteristics of Dowex 11, Dowex 21K and Permutit SK were excellent in the static-bed tests. Each of the resins adsorbed relatively large quantities of uranium at acceptable transfer rates. The results of these static-bed adsorption tests are illustrated in Figure 1.5. Generally, the highest uranium loading was obtained with Permutit SK resin; however, faster uranium transfer rates were obtained with the Dow resins at resin uranium concentration ranges that would be practical for the semicontinuous ion exchange column operation. Uranium elution characteristics of these three resins were similar as illustrated in Figure 1.6, however, slightly faster uranium elution rates were obtained from the Permutit

FIGURE 1.5 Static Bed Uranium Adsorption Tests

FIGURE 1.6 Static Bed Uranium Elution Tests

resin. Uranium elution from all three resins appeared satisfactory for semicontinuous contactor operation.

Plant leach liquors were monitored during a one month period for uranium, HCl, chlorine, fluorine, and cation impurity concentration. The average values of the impurities found in the leach liquor, during this period, are listed below:

U . . . 24.2 g/l	HCl . . . 0.91 M
Cl . . . 125 g/l	F . . . 4.6 g/l
Fe . . . 1.3 g/l	Mn . . . 4.1 g/l
Mg . . . 17.8 g/l	Ca . . . 12.3 g/l

As indicated above, large quantities of alkaline earth metals are present in the leach liquor. Prior Winlo investigations⁷ indicated that very little calcium and magnesium decontamination is achieved in the Winlo precipitation process. Consequently, an ion-exchange process for the recovery of uranium from leach liquor had to exclude these ions from the product stream. Prior work by Kraus⁵ had shown that calcium and magnesium would not be adsorbed on an anionic resin with a trimethyl benzyl ammonium active group. Dowex 21K resin has a trimethyl benzyl ammonium active group, and this resin differs only slightly in the degree of divinylbenzene cross linkage from the resin used by Kraus.⁶ Therefore, Dowex 21K resin (20 to 50 mesh) was chosen for preliminary semicontinuous contactor work. The Higgins contactor work reported in the next few sections was all performed with the Dowex 21K resin (20 to 50 mesh).

Contactors Tests, Uranium Adsorption

The pilot-scale Higgins contactor has been used to investigate the major variables involved in a semicontinuous ion exchange operation. Column profile samples obtained under steady operating conditions were used to evaluate the effect of the variables upon column operation. For example, adsorption section profile samples when shown graphically as in Figure 1.7 illustrate the effect of uranium resin loading upon the length of

FIGURE 1.7 Higgins Contactor Adsorption Section Profile Data

column required for the adsorption of uranium from a given feed solution. The three major adsorption section operating variables (HCl and the H^+ and Cl^- concentration of the feed, total column throughput, and uranium concentration of the adsorption section product resin) were investigated in this manner. A summary of the more important of these tests is presented in Figure 1.8.

Uranium transfer rates were found to be extremely fast in a 7M HCl aqueous feed — adsorption system (Figure 1.8), and only 2 feet of column were required for complete uranium adsorption at a total column throughput of 200 gsfh. Laboratory distribution tests (Table 1.1) indicated that NaCl could be substituted for part of the HCl in a feed

TABLE 1.1 Uranium Distribution Coefficients for the HCl, NaCl - Dowex 21K Resin System

Feed Solution	Uranium Concentration of the Resin Phase (g/l U, Wet Basis)	$\frac{R}{C_A}$
7M HCl	50	83/1
5M HCl	50	38/1*
2½M HCl + 5M Cl ⁻	50	38/1
1M HCl + 5M Cl ⁻	50	16/1

* Average value from several tests.

solution without drastically reducing the uranium distribution coefficient (C_A^R).

Static-bed tests indicated that the uranium transfer rates were only slightly slower for the 2.5M HCl - 5M Cl⁻ system in comparison with the rates obtained in 5M HCl system tests. Consequently, the acidity of Higgins contactor test feed solution was decreased, and NaCl was added to increase the total chloride content of the feeds to 5M. As indicated in Figure 1.8, approximately two additional feet of adsorption column length were required to obtain complete uranium extraction for the altered feed solution system.

FIGURE 1.8 Higgins Contactor Adsorption Section Length Requirement for the Complete Extraction of Uranium*

These tests indicated that increases in total column throughput increased adsorption column length requirements by about 1 foot of column per 100 gsh. Also, that increases in the uranium loading of the resin increased adsorption column length requirements by about 1.9 feet of column per 10 g/l U (wet resin basis). These values remained about the same for all tests within the uranium loading limits of 20 to 45 g/l U and throughput limits of 100 to 350 gsh.

After the above tests had been completed, a series of tests was made to determine the impurity decontamination capabilities of the system. Synthetic leach liquors (25 g/l U solutions with various quantities of cationic and anionic impurities added) and actual plant leach liquors were used in these tests. During this phase of the testing it was noted that the fluoride ion in both the synthetic feed solution and the plant leach liquors hindered uranium transfer. Longer lengths of adsorption column were required to obtain a uranium-depleted raffinate. The adsorption column uranium profiles for two of these tests are represented in Figure 1.9 and are compared with a pure UO₂Cl₂ feed test conducted under the same operating conditions. Laboratory batch contacts indicated that the uranium distribution between the resin and aqueous phases was not significantly affected by the fluoride ion (Figure 1.10); however, the tests did show that the rate of uranium adsorption was hindered by this element (Table 1.2). Further work indicated that an increase in adsorption operating temperatures or an increase in the HCl content of the feed could be used to overcome the detrimental effect of the fluoride ion. The effect of temperature upon the system is also given in Table 1.2.

A series of Higgins contactor tests was consequently made to test the effect of temperature upon the adsorption section operation. The column adsorption and scrub sections were insulated, and the scrub and feed streams were heated to 160°F. Different operating flow rates produced different column temperature gradients, but the effect of

TABLE 1.2 Batch Equilibrium Contacts Between Dowex 21K (20 to 50 Mesh) Resin and 5M HCl - UO_2Cl_2 Solutions

Resin Loading (U-g/l) (At Equilibrium)	8.4	8.6	8.5	8.1	8.3	8.9	9.7	9.3	9.1	8.2
Aqueous Phase F^{+} Concentration (g/l)	0	1	4	8	12	0	1	4	8	12
Temperature ($^{\circ}\text{F}$)	76	76	76	76	76	150	150	150	150	150
Average U Transfer Rate for 5 minutes of Contact (micrograms of U/min/ml of wet resin)	994	1035	830	679	463	1498	1530	1430	1405	1090

FIGURE 1.9 Higgins Contactor Adsorption Section Profile Data

higher operating temperatures upon the uranium adsorption was significant. The effect of temperature upon the adsorption section operation is illustrated in Figure 1.11 for impure synthetic feed solutions. The adsorption section temperature

FIGURE 1.10 Uranium Distribution Between Dowex 21K (20 to 50 Mesh) Resin and an Aqueous Phase Containing 5M HCl

gradient was about 150°F to 125°F in these heated feed tests. However, the adsorption column temperature profile differed in each test because dif-

FIGURE 1.11 Higgins Contactor Adsorption Section Profile Data

***NOTE:** The feed solutions for these four operations were practically identical. The temperature throughout the adsorption section was higher in Test 22 because of a higher feed rate.

ferent feed rates were employed in each test and heat losses through the insulated glass column were significant.

Contactor Tests, Resin Scrubbing

Higgins contactor tests were made to investigate scrub section operating variables. Scrub section length, scrub acid concentration, and scrub acid rates were investigated to determine their

FIGURE 1.12 Distribution of Uranium for Various Acid Conditions in Scrub Section of Higgins Contactor

effect upon product purity (the removal of impurities from the contactor process). The impurity decontamination achieved in these tests is discussed in a later section of this report. Scrub acid concentration was investigated to determine the quantities of uranium that would be refluxed to the adsorption system of the column (for read-sorption). Scrub section aqueous profile samples were analyzed for U and HCl in this investigation. Average U and HCl values of the profile samples were used to construct Figure 1.12. A scrub acid concentration of 3.0M HCl has been generally satisfactory for column operation. A three molar scrub solution fed at a rate equal to $\frac{1}{4}$ of the resin rate (generally satisfactory for decontamination purposes), recycles less than 4 g/l (wet resin loading basis) to the contactor adsorption section.

Contactors Tests, Uranium Elution

Alternate conditions for uranium elution from the Dowex 21K resin were tested in static-bed ion exchange tests. Water, dilute HF solutions, and dilute HCl solutions were used as uranium stripping solutions in these tests. Also, tests were conducted to determine the effect of temperature (76°F or 150°F) upon the uranium distribution coefficients for the elution operation. Ambient temperature water elution appeared best for uranium stripping and these conditions were used to evaluate the elution section of the Higgins contactor. However, the kinetics of uranium elution at 76°F and 150°F are being studied.

Elution section throughput (resin plus aqueous), product uranium concentration, and product acid concentration were studied in a series of Higgins contactor elution tests. Elution section throughput changes between 60 to 180 gsfh made almost no difference in elution section operation. This operation is represented graphically in Figure 1.13. Changes in the acid concentration of the product stream only altered the elution column profile in the first one or two feet of column. The maintenance of a product acid concentration greater than $\sim 0.5M$ HCl requires about one or two extra feet of column in the elution section for the recycle and concentration of uranium. This type of operation produces an aqueous phase uranium concentration higher than the product uranium concentration somewhere in the elution section of the contactor.

Elution tests made to evaluate the effect of higher product uranium concentration upon elution section length requirements are illustrated in Figure 1.14. The results of these tests indicate that very little additional column length is required to concentrate the column product to a uranium concentration four times greater than the loaded resin uranium concentration (resin loading from the adsorption section on a wet resin basis). Even at the relatively high acid product concentrations obtained in these tests, less than 8 feet

FIGURE 1.13 Higgins Contactor Elution Section Profile Results* (Average Profile)

NOTE: This diagram represents only the mid-section of a larger nonlinear plot.

of elution section would have been required to produce a uranium-free resin stream.

Higgins Contactor Product Purity

One contactor test was made to determine if Fe^{+++} would be extracted in the contactor system and carried over into the process product. A synthetic solution containing ferric ion was processed in the contactor, and greater than 95% of the iron in the feed solution appeared in the column product. Therefore, all later tests were conducted with feed solutions that had been reduced to a potential of -300 mv with sodium thiosulfate. At this potential, the greater part of the iron in the feed solution is in the ferrous state. $FeCl_2$ de-

FIGURE 1.14 Higgins Contactor Elution
Section Profile Results

contamination achieved in the contactor system was shown to be acceptable for Winlo precipitation purposes.

Both synthetic leach liquors and actual plant leach liquors have been processed in the semi-continuous ion exchange contactor. The product streams from the contactor (containing approximately 50 g/l U) were evaporated until a 150 to 200 g/l U concentration had been reached. The resultant solutions were then used in laboratory Winlo precipitations to produce samples of green salt. Impurity decontamination for two of these tests is presented in Table 1.3.

The ion exchange system decontamination of the alkali and alkaline earth metals was good. The two major contaminants in leach liquors that are adsorbed to some extent in the system, iron

and lead, are decontaminated well in the Winlo precipitation process. Consequently, the green salts produced from ion-exchange column products thus far, have met all metal-grade green salt product purity specifications.

Several contactor tests have been made to determine how altered scrub conditions affect impurity decontamination in the system. These tests indicated that scrub section length (from 3 to 5 feet of length) has virtually no effect upon product purity. In tests where the same leach liquor was processed in both an ambient temperature operation and a hot operation it was found that alkali and alkaline earth decontamination increased, but iron decontamination decreased, at the higher temperatures. The results of these tests are presented in Table 1.4. Lower scrub acid rates had only a small effect upon product purity in these tests where the rate was decreased from a rate equivalent to one half of the resin rate to a rate equivalent to one quarter of the resin rate. Decreased scrub acid concentration (from 5.0M HCl to 3.5M HCl) apparently improved iron decontamination slightly, however, these tests are being rechecked to obtain more precise data as to the effect of scrub acid concentration upon product purity.

Other Contactor Operating Considerations

The major mechanical operating variables of the column include:

1. control and measurement of the amount of resin pulsed,
2. control of the strip water system, and
3. continuous removal of resin fines.

Control of the resin movement in the column has been satisfactory during contactor testing. The sequence timers and the plant water hydraulic operation have been adequate to maintain a steady resin flow during the tests. As resin rates were increased in some tests, slip water rates also increased. However, no serious back mixing has

TABLE 1.3 Product Purity of Continuous Ion Exchange Product and the Resultant Green Salt Product

Element	Feed Concentration (g/l)	Product Concentration (ppm U-basis)	Decontamination Factor	Material Balance for Test (%)	Green Salt Product (ppm U-basis)
For a Synthetic Leach Liquor					
U	25.9	50.3	—	+8.2	—
Ca	6.82	133	1.8×10^3	+3.69	—
Na	66.0	7	3.3×10^5	+2.70	—
K	3.25	<3	$>4.0 \times 10^4$	-3.10	—
Mg	2.34	74	1.1×10^3	-2.22	6
Fe	0.92	1233	2.7×10	-2.49	15
Zr	1.35	34	1.4×10^3	+4.82	—
Al	1.48	58	9.1×10^2	-6.98	47
Mn	2.52	298	3.3×10^2	-3.83	<4
Sn	0.013	4	1.2×10^2	-80.60*	4
Pb	0.060	1660	1.3	+3.11	2
B ₁	—	<1	—	—	<1
Cd	—	<0.2	—	—	<0.2
Cr	—	<5	—	—	<5
N ₁	—	3	—	—	5
For a Plant Leach Liquor					
U	19.8	51.8	—	-2.59	—
Ca	0.25	25	5.2×10^2	+6.37	20
Na	74.0	20	2.2×10^5	-5.58	25
K	0.10	7	6.9×10^2	+1.99	<3
Mg	4.47	120	2.0×10^3	-0.89	39
Fe	0.378	211	9.6×10	+0.30	8
Zr	—	—	—	—	—
Al	—	14	—	—	<6
Mg	1.75	<4	2.2×10^3	-2.79	<4
Sr	—	1	—	—	<5
Pb	0.455	>50	—	—	<1
B ₁	—	—	—	—	—
Cd	—	<0.2	—	—	<0.2
Cr	—	<5	—	—	<5
N ₁	—	<2	—	—	2

* Material balance indicates that Sn was adsorbed by the resin but was not stripped off with water. A dilute NaOH solution removed the Sn from a sample of the resin.

been encountered in the column; and the integrity of the adsorption, scrub, and elution sections of the column has been maintained.

Strip water control by conductivity measurements of the product stream has been excellent, so long as the acid concentration of the product stream is high (about 1M HCl). However, it is desirable to lower the acid concentration of the product stream to within a range of from 0.1 to 0.3M HCl. At acid concentrations in this range,

the uranium content of the product stream interferes with good control measurements. Conductivity probes between the scrub water inlet and the product take-off point of the column should allow good control of the strip water stream when the product stream contains only a small quantity of HCl.

A critical operating variable of the contactor system is the resin particle size. The resin in the column is continually broken through mechan-

TABLE 1.4 Higgins Contractor
Product Purity Data

Element	Feed Concentration (g/l)	Product from Cold Operation	Product from Hot Operation
		(ppm - U	Basis)
	Synthetic Feed Number 1*		
U	—	—	—
Ca	5.44	90	<12
K	11.10	30	<6
Na	49.0	50	15
Mg	7.47	340	56
Al	0.075	9	<6
Fe	1.00	21**	39**
Mn	2.90	260	110
	Synthetic Feed Number 2*		
U	—	—	—
Ca	5.0	100	12
K	6.8	30	<6
Na	45.0	60	6
Mg	5.19	>120	21
Al	0.07	10	<6
Fe	0.98	—	—
Mn	2.84	>120	53

* Temperature was the only column operating condition changed in the testing of this synthetic leach liquor.

** Analyses of the green salt made from the respective contactor product samples.

cal and chemical action, and a build-up of fine broken particles in the system can cause resin-pulsing difficulties. Consequently, a resin backwash has been utilized to maintain a bed of 20 to 50 mesh particles. A rough resin classification has been achieved through the use of the column backwash system at a water rate of approximately 200 gsfh. Resin particles larger than 50 mesh that have been removed from the column in this backwash stream have been caught on a 50 mesh screen and returned manually to the system.

A 3-day contactor test was conducted to determine what resin attrition rate could be expected from the mechanical operation of the column alone. Only HCl was fed to column during this test. A resin attrition rate of 0.1 v/o per day resulted from this operation. Further tests are to be conducted to ascertain resin attrition rates under the

designed operating conditions of a large-scale contactor flowsheet.

RESIDUE PROCESSING IN A MIXER-SETTLER SYSTEM BY AN ALIQUAT-336 EXTRACTION

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Introduction

Mixer-settler systems are widely used in the uranium process industries for the extraction and purification of uranium. This type of system is relatively trouble-free because of its simple mechanical construction and is generally inexpensive to operate because of a low manpower requirement. Previous work at our laboratory¹ had shown that the Aliquat 336 — Solvesso 100 organic solvent system was suitable for the extraction of uranium from uranyl chloride feed solutions. The work reported herein was undertaken to determine the feasibility of purifying uranyl chloride plant feed solutions (hydrochloric acid leach liquors) for use in the Winlo process by the means of a mixer-settler system.

Summary of Results

A summary of the major results obtained on this project are listed below.

1. A series of uranium distribution curves was developed for the extraction of UO_2Cl_2 in a (1) 10 w/o Aliquat/90 w/o Solvesso 100:1M HCl system, (2) 20 w/o Aliquat/80 w/o Solvesso 100:1M HCl system, and (3) 30 w/o Aliquat/70 w/o Solvesso 100:1M HCl system.

2. The extraction of uranium from a solution containing 30 g/l UO_2Cl_2 and 1M HCl was accomplished by a 20 w/o Aliquat:Solvesso system. Three mixer-settler stages would be required to produce an organic product containing 37 g/l of uranium.

3. The phase disengagement characteristics of the 20 w/o Aliquat extraction system were studied in a single-stage continuous box mixer-settler

system. The major factor contributing to large dispersion bands was throughput rate.

4. Impurity decontamination of the uranium-laden organic phase in a 2M HCl scrubbing operation yielded a product upon re-extraction and evaporation that was amenable for processing to UF_4 via the Winlo process. The finished UF_4 was within the required chemical specifications for a Winlo product.

5. A series of uranium distribution curves was obtained for the re-extraction of UO_2Cl_2 from 20 w/o Aliquat with the following re-extraction agents: H_2O , 0.4M H_2SO_4 , and 0.7M H_2SO_4 .

6. Water stripping of the uranium-laden Aliquat solvent was unsatisfactory because of low uranium concentration; however, product concentrations as 180 g/l U could be obtained when sulfurous acid was used to aid in the re-extraction operation. Relatively stable emulsions were formed in the sulfurous acid stripping tests; centrifugal extractors would be required for such a system.

Experimental Procedure

Distribution Data

The distribution of uranium between the Aliquat-Solvesso phase and the aqueous phase was experimentally determined by a batch shakeout procedure in 250-ml pear-shape separatory funnels. Earlier work⁷ had indicated that a solvent consisting of Aliquat 336, a tricaprylyl monomethyl quaternary ammonium chloride, in an aromatic diluent, Solvesso 100, met the process requirements for the extraction of UO_2Cl_2 . A predetermined volume of the aqueous phase was added to a separatory funnel and then followed by the addition of the proper amount of the 20 w/o organic phase (20 w/o organic phase will be used to designate a solution of 20% by weight of Aliquat and 80% by weight of Solvesso 100). The mixture was vigorously hand shaken for 60 seconds, and the phases were allowed to separate. The phases were drained off separately and analyzed for uranium.

Phase Disengagement

Three batch test procedures were devised for preliminary evaluation of the phase disengagement characteristics of the Aliquat - Solvesso:aqueous* system.

1. *250-ml Pear Shaped Funnel* — The procedure was the same as described in the above distribution data procedure. The disengagement time was the time necessary for the phases to separate completely after shaking.

2. *600-ml Straight Side Open Top Separatory Funnel* — Phase disengagement characteristics when studied at temperatures of 125°F required a heated separatory funnel. The graduated separatory funnel was wound with electrical heating tape to maintain a temperature of 125°F. The two phases were added (aqueous first) and agitated with a four-bladed turbine mixer for 1 minute at ~500 rpm (see Figure 1.15, Turbine Detail). The phase separation time was the time from mixer shut-off to complete phase disengagement.

3. *Box Mixer* — A graduate, 3-inch-square Lucite box, 11 $\frac{1}{8}$ -inches tall with four $\frac{1}{4}$ -inch baffles was also employed to study phase disengagement. The two phases were added (aqueous first) and agitated with the turbine mixer for 2 minutes at ~800 rpm. The amount of phase separation was visually measured every minute until complete separation occurred.

Phase disengagement characteristics of the Aliquat-Solvesso solvent system were also measured under continuous operating conditions in a Lucite box mixer-settler (shown in Figure 1.15 and Figure 1.16). The following general procedure was employed during all continuous runs:

1. The aqueous and organic pumps were started to fill the constant head tanks.

2. The aqueous rotameter was adjusted to the desired flow rate, and the mixer section of the

*Aqueous is used in this report as a generic term which would cover any aqueous solution brought into contact with the organic phase, i.e., 0.7M H_2SO_4 solution would be considered as an aqueous phase.

FIGURE 1.15 Box Mixer-Settler Construction Details

unit was filled to overflow through the weir opening.

3. After the agitator was started and adjusted to the proper speed, the organic rotameter was set to the required flow rate.

4. When the settler section was about filled, the aqueous weir overflow was adjusted to a height to keep an aqueous level 1-inch above the aqueous phase discharge port in the settler.

5. The unit was run until the thickness of the dispersion band reached a steady-state condition (usually in about three total volume changes).

Discussion

Batch Tests, Extraction

Uranium distribution curves are shown in Figure 1.17 for the distribution of uranyl chloride (UO_2Cl_2)

FIGURE 1.16 Continuous Box Mixer-Settler Unit

FIGURE 1.17 Uranium Distribution Curve for Pure UO_2Cl_2 Solutions and Aliquat - Solvesso 100 (Ambient Temperature)

in a 1.0M HCl aqueous phase and an organic phase of 10 to 30 w/o Aliquat dissolved in Solvesso 100. A McCabe-Thiele graphical analysis of the distribution curve was made to determine the number of ideal stages that would be required for the complete extraction of uranium from a plant feed solution (leach liquor). The parameters of this analysis were (1) a 30 g/l U and 1M HCl feed solution, (2) a 95% uranium saturation of the Aliquat, and (3) a final raffinate stream containing <0.05 g/l U. Three theoretical stages resulted from the analysis of the 20 w/o Aliquat system. The graphical analysis is shown in Figure 1.17.

Phase disengagement characteristics were studied principally in the 600-ml separatory funnel and the box mixer. A series of tests was made to determine if a correlation existed between coalescence time and the size of dispersion band formation. A number of factors were studied to find the specific influence that they exerted on

the coalescence rate of the leach liquor:organic mixture. In general, the following factors had no appreciable effect on the rate of coalescence of the dispersion band: agitator speed, length of time of mixing, new organic versus organic that had been used several times, organic-to-aqueous (O/A) ratio, and per cent uranium saturation of the organic phase. The coalescence rate was determined by plotting the heights of the organic, aqueous, and dispersion band phases for given time intervals prior to complete coalescence (Figure 1.18). The coalescence rate was considered to be the sum of the individual organic and aqueous rates as measured half-way through the total coalescence time. In most cases, this rate amounted to the sum of the maximum tangents (disregarding signs) of the upper and lower part of the coalescence curve.

Coalescence tests were continued to investigate the effect of O/A ratio and the uranium saturation of the organic phase on the coalescence rate and water entrainment. A synthetic leach liquor was prepared and run with the 20% Aliquat system. In Table 1.5 are shown the results of these tests.

The only significant trend detected in these tests was an increase in the aqueous entrainment level of the coalesced organic phase with an increased organic-to-aqueous ratio. All of the tests produced a water-in-oil-type dispersion. When the solutions from these tests were remixed, an oil-in-water-type dispersion band formed, and water entrainment in the organic phase increased

FIGURE 1.18 Dispersion Band Height as a Function of Settling Time

two to four times over that of the previous tests. This could create difficulties in the startup of a multistage mixer-settler unit.

Batch Tests, Scrub

A set of tests was made to determine the conditions that would be required (1) to yield a coalescence time of 11 min, (2) to produce a raffinate of 2 g/l U or less, and (3) to sufficiently decon-

TABLE 1.5 Coalescence Times and Rates Using a Synthetic Leach Liquor and 20 w/o Aliquat

Uranium Saturation of the Organic Phase (%)	Organic-to-Aqueous Ratio								
	0.7/1			1/1			1.3/1		
	Time (min)	Maximum Rate (in/min)	Aqueous Entrainment in Organic (v/o)	Time (min)	Maximum Rate (in/min)	Aqueous Entrainment in Organic (v/o)	Time (min)	Maximum Rate (in/min)	Aqueous Entrainment in Organic (v/o)
95	10.92	1.17	0.08	11.23	1.45	0.25	10.92	1.37	0.4
85	11.87	1.18	0.07	12.67	1.15	0.4	11.30	1.37	0.4
75	9.02	1.64	0.05	10.20	1.39	0.2	11.73	1.27	0.5

taminate the organic phase of impurities so that the subsequent stripping operation would be capable of yielding a product acceptable for the Winlo process. The 11 minute coalescence time was based on an average settling time that would be available in the mixer-settler system at a flow rate of 50 gsfh. The tests indicated that good organic impurity decontamination could be achieved at scrub operating conditions of 121°F, 2 minutes mixing time, an O/A ratio of 10/1 and an aqueous solution containing 2M HCl. The resulting aqueous raffinate from this operation contained only 1.6 g/l U.

The above optimum scrub conditions were used to decontaminate an organic product from a continuous extraction run. The impurity decontamination achieved in the continuous extraction run, as well as the decontamination in the scrubbing operation, are presented in Table 1.6.

The data shown in Table 1.6 indicate that the major impurities could be removed by the mixer-settler system and that the Aliquat system is capable of producing a product acceptable for the Winlo process.

Batch Tests, Re-extraction

Uranium distribution curves are shown in Figure 1.19 for the distribution of UO_2Cl_2 in various aqueous solutions and a corresponding Aliquat -

Solvesso organic phase. A McCabe-Thiele graphical analysis of the distribution data was made to determine the number of ideal stages that would be required for the complete re-extraction of uranium from a scrubbed organic product containing 37.5 g/l U. A summary of the graphical analysis is shown in Table 1.7. Emulsions were encountered in the batch tests used to obtain the equilibrium data (Figure 1.19) for these calculations. Observations of the phase disengagement characteristics of each system are included in Table 1.7.

Good phase disengagement characteristics were obtained for water as a stripping agent except for the last re-extraction stage (lowest uranium concentration). Coalescence times of 2 to 3 minutes were obtained for all but the last stage where stable emulsions were formed.

In all of the work with H_2SO_3 as a stripping agent, the aqueous phase was made by bubbling SO_2 into H_2O at $\sim 80^\circ\text{F}$ until the desired acid concentration was reached. The same procedure was used in preparing the SO_2 saturated organic phase. The experimental procedure previously described was then followed. None of the above H_2SO_3 systems appeared conducive to continuous mixer-settler operation. Heavy, stable emulsions formed in a number of the stages of each system, but the emulsion was broken by centrifugation in a DeLaval Gyro Test Unit. The following points may be observed from the data presented in Table 1.7:

TABLE 1.6 Decontamination Factors for Extraction and Scrub Sections of the Laboratory Mixer-Settler System

Impurity	Feed* (AF) (ppm)	Extraction Decontamination Factor	Product (AP) (ppm)	Scrub Decontamination Factor	Organic Product (BP) (ppm)	Winlo Decontamination Factor	Calculated Winlo Product (ppm)	Tentative Winlo Spec (ppm)
Fe	88,000	40	2200	1	2200	200	11	100
Mg	835,000	500	1670	2	835	100	8.3	**
Mn	216,000	100	2160	15	144	200	<1	**
Ca	865,000	1000	865	22	39	0	39	**

* ppm (U basis)-These values are the highest reported for the Scrap Recovery Plant acid filtrate.

** Not established.

TABLE 1.7 Ideal Stages Needed for Uranium Re-Extraction
(20 w/o Aliquat - Solvesso System)

Stripping Agent	Aqueous Uranium Concentration (CP) (g/l)	Number of Ideal Stages	A/O Ratio	Phase Disengagement Characteristics
H ₂ O	27.5	9	1.33 : 1	Dispersion bandbreaks easily except last stage of each system.
	25	5	1.49 : 1	
	20	3	1.89 : 1	
	15	2	2.50 : 1	
0.4M H ₂ SO ₃	73	8	1 : 2	Stable emulsion formed.
	57	5	1 : 1.5	
	37.5	4	1 : 1	
0.7M H ₂ SO ₃	112	7	1 : 3	Stable emulsion formed.
	92	5	1 : 2.5	
	74	4	1 : 2	
	37.5	3	1 : 1	
0.7M H ₂ SO ₃ *	180	2	1 : 5	Stable emulsion formed.
	150	2	1 : 4	

NOTE: Test conducted at ambient temperature (~85°F) except for H₂O which was 126°F.

* Organic phase saturated to 1.4M H₂SO₃.

FIGURE 1.19 Uranium Distribution Curve 20
w/o Aliquat - Solvesso:Aqueous

1. Water as a stripping agent is rather ineffective. The maximum U concentration obtainable in the product is 27.5 g/l, and this would require nine mixer-settler stages.

2. Sulfurous acid (SO₂ in H₂O) when employed as a stripping agent is four times as effective as water. Sulfurous acid of 0.7 molarity will re-extract uranium to produce an aqueous product of 112 g/l U.

3. The product uranium concentration from sulfurous acid stripping can be considerably improved if the organic phase is saturated with SO₂. Uranium concentrations of the aqueous phase (CP) as high as 180 g/l U may be achieved by this method.

Other re-extraction tests were conducted in an attempt to obtain a product highly concentrated in uranium (>150 g/l U) but with no emulsification in the individual re-extraction stages. A 50 w/o Aliquat:Solvesso 100 - sulfurous acid re-extraction system was investigated briefly. Aqueous phase uranium concentrations as high as 280 g/l U could be obtained from this system which is highly sensitive to the H₂SO₃ concentration of each phase. The strong effect of sulfurous acid concentration upon the uranium distribution coefficient (U in the

aqueous/ U in the organic) is illustrated in Figure 1.20. This 50% Aliquat re-extraction system yielded emulsions as stable as those encountered in the 20% Aliquat system and further investigation of the system was discontinued. Hydrofluoric acid and dilute sulfurous acid re-extraction systems as well as alternate diluents were studied to circumvent the emulsification problem. Coalescence tests were conducted for various stages of each re-extraction system. A summary of results from these tests are presented in Table 1.8.

Hydrofluoric acid solutions (0.3M to 0.7M) aided phase disengagement in the 20% re-extraction. However, subsequent continuous box-mixer settler runs employing HF were unsuccessful because of excessive organic entrainment (~ 7 v/o) in the aqueous product. Fairly stable emulsions formed in the dilute H_2SO_3 re-extraction tests and, although they were not as stable as the emulsions formed in the more concentrated H_2SO_3 tests, normal mixer-settler operation would be prohibited. The alternate diluent combinations studied did not improve the phase disengagement characteristics of the Aliquat - water re-extraction operation.

FIGURE 1.20 Effect of H_2SO_3 Concentration on Uranium Distribution (50 w/o Aliquat - Solvesso: H_2SO_3 System at Ambient Temperature)

Continuous Runs, Extraction

A mixer-settler unit was considered as one possible type of extraction system for the extraction of uranium from plant scrap leach liquors. The solvent system employed throughout the following

TABLE 1.8 Re-Extraction Coalescence Times for Various Stripping Agents and Alternate Diluents

Test No.	Organic Phase	Aqueous Phase	Coalescence Time	Comments
1	20% Aliquat :Solvesso	0.7M HF	1½ min	Excellent break
2	20% Aliquat :Solvesso	0.3M HF	1½ min	Excellent break
3	20% Aliquat :Solvesso	0.1M HF	20 min	Both phases cloudy
4	20% Aliquat :Solvesso	$\sim 0.02\text{M}$ H_2SO_3	1 hr	Pieces of emulsion in aqueous
5	20% Aliquat :Solvesso	$\sim 0.06\text{M}$ H_2SO_3	>19 hr	Pieces of emulsion in aqueous
6	20% Aliquat :Solvesso	$\sim 0.3\text{M}$ H_2SO_3	~ 5 min	Pieces of emulsion in aqueous
7	20% Aliquat :Solvesso	H_2O	>19 hr	95% of organic — very milky
8	20% Aliquat 20% Dibutyl butyl phosphonate 60% Kerosene	H_2O	>19 hr	40% of organic — very milky
9	20% Aliquat 20% Isodecanol 60% Kerosene	H_2O	>19 hr	20% of organic — very milky

NOTE: All tests made at $\sim 120^\circ\text{F}$ except No. 4 through 6 which were made at 100°F .

continuous runs was a 20 w/o Aliquat - 80 w/o Solvesso 100. Several designs of mixer-settler systems were examined, and a single stage laboratory mixer-settler unit was constructed. This unit was similar to one stage of the British mixer-settler system⁸ for the uranium concentrate purification in the TBP-nitric acid system. The British mixer-settler system utilizes gravity countercurrent flow for all interstage liquid transportation. Details of the stage are shown in Figures 1.15 and 1.16.

Early in the operation, it was realized that several factors could contribute materially to the dispersion band formation. A study of these factors and their numerical effect on the dispersion band was undertaken.

Throughput Rate

The total liquid flow through a mixer-settler system affects the dispersion band formation in the system in an exponential manner.⁹ An early test run showed that this relationship existed in the Aliquat:Solvesso - UO_2Cl_2 system. The effect of total throughput rate on the dispersion band size for a 20 v/o Aliquat - Solvesso:uranyl chloride extraction is presented in Table 1.9.

TABLE 1.9 Effect of Total Throughput Rate on the Dispersion Band Size (Ambient Temp & O/A = 3/4)

Total Flow (gsfh)	Dispersion Band (inches)
27	1.00
40	2.00
53	5.35
60	8.10
66	8.5 (flooded) in 40 min
79	8.5 (flooded) in 14 min

Later tests (Figure 1.22) support the above exponential dispersion band increase with increased flow rates for different conditions of settler length and O/A ratios.

Uranium Concentration

A McCabe-Thiele graphical analysis of the uranium distribution curve for the 20 v/o organic - UO_2Cl_2 extraction system indicated the requirement for three theoretical stages. The individual ideal stage uranium concentrations (g/l) are shown below for 95% uranium saturation of the organic phase.

Stage	Incoming Organic	Incoming Aqueous
1	0.00	0.32
2	0.39	3.5
3	4.3	30.0

Each of the three stages was operated at the concentrations shown above to determine the uranium concentration effect on the dispersion band formation. The results of these runs were as follows:

Stage	Total Flow Rate (gsfh)	O/A	Dispersion Band (in.)	Organic Appearance
1	50	0.75	2.35	Hazy
2	50	0.75	1.75	Clear
3	43	0.51	0.10	Very cloudy

The cloudy organic phase of the third stage contained 2% entrained water. No further study was made on Stages 1 and 2 since it was felt that the low aqueous entrainment and the relatively small dispersion band yielded operable stages. Several tests were made at various operating conditions to lower the aqueous entrainment associated with the Stage 3 organic product. Altered stage operating conditions did little to reduce this entrainment. However, it was determined that Stage 3 aqueous entrainment was reduced to <0.3 v/o when actual plant leach liquors were used in the system rather than pure UO_2Cl_2 solutions. The additional salt strength of the leach liquors probably was responsible for better coalescence.

Agitator Speed

A study of the effect of mixer agitator speed on the dispersion band was made under constant throughput conditions. The results of this study are shown in Figure 1.21.

FIGURE 1.21 Effect of Agitation Speed on Dispersion Band Thickness

The effect of agitator speed was considered to be of minor importance in the dispersion band generation since a change in agitator speed from 500 rpm to 800 rpm increased the dispersion band by only $\frac{1}{2}$ inch. Hence, all ensuing runs were made at a constant 800 rpm to eliminate mixer speed as a variable.

A series of tests was made to study the effect of the horizontal settler area on the dispersion band thickness as a function of throughput. This was accomplished by varying the length of the settler while the other box dimensions were kept the same. The results of these tests are presented graphically in Figure 1.22. The effect of dispersion band as a function of settler length appears to be small in the range investigated.

An analysis of continuous runs had indicated that the rate of dispersion band growth could be used to calculate a steady-state dispersion band thickness. An equation was developed which gave good agreement with the available experimental data

FIGURE 1.22 Effect of Total Throughput Rate on the Extraction Dispersion Band (20 w/o Aliquat - Solvesso:Leach Liquor)

$$\ln\left(\frac{\alpha_s - \alpha_t}{\alpha_s}\right) = kt$$

where α_s = steady-state dispersion band width
 α_t = dispersion band width at time t
 k = proportionality constant for the run
 t = time

The equation was utilized (1) to predict the dispersion band size when conditions were encountered that caused bands larger than the 9-inch available height of the laboratory settler chamber, and (2) to shorten (in some cases) the experimental time required for certain mixer-settler tests. The departure of calculated curves from the experimentally derived curves are shown in Figure 1.23. The equation proved useful and accurate when used during a time range extending from the time required for one complete volume change to the time required to reach 99% of steady-state operation.

The conditions of a typical continuous extraction run are shown in Table 1.10, and the disper-

FIGURE 1.23 Calculated and Experimental Extraction Dispersion Band Curves for the Equation $\ln\left(\frac{\alpha_s - \alpha_t}{\alpha_s}\right) = kt$ (See discussion in text.)

sion band growth curve is the largest dispersion band curve shown in Figure 1.23.

In general, the dispersion band reached a steady-state condition by the end of the third volume change, although in some cases where the band thickness was relatively small, steady-state was reached just prior to the end of the first volume change.

Product Purity

A green salt (UF_4) was prepared from an Aliquat - Solvesso extraction system product in a laboratory Winlo precipitation. An organic product (AP) and a scrubbed organic product (BP) were con-

TABLE 8.10 Operating Conditions of a Typical Continuous Extraction Run (Box Mixer-Settler System)

Aqueous Phase Composition (g/l)				Organic Phase	
U	37	Fe	1.0	20 w/o Aliquat 330	
H ⁺ (N)	1.1	Mn	5.4	80 w/o Solvesso 100	
F	5.5	Ca	7.8		
Cl	115	Mg	16.0		
Run Conditions					
Mixer Speed (rpm)				800	
Aqueous Rate (ml/min)				273	
Organic Rate (ml/min)				319	
Organic Entrainment (v/o H ₂ O)				0.25	
Temperature (°F)				78	
Dispersion Band Formation					
Time (min)	0	10	20	30	40
Volume Change	0	1	2	3	4
Band (inches)	0	4.38	5.93	6.90	7.38

tinuously prepared in the mixer-settler unit. The conditions of the AP product generation were similar to those shown in Table 1.10, and the scrubbed organic product (BP) conditions were similar to the conditions shown in the subsection, Batch Test, Scrub. The product for Winlo precipitation was generated by a batch re-extraction of the BP and subsequent evaporation. The spectrochemical analysis of the resultant Winlo product is shown in Table 1.11.

The above spectrochemical analysis of the Winlo product has shown that the product is comparable chemically to a control sample (a pure UO_2Cl_2 solution converted to UF_4) and within the proposed specifications for Winlo UF_4 .

TABLE 1.11 Analyses of Winlo UF_4 From Pure UO_2Cl_2 and Mixer-Settler Winlo UF_4 (ppm on U Basis)

	Al	Cd	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Sn	Zn	Tap Density	AOI (%)
Control	<6	<0.2	<5	63	11	<4	<4	4	1	<1	<20	3.08	<0.01
Mixer-Settler Winlo UF_4	<6	<0.2	<5	21	22	<4	<4	2	1	<1	<20	3.08	<0.01
Tentative Winlo UF_4 Specifications	125	*	15	50	100	*	*	15	*	*	*	*	1.0

* Not established

Reduction of Leach Liquors

Preliminary Aliquat extraction experiments⁷ indicated that leach liquors must be reduced to prevent ferric chloride extraction. Subsequent work¹⁰ indicated that leach liquors could be reduced with a hydrochloric acid metal dissolver product (UCl_4) to a electrical potential of -300 mv. At this point almost all of the ferric chloride had been converted to ferrous chloride; consequently all of the leach liquors tested in these box mixer-settler tests were reduced to a potential of 300 ± 10 mv. An initial test showed that a leach liquor (composition, g/l: U 30, Fe 1.62, Mg 6.84, Mn 2.67, HCl 0.8M) could be reduced from 670 mv to 290 mv with 2.0 ml of filtered metal dissolver product (200 g/l U) per 100 ml of acid filtrate.

A series of experiments were made to determine the degree and rate of reoxidation that could be expected from chemically reduced leach liquors. Reoxidation rates for various samples of leach liquor were fairly slow (one sample reoxidized from 290 to 375 mv in 16 hours), but reduced feed solutions had to be kept covered to prevent air oxidation.

Solvent Losses

A preliminary study was made to determine probable solvent evaporation losses in the handling and storing of a 20% Aliquat in Solvesso 100 solution. An experiment was conducted in which a controlled rate of air was drawn over the 20 w/o organic solution contained in a 1000-ml flask, and the weight loss for a given time was noted. The following solvent losses were determined:

Temperature (°F)	Air Rate (Volume Changes per Hour*)	Solvent Loss (lb/hr/sq ft)
85	12-36	0.0033
120	12	~0.015

*Linear air velocity approximately 0.05 to 0.16 ft/min.

Materials of Construction

A preliminary evaluation was made of materials of construction for the 20 w/o Aliquat - Solvesso organic system and the aqueous UO_2Cl_2 (0.9M HCl) system. The following materials appear to be satisfactory for use in an extraction system which uses these solutions.

Organic Phase	Aqueous Phase	
	Metallic	Non-metallic
Penton	Hastelloy 25	Penton
polypropylene	Hastelloy C	polypropylene
polyethylene		polyethylene
Kel F		Kel F
Teflon		Teflon
glass		glass
Lucite		Lucite

Future Work

Pilot-scale ion-exchange tests will be continued to develop fully all necessary data for a plant-scale prototype ion-exchange column. Resins other than Dowex 21K will be evaluated in the pilot-scale contactor for possible use in a prototype contactor flowsheet.

Uranium re-extraction from the Aliquat - Solvesso solvent will be investigated further. A complete cost evaluation of a finalized liquid extraction process will be made and the flowsheet, if economically attractive, will be tested on a pilot scale.

References

¹E. O. Rutenkroger and J. H. Cavendish. "Scrap Processing by an Amine Extraction - Aqueous UF_4 Process," Summary Tech. Rpt. for the Period January 1, 1959 to March 31, 1959, USAEC report NLCO-785, pp. 61-72, April 15, 1959 (Classified).

²C. S. Cronan, ed. "Ion Exchange Column Runs Continuously," Chem. Eng., 64:184. July, 1957.

³"Novel Process Tools Win First Job," Chem. Eng., 66:84. July 13, 1959.

⁴N. J. Setter, J. M. Googin and G. B. Marrow. The Recovery of Uranium from Reduction Residues by Semi-

continuous Ion Exchange, USAEC Report Y-1257. July 9, 1959.

⁵K. A. Kraus and F. Nelson. "Anion Exchange Studies of the Fission Products," International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955, Proceedings, Vol. 7, p. 113. Geneva:United Nations Press, 1956.

⁶K. A. Kraus and F. Nelson. "Metal Separations by Anion Exchange," Symposium on Ion Exchange and Chromatography in Analytical Chemistry, ASTM Special Technical Publication No. 195, pp. 27-57. Philadelphia:American Society for Testing Materials, 1958.

⁷T. J. Collopy, J. H. Mueller, W. S. Miller, R. K. Klopfenstein and W. P. Tolos. "Conversion of Scrap Materials to Uranyl Chloride," Summary Tech. Rpt. for the Period April 1, 1962 to June 30, 1962, USAEC report NLCO-855, pp. 19-26. July 25, 1962.

⁸A. Price and W. L. Wilkinson. The Purification of Crude Uranyl Nitrate Liquors at Springfields Works by Solvent Extraction, Paper Presented to the Graduates and Students Section of the Institution of Chemical Engineers in Manchester, England, February 23, 1961.

⁹A. D. Ryan, F. L. Daley and R. S. Lowrie. "Scale-up of Mixer-Settlers," Chem. Eng. Progress, 55:70. October, 1959.

¹⁰J. H. Mueller, W. P. Tolos, J. H. Cavendish and T. J. Collopy. "Uranous Chloride as a Reducing Agent for Iron in Scrap Recovery Plant Leach Liquor," Summary Tech. Rpt. for the Period October 1, 1962 to December 31, 1962, USAEC report NLCO-865, pp. 7-11. February 1, 1963.

2. CLEANING DERBIES WITH AN AIRLESS BLASTER USING URANIUM SHOT

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Abstract

A commercial airless shot blaster was installed in the Pilot Plant to clean surface slag from uranium derbies. Uranium shot, a by-product of slag processing, was selected as the blasting medium. Both enriched and normal derbies having various amounts of adhering slag were adequately cleaned.

Introduction

In the production of uranium ingots at the National Lead Company of Ohio, a composite charge of uranium consisting of derbies, briquetted machining chips, and solid scrap is melted in a graphite crucible and then cast in a refractory-coated graphite mold in a vacuum induction furnace. The uranium and the slag on the derbies attack the graphite crucible. The attack is reduced by the use of refractory coatings, but a stable coating has not yet been developed. Present practice is to use uncoated crucibles and tolerate an increase in carbon in the ingot.

It was reasoned that the removal of the magnesium fluoride slag from the derbies before the remelting operation would reduce the attack on the crucible and thereby decrease the carbon pickup, increase the crucible life, and result in better ingots. Previous efforts were made to remove the slag by leaching, acid pickling,¹ and heat shocking.² These methods were costly and resulted in decreased derby yields. Airless blasting was selected as a likely method because it is a dry, cold method, the base metal is not attacked, and the blasting medium is a by-product of one of the plant processes.

Objectives for This Quarter

The objectives were as follows:

1. To determine the ability of the airless blaster to clean both enriched and normal derbies having

various amounts of adhering slag.

2. To select a blasting medium having suitable cleaning power. This material should be of reasonable cost and should not contaminate the metal being blasted.

Summary of Results

The derby cleaning program was carried out in the Pilot Plant in three phases.

In the first phase, 27 Grade III (lowest grade, most slag) derbies were blasted with steel shot. Ingots cast from these derbies analyzed from 26 to 72 ppm higher in iron than the derbies in the charges. This iron contamination was attributed to the entrapment of steel shot in the interstices of the derbies.

In the second phase, 136 enriched derbies were cleaned with uranium shot. These derbies were melted in charges containing two or three derbies with sufficient other scrap to make 1400 pounds. As a control, manually cleaned derbies plus briquettes and scrap were used in other charges. The results showed that the crude ingot yield was higher, and the hydrogen content was lower, when shot-blasted derbies were used as part of the charge.

In the third phase, 145 normal derbies were cleaned with uranium shot. The results showed that the top of the derby must be blasted a minimum of 5 minutes, and the bottom for 3 minutes, to assure adequate slag removal.

Equipment

The airless shot blasting machine used in this test was installed in the Pilot Plant. The machine is a commercial model, called a Rotoblast, manufactured by the Pangborn Corporation. It consists of a fully enclosed work table, an airless blaster,

an abrasive elevator, and a pneumatic abrasive separator. All are adequately ventilated (see

Figures 2.1 and 2.2). A description of these major components follows.

1297 - 1

FIGURE 2.1 Rotoblast Airless Blasting Equipment

1297 - 2

FIGURE 2.2 Interior View of Equipment Showing Work Table Loaded with Derbies

Work Table

The work table is 4 feet in diameter, providing 12.6 square feet of work area. It can accommodate work 2 feet in height with a maximum weight of

4000 pounds. The steel cabinet and door surrounding the work table are protected from the blast stream by wear pads. The surface of the table is protected by replaceable rubber mats. The table rotates at 4 rpm in a counterclockwise direction.

PHOTO CREDIT - PANGBORN CORPORATION

FIGURE 2.3 Cutaway View of Rotoblast Showing Operating Parts. Visible are the Feed Spout, the Feed Slot which Lengthens the Abrasive Stream, the Vaned Rotor which Imparts Velocity to the Abrasive by Centrifugal Force, and the Protective Wear Plates in the Wheel Housing.

Airless Blaster

This unit uses the principle of controlled centrifugal force for its blasting power. In operation,

an abrasive is fed by gravity down a spout to a cage housing a rotating impeller (Figure 2.3). The abrasive is picked up by the rotating paddles on the impeller, discharged through a slot in the cage

onto the path of the rotating vanes. Since the vanes are operating at the same speed, the abrasive slides radially along the surface of the vane and is discharged from the outer edge with both radial and tangential velocity.

The blaster is driven at 3000 rpm by a 15 hp motor and propels 22,000 pounds of abrasive per hour.

Elevator

Scrapers are attached to the underside of the work table to move the accumulated abrasive into the elevator boot. There the abrasive is picked up by a bucket elevator and carried up to a pneumatic abrasive separator.

Pneumatic Abrasive Separator

As the abrasive enters the pneumatic abrasive separator, it passes over a stratification plate and

then through an air wash. Dust and fines are removed by the air current. The large particles are retained on a $\frac{3}{8}$ -inch scalping screen. The shot then passes to a storage bin where it is retained until required for blasting.

Ventilation

The grill work in the upper left-hand corner of the enclosure (Figure 2.2) is the opening to the exhaust duct. One thousand cfm of air sweeps in through louvered intakes on top of the door (Figure 2.2). Five hundred cfm of air passes through the pneumatic separator.

Blasting Media

Source of Blasting Media

Steel shot for the test (Figure 2.4) was purchased from the Pangborn Corporation, manufacturers of the Rotoblast machine.

FIGURE 2.4 Uranium Shot (-8 Mesh) Compared with Commercial Steel Shot (Actual Size Photograph)

The uranium shot used (Figure 2.4) was a by-product of a plant process. In the reduction of green salt with magnesium, the reaction products are liquid uranium and magnesium fluoride. During the cooling period, the uranium sinks down through the slag to settle at the bottom of the reduction vessel as a derby. During this settlement, small droplets of uranium are entrapped in the slag as it solidifies.

The uranium derby and slag are broken out of the reduction pot, the derby is cleaned for remelting, and the slag is processed for reuse as liner material for the reduction pot. When the slag is crushed, the small uranium droplets and the unreacted magnesium are freed. The metallic particles are separated from the slag liner fines. This by-product, formerly returned to the production stream as oxide, is the material now used as shot for cleaning derbies.

Charging the Machine with Shot

Steel Shot. Approximately 1800 pounds of steel shot were required to charge the system. The scrapers under the table cleared the floor of the enclosure by 1 inch. The shot was poured on the work table and the scrapers moved it into the elevator boot. When the storage bin was full, the system was considered charged with shot, and the table was ready to be loaded with derbies.

Uranium Shot. To reduce the amount of uranium shot required to charge the machine, all the voids in the machine were filled with slag liner. Slag liner was poured onto the table top for distribution beneath the work table. All of the corners in the enclosure were filled with slag liner. The charging of slag liner was continued until the slag started to discharge into the pneumatic abrasive separator.

The magnesium and uranium shot mixture, previously screened through an -8-mesh screen, consisted of approximately 75% to 85% magnesium by volume. To remove the magnesium, the mixture was poured directly into the elevator boot. From

there it passed through the pneumatic abrasive separator where approximately 99% of the magnesium particles was removed by the air stream. The storage bin was loaded with approximately 1000 pounds of shot, and the system was ready to be loaded with derbies.

Cleaning Procedure

Both enriched and normal derbies of Grades I, II, and III were cleaned. (Derbies are graded visually according to the amount of slag on their surfaces. Grade I derbies are nearly slag free. Grade II derbies are of intermediate quality. Grade III derbies have large amounts of adhering or entrapped slag.) The derbies were handled by means of a scissors grab and were lifted with a hoist.

Six or seven derbies were loaded around the perimeter of the work table, and one derby was placed in the center. The number of derbies loaded depended on the derby grade. If the load consisted primarily of Grade II or III derbies, six were loaded around the perimeter, close to the center derby as shown in Figure 2.9. However, when Grade I derbies were loaded, seven were placed around the perimeter as shown in Figure 2.5. The area in the center of the work table receives the most concentrated flow of abrasive. Therefore, the derby with the most slag was placed at the center of the table.

After the derbies were loaded on the work table, the door was closed and the derbies were blasted. The tops of Grade II and III derbies were usually blasted in increments of 5 minutes until clean. Grade I derbies were blasted for 3 minutes and then for 2 additional minutes, if required.

After their tops were cleaned, the derbies were turned over. The bottoms of enriched derbies usually required 5 minutes blasting time; the bottoms of normal derbies were usually clean after 3 minutes blasting.

The cleaned derbies were then numbered, weighed, and placed on skids for shipment.

1289-14

FIGURE 2.5 Top View and Loading Arrangement of Grade I Derbies Before Cleaning

Discussion of Results

Phase I, Cleaning Normal Derbies with Steel Shot

Twenty-Seven Grade III derbies were cleaned with steel shot. They were blasted during the machine startup period for undetermined time intervals until all the slag was removed.

After the derbies were cleaned, they were sampled by drilling to ascertain the iron content of each derby. These derbies were then remelted alone to produce six ingots. The ingots were sampled and analyzed for the usual contaminants.

The blast cleaning resulted in an average weight loss per derby of 29 pounds. Individual weight losses ranged from 9 to 77 pounds per derby.

The average iron content of the derby charge and the resulting ingot together with the iron pick-

up attributable to the steel shot is given in Table 2.1.

TABLE 2.1 Iron Contamination,
Phase I Ingots

Ingot No.	Average Derby Analyses (ppm Fe)	Ingot Analyses (ppm Fe)	Contamination from Steel Shot (ppm Fe)
1	77	144	67
2	84	112	28
3	96	122	26
4	95	169	74
5	52	120	68
6	66	103	37

Phase II, Cleaning Enriched Derbies with Uranium Shot

One hundred thirty-six enriched derbies were cleaned with uranium shot. These derbies were

used to produce 8-inch and 9-inch diameter solid ingots. The charges consisted of two or three derbies, 20% briquettes, and solid scrap to complete a 1400 pound charge. Approximately the same number of control ingots were produced using manually cleaned derbies instead of shot-blasted derbies.

The average weight loss per derby after blast cleaning was 7.2 pounds and ranged from 2.5 to 15.5 pounds. Cleaning times were 3 minutes for the tops of the derbies and 5 minutes for the bottoms.

The crude ingot yields and hydrogen levels in the ingots produced from the two types of charges were compared (see Table 2.2).

TABLE 2.2 Comparison of Ingots from Shot Blasted and Control Derbies, Phase II

Ingot Diameter (in.)	No. of Derbies Per Charge	Cleaning Method	No. of Ingots Cast	Ingot Hydrogen Analyses (ppm)	Crude Ingot Yield (%)
8	2	Manual	6	1.8	95.1
8	2	Shot Blasted	5	1.5	97.1
9	2	Manual	11	1.9	92.1
9	2	Shot Blasted	10	1.4	97.7
8	3	Manual	7	2.1	95.6
8	3	Shot Blasted	6	1.4	97.6
9	3	Manual	16	2.6	95.1
9	3	Shot Blasted	11	1.4	97.6

An evaluation of the data in Table 2.2 indicated that there was a real difference in the hydrogen levels and crude ingot yields. Ingots produced from charges consisting of two shot-blasted derbies plus other scrap analyzed 0.4 ppm lower in hydrogen, and the crude ingot yield was 4.2% greater than control ingots produced from manually-cleaned derbies. When the charges contained three shot-blasted derbies plus other scrap, the ingots analyzed 0.95 ppm lower in hydrogen, and the crude ingot yield increased 2.25%. The significance of these differences was ascertained by using the statistical test of equality of two means.³

Phase III, Cleaning Normal Derbies with Uranium Shot

One hundred forty-five normal derbies, including 69 Grade III derbies, were cleaned with uranium shot. These derbies went into the regular production stream for remelting in the Metals Production Plant.

The weight loss per derby resulting from the shot blasting was as follows:

Derby Grade	Average Weight Loss Per Derby (lb)	Range of Individual Weight Losses (lb)
I and II	5.7	1 to 8.5
III	15.8	up to 29

The cleaning time required to remove the adhering slag depended on the amount of slag present. The average cleaning times for the derbies cleaned in the test were as follows:

Derby Grade	Average Cleaning Time (minutes)	
	Top of Derby	Bottom of Derby
I	3	3
II	4 to 8	3
III	10 to 25	3

In Phase III of the test, a number of photographs were taken during operation of the Rotoblast machine. A load of Grade I derbies with the slaggiest derby in the center is shown before cleaning (Figure 2.5) and after 3 minutes of blasting (Figure 2.6). Figures 2.7 and 2.8 show the bottoms of the same derbies before cleaning and after 3 minutes of blasting. The weight losses of each derby shown in the photographs were as follows:

Derby No.	Weight Loss (lb)
5330	1
5331	1.5
5303	2
5295	2
5409	3.5
5294	4
5217	5
4913	5.5

1289 - 13

FIGURE 2.6 Top View of Grade I Derbies After 3 Minutes Cleaning with Uranium Shot

1289 - 11

FIGURE 2.7 Bottom View of Grade I Derbies Before Cleaning

FIGURE 2.8 Bottom View of Grade I Derbies After 3 Minutes Cleaning with Uranium Shot

A series of photographs was taken at 5-minute intervals during cleaning of a table load of Grade III derbies (except for one Grade II derby, No. 9518). The table was loaded for optimum cleaning, (six around the perimeter) (Figure 2.9). The derbies were then blasted for 5 minutes. Note that the Grade II derby (No. 9518) is almost clean (Figure 2.10). In Figure 2.11 the derbies have been blasted for a total of 10 minutes. The Grade II derby (No. 9518) is clean. After the photograph was taken, a sledge hammer was used to break up the slag on Derby No. 128. A platelet of uranium under this slag was also pried loose. In Figure 2.12 the derbies have been blasted for 15 minutes. Note Derby No. 128. The top is now becoming clean. After the photograph was taken, a sledge hammer was used on the bulge on the top of Derby No. 9544, and a platelet of uranium was pried off the top of Derby No. 107. After blasting for 20 minutes,

the derbies appear almost clean (Figure 2.13). In Figure 2.14 the derbies have been blasted for a total of 25 minutes. They are now considered to be clean.

The derbies shown in Figures 2.9 through 2.14 were then inverted on the work table to shot-blast their bottom surfaces. Figure 2.15 shows these derbies before cleaning. Figure 2.16 was taken after 3 minutes of blasting.

The weight lost in blasting by each of these seven derbies was as follows:

Derby No.	Weight Loss (lb)
9518	3.5
128	8.5
9408	12.0
8994	16.0
8854	17.0
107	25.5
9544	26.5

1289 - 1

FIGURE 2.9 Top View and Loading Arrangement of One Grade II (No. 9518) and Six Grade III Derbies Before Cleaning with Uranium Shot. The Derby Having the Most Slag is Located at the Center of the Table

1289 - 2

FIGURE 2.10 Top View of Grade II and III Derbies After 5 Minutes Cleaning. Note that Grade II Derby (No. 9518) is practically clean

1289-3

FIGURE 2.11 Top View of Grade II and III Derbies After 10 Minutes Cleaning. The Grade II Derby (No. 9518) is Considered Clean. Enough Slag Has Been Removed from the Grade III Derbies to Detect Uranium Platelet in Derbies No. 128 and 107 and a Heavy Metal Slag Skull on Derbies No. 9544 and 9408. These were Subsequently Removed with a Sledge Hammer

1289-4

FIGURE 2.12 Top View of Grade II and III Derbies After 15 Minutes Cleaning The Uranium Platelet has Been Removed from Derby No. 128.

1289 - 5

FIGURE 2 13 Top View of Grade II and III Derbies After 20 Minutes Cleaning Note the Uranium Platelet has Been Removed from Derby No 107 and is Lying on the Table. The Skull on Derby No. 9544 has Been Removed down to Solid Metal

1289 - 6

FIGURE 2 14 Top View of Grade II and III Derbies After 25 Minutes Cleaning The Derby Tops are Considered Clean.

1289-7

FIGURE 2 15 Bottom View of One Grade II (No. 9518) and Six Grade III Derbies Before Cleaning with Uranium Shot

1289-8

FIGURE 2 16 Bottom View of Grade II and III Derbies After 3 Minute Cleaning

Conclusions

1. Uranium shot of -8-mesh size can be used in an airless blaster to adequately clean adhering slag from the surface of derbies.

2. Derbies cleaned by shot blasting reduce the amount of slag in the remelt crucible by an average of 5 pounds per derby in the charge.

3. The hydrogen in the resulting ingots is lower because of the elimination of the slag cover over the melt in the crucible. (A slag cover apparently inhibits the evolution of hydrogen from the surface of the uranium.)

4. The crude ingot yield is higher with shot-blasted derbies because the charge weight will represent more actual uranium.

References

¹S. Cseplo and C. C. Fogel. "Method of Cleaning Derbies Produced in Slag-Lined and Dolomite-Lined Furnace Pots," Summary Tech. Rpt. for the Period July 1 to September 30, 1956, USAEC Report NLCO-650, p. 85. October 15, 1956.

²V. G. Minutolo and S. O. Samoriga. "Slag Removal from Uranium Derbies," Summary Tech. Rpt. for the Period July 1 to September 30, 1958, USAEC Report NLCO-760, p. 81. October 24, 1958.

³J. E. Freund, P. E. Livermore and I. Miller. Manual of Experimental Statistics, pp. 16-18. Englewood Cliffs, N. J.: Prentice-Hall, 1960.

3. INSTALLATION AND INITIAL OPERATION OF PLASMA-SPRAYING EQUIPMENT

D. L. Elston

Abstract

Plasma-Spraying equipment for coating graphite remelt crucibles and molds with high-temperature protective materials was installed in the Pilot Plant. The equipment was tested, and small-scale graphite crucibles were coated.

Introduction

An important step in the manufacture of uranium fuel cores at the National Lead Company of Ohio is the vacuum remelting and casting operation for producing uranium ingots. In this process, uranium feed material is vacuum-induction melted in a graphite crucible and poured at 2550°F into a graphite mold. Many problems are being encountered because the graphite is insufficiently protected against the action of the molten uranium. Among these problems are the following:

1. The expensive graphite parts are subject to excessive corrosion and abrasion and require frequent replacement.
2. Impurity levels in the metal are difficult to maintain or control.
3. The molten uranium is contaminated by the graphite, and this contamination frequently results in ingots with more carbon than is allowed by specification.
4. The higher carbon content results in ingots with large carbide agglomerates, and the reactor sites have shown this condition to be undesirable.

Refractory materials are available that do not react with molten uranium, if they can be applied to graphite as well-bonded impervious coatings. Off-site, small-scale, exploratory work¹ showed plasma spraying to be a promising method of application. To continue this work, plasma-spraying equipment was installed in the Pilot Plant.

Objectives for This Quarter

The objectives for this quarter were as follows:

1. To test the operation of the newly installed equipment.
2. To do preliminary small-scale spraying.
3. To make preparations for coating production crucibles and molds.

Summary of Results

The results were as follows:

1. The plasma spraying equipment with its auxiliaries is now in operation.
2. Small-scale crucibles (6¼ inches in diameter and 6¼ inches deep) were successfully coated with magnesium zirconate.
3. A gun extension and positioner were installed for coating the inner surfaces of large, deep crucibles and molds.

Plasma-Spraying Process

The plasma-spraying process uses an electrically neutral inert gas (argon, helium, or nitrogen) that is heated and ionized in a high-intensity electric arc contained in a water-cooled gun. The resulting plasma gas stream is expelled through an orifice at temperatures up to 30,000°F and a velocity of approximately 1200 fps. (The plasma temperature can be controlled by adjusting the arc current and gas flow.) Powdered material is fed into the high-velocity plasma gas stream where it is melted and propelled to the substrate. Because of the high temperatures obtainable, it is possible to melt or vaporize any known material.

Description of Equipment

Major Components (see Figure 3.1):

1. Gun — 40 kw, Type 2MB, Plasma-Spray Gun manufactured by METCO, Inc. The gun consists

1312-9

FIGURE 3.1 Over-All View of the Plasma-Spray Installation. (1) Gun, (2) Control Unit, (3) Power Supply, (4) Powder Feed Unit, (5) Large Welding Positioner, (6) Spray Booth.

of a three piece water-cooled body with the following components:

- a. Thoriated tungsten electrode assembly.
- b. Phenolic gas chamber which also acts as an insulator between the electrode and nozzle.
- c. Copper alloy nozzle.

2. *Control Unit* — METCO, Type 2MC, Plasma-Flame Control Unit that houses in one cabinet all of the operating controls for gas flow, powder supply, powder feed, water flow, and arc current.

3. *Power Supply Unit* — Miller SR-1000 — CIM

welder (supplied by METCO) that converts 230/460 volts, 3 phase, 60 cycle ac into 1000 ampere dc continuous service at 80 volts, open circuit, and 40 volts, load.

4. *Powder Feed Unit* — A SYLCO CCC, Mark VII, fine powder feeding apparatus consisting of a sealed powder container and a variable-speed feed-screw assembly mounted on an electromagnetic vibrator. The equipment is designed to operate with a carrier gas rate between 15 and 100 cubic feet per hour.

1312-10

FIGURE 3.2 Gun Extension Mounted on Positioner

Auxiliary Equipment (see Figure 3.1):

1 *Large Welding Positioner* — A modified welding positioner fitted with a lathe chuck is used to rotate workpieces during spraying. The positioner is mounted on a track and has a variable drive mechanism for uniform traversing rates while large pieces are being coated. Controls for starting and stopping, tilting, and changing rotation speed and traverse rates are within easy reach of the operator.

2 *Spray Booth* — A ventilated paint spray booth was modified to enclose the plasma spraying. The existing plant ventilation system is used to exhaust all air borne particles.

3 *Small Welding Positioner* — A small welding positioner was acquired for positioning the gun when the extension (Item 4 below) is used. The positioner can be fitted with a lathe chuck for rotating small workpieces during spraying.

4 *Gun Extension* — A METCO Type 2MS extension unit was acquired for coating inside surfaces of large deep pieces. Figure 3.2 shows the extension

mounted on the small welding positioner.

5 *Grit Blasting Cabinet* — A modified blasting cabinet (Figures 3.3 and 3.4) is used to clean and roughen surfaces in preparation for coating. Modifications include:

a Mechanically driven rollers in the cabinet to rotate the workpieces during blasting.

b. A variable drive motor to regulate the rotation speed

c. A blast hose mounted on the way of a lathe bed for regulated traversing rates.

d A length of expendable metal pipe with a 45-degree elbow attached to the end of the blast hose. The elbow directs the blast stream onto the workpiece.

6 *Gas Manifold System* — To assure a regulated flow of primary and secondary gases, a special manifold system was installed outside the building. There are four outlets for connecting two cylinders of nitrogen, one of hydrogen, and one of argon or helium. The argon and helium outlets can also be used for nitrogen.

1312-8

FIGURE 3.3 Over-All View of Modified Grit Blasting Equipment

Preliminary Plasma Spraying

Small-scale graphite crucibles ($6\frac{1}{4}$ -inches inside diameter by $6\frac{1}{4}$ -inches deep) were coated with magnesium zirconate (see Figure 3.5). This material had given the best over-all results in the previous investigations.¹ Precautionary measures were taken to protect the equipment and the operator from the heat forced out of the crucible during spraying. The gun was mounted on a bicycle handle bar which kept the operator's hands out of the heat, and the gun and connecting hoses were wrapped with high temperature insulation.

Good coatings were obtained with the following procedures:

1. The refractory powders were screened and the -250 +325 mesh fractions used.
2. The graphite surfaces were roughened by light grit blasting and cleaned to remove the embedded blasting medium and other loose materials.
3. The prepared surface was heated to 400°F prior to coating.
4. Spraying distances of 3 to 7 inches were used (3 to 4 inches was the desired distance, but could not be maintained when spraying the bottom area of the crucible).

1312-6

FIGURE 3.4 Interior View of Grit Blasting Cabinet Showing a Graphite Mold in Position for Blasting.

5. The plasma gas flow rates, arc currents, and voltages used were as follows:

Plasma Gas	Flow Rate (cfh)	Arc Current (amp)	Voltage (dc)
Nitrogen	100	400 to 420	60 to 65
Hydrogen*	15	—	—

* Secondary gas added to increase heat content of plasma flame and to provide additional atmospheric protection for the workpiece.

Future Work

The small-scale investigations of coating materials and bonding mechanisms will be continued. Large-scale evaluations of coatings on production equipment will also be made, as well as an investigation of possibility of other uses for plasma-sprayed coatings on process equipment.

1312-5

FIGURE 3.5 View of a Small-Scale Graphite Remelt Crucible Being Plasma-Spray Coated.
Note gun mounted on bicycle handle bar.

Reference

¹D. L. Elston, and G. Brodi. "Plasma-Sprayed Refractory Coatings on Small-Scale Graphite Crucibles,"

Summary Tech. Rpt. for the period April 1, 1962, to June 30, 1962, USAEC Report NLCO-855, p. 33. July 25, 1962.

4. CONSUMABLE-ELECTRODE ARC-MELTING OF URANIUM

R. L. Schardt

Abstract

Consumable-electrode arc-melting was used to produce production-size uranium ingots. Procedures for the arc melting of uranium in a vacuum were established, and the effects of the process on the residual impurity levels in the uranium ingots were determined. Metallographic studies showed that the inclusions were finely divided and evenly distributed. Chemical analyses indicated that no chemical refinement could be attributed to the arc-melting process.

Introduction

Recent concern by the reactor sites with the variation in reactor performance from ingot to ingot has generated interest in consumable-electrode arc melting in a vacuum as a possible means of improving ingot consistency. In addition, the reactor sites have expressed concern about the segregation of chemical contaminants and the size and the distribution of the carbide particles found within each induction-melted uranium ingot.

Previous small-scale tests^{1,2,3} made under the supervision of the National Lead Company of Ohio showed that a substantial improvement can be made in chemical homogeneity and in the control of carbide size and distribution by the consumable-electrode arc melting of induction-melted uranium feedstock. These previous tests also

indicated that excellent fuel-core-to-good-fuel-core yields were obtainable.

To test these conclusions, a contract was made with the National Lead Company, Nuclear Metals Division in Albany, New York, to arc-melt induction-melted uranium electrodes into ingots of various sizes.

Objectives

The over-all purpose of this test is three-fold:

1. To compare the effect of consumable-electrode arc melting on the chemical impurity levels of ingots so produced with those produced by vacuum-induction melting.
2. To compare the metal quality of NPR, Mark V-B, and I and E fuel cores produced from these two types of ingots.
3. To provide fuel cores for a reactor performance test.

The work reported this quarter covers the first of these three objectives.

Summary of Results

The arc-melting test was divided into five phases according to the sizes of the ingots required (see Table 4.1).

This report summarizes the work completed and the results obtained on Phases III, IV, and V.

TABLE 4.1 Summary of Consumable Arc-Melted Ingot Requirements

Test Phase	Number of Ingots	Nominal Diameter (in.)	Nominal Length (in.)	Enrichment	Est Ingot Weight (lb)	Core Type
I	11	11	22	0.94% U ²³⁵	1430	NPR
II	6	11	22	Normal	1430	I and E
III	5	10	25	Normal	1340	V-B
IV	10	7 ³ / ₈	22	Normal	640	V-B
V	10	7	25	Normal	660	I and E

Sufficient data have not been generated on Phases I and II to be reported at this time.

Arc-Melting Conditions

The optimum power required to form the 7 and $7\frac{3}{8}$ -inch-diameter ingots was determined to be 25 volts with a total current input of 5600 amperes. The optimum power for the 10-inch-diameter ingots was determined to be 25 volts with a total current input of 8000 amperes.

Metallography

Metallographic examinations were made on the as-cast 7, $7\frac{3}{8}$, and 10-inch-diameter ingots. Vertical ingot sections revealed primary pipe, center-line voids, rimming, and scattered voids measuring $\frac{1}{16}$ inch or less in diameter. Etched sections at 100X showed a finely dispersed, evenly distributed pattern of carbides and other nonmetallics.

Chemical Analyses

Chemical analyses were made on samples taken from the top and bottom of the electrodes (feedstock) prior to arc melting and from corresponding positions in the arc-melted ingots. A "within ingot" chemical analysis study was also made. Both investigations indicated that there were no significant changes in the level of chemical impurities of the uranium attributable to arc melting.

Equipment and Procedures

Arc-Melting Equipment

The consumable-electrode arc-melting furnace (See Figure 4.1) used was manufactured by the Lectromelt Corporation, Pittsburgh, Pennsylvania. It was designed for melting refractory and reactive metals under vacuum or in controlled atmospheres. The furnace contains the following principal components:

1. An electrode drive assembly equipped with both automatic and manually controlled feed sys-

tems. The drive system, bus bars, and electrode stem were air cooled.

2. A crucible assembly (Figure 4.2) consisting of a massive copper cylinder and base plates. (This mass of copper provided the only source of ingot cooling.)

3. A vacuum system consisting of a blower and a roughing pump.

4. Furnace instrumentation consisting of:

a. A thermocouple vacuum sensing element located in the fore line between the furnace shell and the exhaust valve. The meter is located on the instrument panel (Figure 4.3).

b. Electrical meters (see Figure 4.3) consisting of a voltmeter, an ammeter, and a watt-hour meter.

c. A multipoint recorder attached to chromel-alumel thermocouples for recording the crucible temperatures.

The maximum current capacity of the furnace was 10,000 amperes. The maximum electrode size was 9 inches in diameter by 55-inches long. The furnace could produce uranium ingots as large as 11 inches in diameter by 27-inches long.

Electrode Preparation

Electrodes of two sizes and of various charge compositions were produced by vacuum-induction melting. A summary of the conditions used in preparing the electrodes appears in Table 4.2.

TABLE 4.2 Consumable Arc-Melting
Electrode Requirements*

Test Phase	Electrode Diameter (in.)	Finished Length (in.)	Feedstock for Electrode	Charge Weight (lb)
III	8	46	Three derbies, solid scrap	1800
IV	5.5	48	One derby, solid scrap	900
V	5.5	48	One derby, solid scrap, briquettes (25% max)	900

* Crucibles were uncoated graphite; molds were graphite wash-coated with MgO.

1262-17

FIGURE 4.1 Lectromelt Consumable Arc-Melting Furnace

1262-8

FIGURE 4.2 Copper Crucible for 7-Inch Diameter Ingot with Copper Base Plate and Uranium Starting Pad

The induction furnace operating conditions were as follows:

1. The furnace starting pressure was maintained at 50 microns or less with a leak rate of less than 20 microns per minute.
2. The melting cycle was 165 kw to the melting point, 100 kw to approximately 2450°F, and pour.
3. Unheated graphite molds were used.

All of the electrodes (see Figure 4.4) were grit blasted with MgF_2 slag to remove surface oxidation and were machined to provide a groove for attaching the electrode holder.

Arc-Melting Procedure

The arc melting was performed in the Lectromelt furnace using the following procedure:

1. A 1-inch-thick uranium pad (see Figures 4.2 and 4.5), previously cast and machined at National Lead Company of Ohio, was placed in the bottom of the crucible.
2. Approximately one pound of chips or small pieces of scrap uranium was placed on top of the uranium pad. This metal was used as starting material to strike the arc.
3. The electrode was placed in the furnace and attached to the drive assembly. The furnace was evacuated to less than 40 microns before melting was started.
4. The electrode was lowered to strike the arc, and melting proceeded.
5. Amperage, voltage, pressure, and thermocouple readings taken periodically.*
6. The arc was controlled according to the conditions outlined in Table 4.3.

**Thermocouple readings were taken at three locations in the crucible. Temperature measurements were made on only five heats, since the readings appeared to be consistent from heat to heat.*

TABLE 4.3 Arc-Melting Conditions

	Test Phase		
	III	IV	V
Weight Copper Crucible (lb)	4159	1736	2060
Crucible Dimensions (in.)			
ID	10.250	7.650	7.187
OD	24.5	17	17
Height	34.5	29	32
Pressure (microns)			
Starting (max)	—	40	40
Operating Range	15 to 170	14 to 42	10 to 250
Current (kiloamperes)	7.9 to 8.1	5.5 to 5.7	5.5 to 5.7
Voltage	24 to 26	24 to 26	24 to 26
Melting Rate (lb/hr)	2244	1536	1587
Ingot Weight (lb)	1388	687	678
Maximum Breakout Temperature (°F)	750	750	750

1262-4

FIGURE 4.3 Instrument Panel

7. Near the completion of the melt, the power was reduced by a predetermined amount at 30-second intervals until the arc was extinguished. (This procedure, known as hot topping, reduces the formation of voids as the ingot solidifies.)

8. After melting was completed, the ingot was cooled in the furnace to 750°F (under one-half atmosphere of argon) before removal (see Figure 4.6).

Control Ingots

An important objective of this program was to compare the arc-melted ingots with the induction-melted ingots currently being produced at the National Lead Company of Ohio. Therefore, induction-melted control ingots were cast from the same types of charge materials as were used to cast the arc-melted electrodes. Standard production procedures were employed in melting and casting.

1214-3

FIGURE 4.4 Typical Grit-Blasted Electrodes, 8 Inches in Diameter

1214-1

FIGURE 4.5 Uranium Starting Pad 10 Inches in Diameter

The control ingots were processed concurrently with the arc-melted material to eliminate any effects due to aging.

Sampling Procedure

Ingots from each of the three test phases reported were selected for metallographic and chemical examination. Several ingots were cut longitudinally through the axis to expose a half section; ingots were cut transversely to expose the top and bottom. Each of the vertical and transverse surfaces were etched to show voids, grain structure, and inclusions. Photographs were made of representative sections. For each arc-melted ingot sampled in this manner, a vacuum induction-melted (control) ingot was sampled in a like manner.

Specimens were taken from the ingot sections described above for wet chemical analyses. Each specimen was analyzed for the same elements that were determined in the electrodes; namely: carbon,

1262-9

FIGURE 4.6 Typical As-Cast Arc-Melted Ingot, 7 Inches in Diameter by 25 Inches Long

nitrogen, hydrogen, oxygen, density. Spectrochemical analyses were also made for other elements.

Discussion of Results

Furnace Performance

Ingots of reactor grade and production size were produced by vacuum consumable arc melting. Particular

attention was paid to the stability of the arc and evolution of volatiles during the melt. The following observations were made:

1. Occasionally, bubbling was visible on the pool surface accompanied by much greater splattering from the electrode surface.

2. In all ingots, regardless of size, the phenomenon known as "glow-discharge" occurred approximately half-way through the melting cycle. A glow-discharge arc is one displaced up the electrode and crucible from its intended position at the electrode tip. This displaced arc does not melt the electrode, but does appreciably heat the crucible wall. Glow-discharge is apparently caused by a combination of instability of the anode and positional instability of the cathode. Observations made by Johnson, Hahn, and Itoh⁴ indicated that:

- a. At pressures down to 30 mm Hg, the anode is positionally stable.
- b. At pressures below 30 mm Hg, the anode becomes positionally unstable.
- c. At approximately 0.4 mm Hg, the cathode becomes stably affixed to the electrode tip thus restoring the arc stability.

The periods of "glow" became more frequent and lasted longer as the melt progressed. During these longer periods of "glow", the metal could be seen to solidify radially from the walls of the crucible.

3. Generally, the arc remained hard and stable except during the periods of "glow" described above and during the hot-topping period. An examination of the crucible after use showed that the unstable arc during hot topping had etched the crucible wall. This etching had no deleterious effect other than producing a rougher ingot surface on the succeeding melt.

The use of massive copper crucibles without the aid of external cooling media, such as fins, water, etc., is unique with this furnace installation. The crucibles proved satisfactory for the smaller diameter ingots, i.e., 7, 7 $\frac{3}{8}$ and 10 inches. A difficulty that occurred with the crucibles used to produce ingots of the sizes mentioned was growth of

the copper from thermocycling. The inner diameter of the crucibles decreased with each succeeding melt. This growth made it necessary to rebore the crucibles after every fifth melt.

Metallography

The induction-melted and the arc-melted ingots were evaluated for inclusion content, and a comparison of the two types of ingots was made (see Figures 4.7 through 4.11).

In the arc-melted ingots, the carbides and other nonmetallics were fairly evenly distributed over the entire area of the samples. They were small in size and not elongated. The carbide clusters were also small and were sparse.

In the induction-melted ingots, the carbides and other nonmetallics were large. Some of the inclusions (see Figure 4.11) were elongated and tended to form a network type of structure. The clusters were also much larger and more numerous than those of the arc-melted ingots.

A peppery network was noted in the background of both types of ingots at higher magnifications. The inclusions in the induction-melted ingots were much larger and turned dark after a HNO_3 rinse, thus identifying this background material as carbide. Several small hydrides were also found in each of the two types of ingots. These hydrides were smaller but more numerous in the arc-melted ingots.

The nonmetallic inclusions found in the 10-inch-diameter arc-melted ingots (Figures 4.10) were larger than those of the 7 and $7\frac{1}{8}$ -inch-diameter ingots (Figures 4.7 and 4.9). The increase in the particle size was attributable to the slower cooling rate of the 10-inch ingots.

The metallographic evaluation revealed voids present in a rather scattered pattern. The major voids occurred along the centerline and as primary pipe; however, there were many smaller holes ($\frac{1}{16}$ -

inch diameter or less) scattered throughout the ingots.

Chemical Analyses

The within-ingot chemical analyses given in Figures 4.7 through 4.11 and the ingot and electrode analyses given in Table 4.4 indicate that arc melting did not result in any chemical refinement other than a slight reduction in hydrogen (less than 0.3 ppm average). The significance of these results cannot be determined at this time because of the small number of ingots sampled; however, the results were consistent with the small-scale, arc-melting feasibility study⁵ previously conducted.

TABLE 4.4 Chemical Analyses of Electrodes and the Arc-Melted Ingots Produced

	Element (ppm)						Density (g/cm ³)
	C	N ₂	H ₂	O ₂	Fe	Si	
Electrode	554	44	0.6	26	111	67	18.91
Ingot No. BB-30	580	70	0.9	32	108	66	18.91
Electrode	476	62	0.8	40	120	61	18.91
Ingot No. BB-34	537	76	0.7	47	165	64	18.92
Electrode	415	28	1.2	18	118	34	18.93
Ingot No. C-24	451	30	1.0	23	115	46	18.95
Electrode	415	31	1.2	17	125	37	18.94
Ingot No. C-29	368	31	0.9	19	141	42	18.92
Electrode	316	27	1.2	20	108	50	18.94
Ingot No. D-0	327	34	0.9	26	124	62	18.94
Electrode	467	29	1.9	25	119	35	18.94
Ingot No. D-5	419	33	0.8	26	132	48	18.90

Conclusions

1. The arc melting of uranium into production-sized ingots (7 to 10 inches in diameter) is feasible.

2. The principal advantage in the arc melting of uranium is the production of extremely fine carbide particles and the uniform distribution of

921 (79 THRU 93)			C	N ₂	H ₂	O ₂	Fe	Si	Den.
E	527	30	1.2	21	120	51	18.88	
	C	463	30	1.0	24	138	50	18.93
E	469	38	0.6	30	138	50	18.93	
	C	455	36	0.7	45	141	45	18.93
E	443	36	0.7	25	125	45	18.80	
	C	425	31	0.7	22	127	45	18.96
E	365	26	0.8	26	126	47	18.84	
	C	382	23	1.1	27	143	49	18.95
E	430	33	0.5	22	144	47	18.76	
	C	424	28	0.9	24	119	46	18.95	

EDGE

MID-RADII

CENTER

NOTE: Photograph at left was taken actual size; photographs above were taken at 100X magnification; all were reduced 66% in reproduction.

FIGURE 4.7 Arc-Melted Ingot 7 Inches in Diameter

NOTE: Photograph at left was taken actual size; photographs above were taken at 100X magnification; all were reduced 66% in reproduction.

FIGURE 4.8 Induction-Melted Control Ingot 7 Inches in Diameter

NOTE: Photograph at left was taken actual size; photographs above were taken at 100X magnification; all were reduced 66% in reproduction.

FIGURE 4.9 Arc-Melted Ingot 7³/₈ Inches in Diameter

NOTE: Photograph at left was taken actual size, photographs above were taken at 100X magnification, all were reduced 66% in reproduction.

FIGURE 4.10 Arc-Melted Ingot 10 Inches in Diameter

NOTE: Photograph at left was taken actual size; photographs above were taken at 100X magnification; all were reduced 66% in reproduction.

FIGURE 4.11 Induction-Melted Control Ingot 10 Inches in Diameter

these carbides from top to bottom and from edge to center of the ingot. It is thought that the shallow pool of molten metal and the rapid solidification effectively eliminate the agglomeration or growth of nonmetallic particles.

3. No contaminants are added to the metal by the arc-melting process. In fact, by eliminating the graphite ingot mold, a major source of carbon contamination is avoided. Furthermore, in the work reported here, the hydrogen content was reduced slightly (0.3 ppm) by arc melting.

4. The chemical homogeneity of the ingots produced is currently under investigation. Insufficient data prevent the evaluation of the significance of the results at this time. Resampling and further study will be required.

5. Internal voids were formed during the solidification of the ingots. Such porosity has been reported as a frequent result of an unstable arc (glow discharge).⁶ Further experimental work is required on this problem.

Future Work

Work is now in progress on the metallographic and chemical analyses of Phase I and II ingots (11-inch diameter). The ingots produced in all five phases of the test will be fabricated to fuel cores, and their metal quality will be compared with control cores fabricated from regular induc-

tion-melted ingots. The cores from the arc-melted ingots will also be evaluated in reactor tests.

Longer range objectives in the arc-melting program are to determine the effect of the following variables on ingot quality:

1. Crucible-to-electrode size ratio.
2. Power input and circuitry.
3. Melting pressures.
4. Control of the solidification pattern.

References

¹H. M. Eikenberry and T. D. Nixon. Consumable-Electrode Arc-Melting of Uranium, USAEC Report, NLCO-849. June 15, 1962.

²E. S. Noe' and J. F. Schiltz. "Arc-Melting of Uranium Metal," Summary Tech. Rpt. for the Period January 1, 1959 to March 31, 1959, USAEC Report NLCO-785, p. 95. April 15, 1959. (Classified).

³E. S. Noe' and J. F. Schiltz. "Evaluation of Arc-Melted Uranium Metal," Summary Tech. Rpt. for the Period July 1, 1959 to September 30, 1959, USAEC Report NLCO-795, p. 63. October 20, 1959 (Classified).

⁴E. W. Johnson, G. T. Hahn, and R. Itoh. "Characteristics of Consumable Electrode D. C. Arcs in Argon, Helium and Vacuum," Arcs in Inert Atmospheres and Vacuum, edited by W. E. Kuhn, p. 38. New York: Wiley 1956.

⁵H. M. Eikenberry and T. D. Nixon. op. cit , p. 32.

⁶W. H. Smith. "The Effect of Variables on the Melting Rate of Metals in the Consumable Electrode Arc Furnace," Arcs in Inert Atmospheres and Vacuum, edited by W. E. Kuhn, p. 49. New York: Wiley, 1956.

5. THE EFFECTS OF ROLLING MILL VARIABLES ON URANIUM FUEL CORE STRUCTURE AND TEXTURE

C. A. Neu

Abstract

Variations in uranium billet temperatures prior to rolling were found to cause significant differences in the amount of recrystallization and in the texture coefficients in the alpha-rolled rods. After beta heat treatment, significant differences were detected only in grain size. The effects of carbon content were also observed.

Introduction

Fuel cores shipped to the reactor sites are known to vary in structure and texture.^{1,2,3} The effects of these variations on reactor performance are only partially known. Since the fabrication processes at National Lead Company of Ohio may be an important source of these variations, a preliminary test was performed to determine the effects of rolling mill variables on uranium fuel core structure and texture.

In the rolling mill, uranium billets after the first rolling (blooming) are reheated in molten salt to bring them to the proper temperature (high alpha range) for rolling to rods in a six-stand continuous mill. The reheated billet drops in temperature during the transfer from the salt bath to the mill. This transfer time, or air delay time, varies in production; but the effect of this variable, as measured by the drop in billet temperature, was not known.

Objectives for This Quarter

The principal objective of this preliminary test was to determine the effects of air delay times (billet temperatures) on the structure and texture of alpha-rolled rods and on beta heat-treated fuel cores fabricated from the rods. A secondary objective was to determine the effect of carbon content on the structures of the rods and cores.

Summary of Results

The following significant effects were attributable to the variation in air delay time:

1. Rods rolled from billets delayed 2 minutes after removal from the salt bath furnace were not as completely recrystallized as the rods from billets that were rolled as quickly as possible after removal from the furnace.
2. Texture coefficients of the two types of rods were different.
3. After fabricating the rods to cores and beta heat-treating the cores, it was found that the grain size was smaller in the cores from the billets delayed prior to rolling (as measured by the UT-2B ultrasonic tester).

The following significant effects were attributable to the differences in carbon content:

1. The rods from the high carbon ingot (571 ppm) were more completely recrystallized than those from the low carbon ingot (231 ppm).
2. Texture coefficients in the 110 plane between rods from the high and low carbon ingots were different.
3. The grain size of cores from the high carbon ingot was smaller than that of the cores from the low carbon ingot (UT-2B tester).

Experimental Procedure

Two 7-inch-diameter ingots which had been produced in sequence from the same lots of charge materials in the Metals Production Plant were chosen for the preliminary rolling test because of their similar impurity contents, except for carbon (Table 5.1). Using regular rolling procedures, the ingots were heated in a salt bath (75% K_2CO_3 , 25% Li_2CO_3) to the high alpha range and bloomed in a two-high reversing mill. Ingot temperatures and rolling times were similar for the two ingots.

TABLE 5.1 Chemical Analyses of Billet Samples

Analyses (ppm)	Ingot Number 59842			Ingot Number 59843		
	Sample Location			Sample Location		
	Top	Middle	Bottom	Top	Middle	Bottom
C	218	224	250	524	565	623
N	23	24	40	18	43	47
Al	14	11	13	7	7	8
Cr	15	14	15	17	17	17
Cu	5	5	4	5	5	5
Fe	145	147	143	144	148	143
Mg	8	6	5	<4	<4	6
Ni	40	41	39	41	43	43
Si	57	58	57	64	57	59
H*	0.8	1.3	1.2	0.7	0.8	0.6
O*	21	31	18	16	38	35

* Alpha rolled rod samples.

The long billet from each ingot was cut into two equal lengths, and samples were removed from the lead, center, and trailing ends for chemical analyses and metallographic evaluation of per cent recrystallization. The four billets, two from each ingot, were then reheated in the billet salt bath furnace (75% K_2CO_3 , 25% Li_2CO_3) to the high alpha range for further reduction to $1\frac{1}{2}$ -inch-diameter rods in the six-stand continuous mill.

The first billet from the first ingot and the second billet from the second ingot were transferred as quickly as possible from the furnace to the continuous mill. The other two billets were delayed for 2 minutes on the discharge trough of the furnace prior to rolling in the continuous mill. The surface temperatures of the billets were measured by a Thermidot infrared radiometer. An emissivity value of 0.925 was used for the molten-salt-coated uranium. The average surface temperature of the two delayed billets just prior to their entry into Stand No. 1 of the continuous mill was approximately $80^\circ F$ lower than the average surface temperature of the two billets not delayed. The peak amperage required for each of the four billets in each of the six stands was recorded. The av-

erage surface temperature of the delayed billets, as measured by a Radiamatic radiometer at the exit of Stand No. 1, was approximately $60^\circ F$ lower than the average surface temperature of the billets which were not delayed. No readings were obtained at the exit of Stand No. 6 because the radiometer was misaligned just prior to the test. Based on analysis of previous production temperature data, it is estimated that the temperature difference between the delayed and non-delayed rods was no greater than $30^\circ F$. Total reduction in area in the continuous mill was approximately 60%. The $1\frac{1}{2}$ -inch-diameter rod produced from each billet was sheared into three equal rod lengths and quenched with a water spray about 19 seconds after passing through Stand No. 6. Samples for metallographic evaluation of per cent recrystallization and X-ray diffraction were removed from the lead end of each rod and the trailing end of the third rod of each billet.

The rods were machined into fuel core blanks and beta heat-treated by heating in 50% NaCl — 50% KCl salt and quenching in water at $140^\circ F$ in the regular production facilities. Sixteen core blanks, four from each of the four billets, were heat-treated in two adjacent racks. These core

blanks were used for visual grain size rating and X-ray diffraction examination.

The remainder of the blanks were machined to finished fuel cores. The cores were rated for grain size on the UT-2B grain size tester, an ultrasonic production control instrument. The cores were visually rated for metal quality, that is, rejectable surface seams and striations.

The X-ray diffraction work was performed at Hanford by techniques which are used for regular production control of uranium fuel cores prior to charging into their reactors.

The data were evaluated statistically using the analysis-of-variance method whenever feasible.

Results and Discussion

The two ingots rolled in this test were very similar in impurity contents, except for the carbon levels (Table 5.1). The high carbon ingot was

more typical of regular production than the low carbon ingot. The carbon and nitrogen segregation from top to bottom of these ingots was normal for ingots cast in heated graphite molds. The other impurities were not found to be segregated to any significant extent.

Metallographic examination of the billet samples showed that their structures were 56% to 90% recrystallized. No significant differences were found. The total reduction in area from ingot to billet is approximately 89%.

As shown in Table 5.2, the average surface temperature of the delayed billets was about 80°F lower than the non-delayed billets just prior to rolling. The peak amperage, which is indicative of the power required for each stand of the continuous mill, was higher for the delayed billets than for the non-delayed billets and was also higher for the billets from the high carbon ingot than for those from the low carbon ingot.

TABLE 5.2 Rolling Mill Data – Billet to Rod

	Ingot Number 59842		Ingot Number 59843	
	Billet Number		Billet Number	
	1	2	1	2
Billet Furnace Salt Temperature (°F)	1160	1160	1160	1160
Time in Billet Furnace (min)	18	18	29*	32*
Desired Air Delay Time (sec)	0	120	120	0
Actual Air Delay Time (sec)	17	128	125	15
Billet Temperature Immediately Prior to Rolling (Therm-dot °F)	1090	1010	1030	1110
Continuous Mill Peak Amperes:				
Stand 1	230	260	280	230
Stand 2	340	440	450	380
Stand 3	310	360	400	300
Stand 4	290	400	380	320
Stand 5	550	620	680	540
Stand 6	480	540	540	520
Rod Temperature at Exit of Stand 1** (Radiamatic °F)	1122	1072	1042	1122

* Billets remained in furnace longer than usual because of a breakdown in continuous-mill equipment.

** No rod temperatures were obtained at the exit from Stand 6 because of misalignment of the Radiamatic unit.

NOTE: All rods were spray-quenched with water.

Recrystallization of Rod Samples

The recrystallization data of the 16 alpha-rolled rod samples obtained by metallographic observation were statistically evaluated by analysis of variance using the chi-square method of treatment (Figure 5.1). The following significant differences (at the 99% confidence level) were found:

1. The rod samples from the two billets which were not delayed prior to finish rolling were more completely recrystallized than those which were delayed 2 minutes.
2. The rod samples from the high carbon ingots were more completely recrystallized than those from the low carbon ingot.
3. The center area (from the axis to one-half of the radius) of the rod samples which were delayed were more completely recrystallized than the outer area of these same samples.

FIGURE 5.1 Effect of Air Delay Time, Carbon Content, and Location Within Delayed Samples on the Recrystallization of Alpha-Rolled Rods

Texture of Rod Samples

The texture coefficient data of the three hkl planes as reported by HAPO from the 16 alpha-rolled rod samples were statistically evaluated by analysis of variance. The results of the statistical evaluation are shown schematically in Figure 5.2. These results were interpreted as follows:

FIGURE 5.2 Mean Texture Coefficient of Alpha Rolled Cores (With 95% Confidence Limits) Longitudinal - Midwall Technique

1. *200 Plane.* The mean texture coefficient of the samples from delayed billets was significantly different at the 99% confidence level from those of the non-delayed billets. No significant difference was found in the mean texture coefficients at the two carbon levels.

2. *020 Plane.* The mean texture coefficient of the samples from delayed billets was significantly different at the 99% confidence level from those of the non-delayed billets. Again, there was no

significant difference in the mean texture coefficients at the two carbon levels.

3. *110 Plane*. The carbon content-air delay time interaction had a significant effect on the mean texture coefficients at the 99% confidence level. The mean texture coefficient of the high carbon samples which were delayed were significantly different from the mean texture coefficient of the high carbon samples which were not delayed. However, there was no significant difference between the low carbon samples due to delay time.

The significant differences in the mean texture coefficients of the delayed and non-delayed samples indicate that somewhat different deformation mechanisms occur at these two temperature conditions. The carbon content has a lesser, but significant, effect.

Grain Size of Cores

The 16 beta heat-treated core blanks that were visually rated for grain size tended to reveal a smaller grain size in the samples from the delayed billets than in the samples from the non-delayed billets. A smaller grain size was observed in the samples from the high carbon ingot than in the samples from the low carbon ingot. Since the precision of the visual rating method is low, all the remaining beta heat-treated cores were rated for grain size by the UT-2B ultrasonic tester. Figure 5.3 shows the mean "average grain size value" (in volts) with 95% confidence limits. An analysis of variance of the data confirmed that (1) the air delay, (2) the carbon content and (3) the air delay - carbon content interaction had significant effects on the means of the "average grain size value." Note that with the UT-2B, the higher the voltage reading, the smaller the actual grain size. The delay time had a greater effect on the cores from the high carbon ingot than those from the low carbon ingot.

FIGURE 5.3 Means of "Average Grain Size Rating" of Beta Heat-Treated Cores as Measured by a UT-2B Tester (With 95% Confidence Limits)

Texture of Cores

The texture coefficient data of the three hkl planes reported by HAPO from the 16 beta heat-treated cores were statistically evaluated by analysis of variance. No significant differences in mean texture coefficients were found for the 200 plane and the 020 plane. Slight but statistically significant differences were found in the mean texture coefficients of the 110 plane (Table 5.3). Although the effect due to delay time was significant at the 99% confidence level and the effect due to carbon level was significant at the 95% confidence level, the actual differences in the mean texture coefficients occur in only the third significant figure. It is thought that these small differences are of no practical significance.

TABLE 5.3 Mean Texture Coefficients (with 95% Confidence Limits) 110 Plane of Beta Heat-Treated Cores; Longitudinal – Midwall Technique

Delay Time (min)	0	2	Difference	Total Mean
High Carbon (571 ppm)	1.147 ± 0.058	1.054 ± 0.058	$0.093 \pm 0.082^*$	1.100 ± 0.041
Low Carbon (231 ppm)	1.065 ± 0.058	0.985 ± 0.058	0.080 ± 0.082	1.025 ± 0.041
Difference	0.082 ± 0.082	0.069 ± 0.082	0.013 ± 0.116	$0.075 \pm 0.058^*$
Total Mean	1.106 ± 0.041	1.019 ± 0.041	$0.087 \pm 0.058^*$	

* The statistically significant differences occur in the third significant figure of the texture coefficient data.

Metallography

Typical inclusions in cores fabricated from the low and high carbon ingots are shown in Figure 5.4. The metallographic examination of longitudinal sections of cores from the two ingots disclosed numerous discontinuous carbide stringers in the cores from the high carbon ingot and a few carbide stringers, some of which were of the continuous type, in the cores from the low carbon ingot. Some uranium oxide inclusions were found in the cores from both ingots.

Conclusions

Even in the narrow range investigated, variation in the air delay time, that is, billet temperature prior to finish rolling, was shown to have significant effects on the recrystallization and the texture coefficients of the alpha-rolled rods. The carbon content also was shown to have significant effects on the recrystallization and on the texture coefficient of the 110 plane. However, after beta heat treatment, the only significant effects due to air delay times and carbon content were the effects on the "average grain size rating" as measured by the UT-2B grain size tester.

Although air delays of as long as 2 minutes prior to finish rolling do not occur frequently during regular production, such delays are quite possible when a malfunction of the billet pusher occurs. Hence, it is believed that this test has

has valid application to the current production rolling process.

Previous studies have shown that iron and silicon contents have significant effects on recrystallization. Also, the effects of iron and/or silicon contents on the grain size of beta heat-treated cores are well known.⁴ These effects appear to be greater than the effects due to the air delay time investigated in this test.

Future Work

Since this test was performed, the ingot diameter in production has been increased to 8 inches, and iron and silicon levels have been increased. Hence it is deemed advisable to repeat certain portions of this test with the new production material.

Future work is planned to include investigation of the following variables:

1. Air delay time prior to finish rolling at two levels.
2. Carbon content at two levels, near the maximum and the minimum of present production material.
3. Iron content at two levels, near the maximum and the minimum of the current specifications.
4. Silicon content at two levels, near the maximum and the minimum of the current specifications.

938-3

A. LOW CARBON INGOT (231 ppm)

938-7

B. HIGH CARBON INGOT (571 ppm)

FIGURE 5.4 Typical Inclusions in Longitudinal Section of Finished Fuel Cores (100X)

Comprehensive power recording instrumentation is planned for each of the six stands of the continuous mill.

References

¹Report of the Working Committee of the Fuel Element Development Committee, January 16-18, 1962, USAEC Report DPST-62-134, pp. 4-5. February, 1962 (Classified).

²Report of the Working Committee of the Fuel Element Development Committee, May 1-3, 1962, USAEC Report MCW-1474, p. 5. May, 1962 (Classified).

³Report of the Working Committee of the Fuel Element Development Committee, September 18-20, 1962, USAEC Report HW-74822, pp. 65-66. September 20, 1962 (Classified).

⁴W. G. Weber. "Alloying to produce fine-grained dingo uranium," Process development quarterly report. Part II - Pilot Plant work, USAEC Report MCW-1429, pp. 85-87. May 1, 1959 (Classified).

6. TEXTURE GRADIENTS IN WATER-QUENCHED HAPO I AND E FUEL CORES

C. A. Powell

Abstract

Four HAPO I and E uranium fuel cores, heated into the beta phase and quenched in water, were examined for texture gradients in the longitudinal, tangential, and radial directions as functions of radial position. G_2 , G_3 , and J data are tabulated; and plots of statistically combined G_3 values for the four cores examined are presented.

Introduction

To permit more accurate predictions of dimensional changes of uranium fuel cores during thermal neutron irradiation, techniques for texture gradient studies^{1,2,3} in the radial, tangential, and longitudinal directions have been developed. Fuel cores from various fabrication processes having different heat treatments are being evaluated in order to establish typical reactor growth tendencies of each. In previous work, cores having the same dimensions, but varying heat treatments, have been examined.^{1,3,4}

Objectives for This Quarter

The objectives for this quarter are:

1. To improve sampling techniques.
2. To collect X-ray preferred orientation data on four HAPO I and E fuel cores that had been beta heat-treated and quenched in water.
3. To combine these data from the four cores and, by means of a statistical technique, to fit the data to a polynomial curve for each direction examined.

Summary of Results

Sampling plans were devised to permit examination of surfaces normal to the three mutually perpendicular directions of interest in the fuel cores. Specimens were machined from the sample cores,

preferred orientation data were collected, and growth indices (G_2 and G_3) were calculated.^{5,6,7}

Tabulations of individual G_2 , G_3 , and J values, with their respective 95% confidence limits for each radius scanned, are shown in Tables 6.1 through 6.4.

The data from all samples from a particular direction were combined into a single set and fitted to a polynomial curve by the least squares method.⁴ Curves of these values (G_3) with σ limits are shown in Figures 6.1, 6.2, and 6.3.

Growth index values in the tangential direction were all positive (Figure 6.1) with a gradual decline from a more positive tendency at the inner surface to less positive growth index values at the outer surface. In the longitudinal direction (Figure 6.2), severe negative growth index values were displayed at the ID, rising steadily to large positive values near the outer wall and then falling slightly at the outer surface. In the radial direction (Figure 6.3), all growth index values were negative.

FIGURE 6.1 Polynomial Curve of Best Fit for Combined G_3 Data in Tangential Direction

TABLE 6.1 Preferred Orientation Data for
Core from Bottom of Ingot

Radius	G ₃	G ₂	J
<u>Radial Direction</u>			
.282	-.011 ± .005	-.017 ± .014	1.017 ± .007
.305	-.000 ± .009	-.005 ± .006	1.004 ± .000
.339	-.013 ± .008	-.020 ± .006	1.016 ± .003
.371	-.010 ± .028	-.015 ± .024	1.017 ± .021
.403	-.027 ± .015	-.028 ± .011	1.028 ± .005
.433	-.045 ± .010	-.055 ± .011	1.056 ± .006
.468	-.032 ± .012	-.042 ± .020	1.064 ± .006
.498	-.006 ± .008	-.012 ± .007	1.054 ± .006
.528	-.069 ± .013	-.068 ± .012	1.082 ± .013
.558	-.054 ± .010	-.049 ± .022	1.082 ± .033
.588	-.057 ± .014	-.066 ± .016	1.113 ± .020
.625	-.084 ± .015	-.082 ± .003	1.084 ± .008
.655	-.138 ± .005	-.143 ± .007	1.124 ± .013
.686	-.162 ± .019	-.157 ± .034	1.155 ± .049
.716	-.100 ± .020	-.103 ± .023	1.355 ± .038
.721	-.138 ± .011	-.101 ± .014	1.143 ± .022
.726	-.093 ± .016	-.094 ± .014	1.132 ± .019
.731	-.132 ± .019	-.138 ± .022	1.208 ± .033
.737	-.159 ± .015	-.168 ± .015	1.382 ± .053
<u>Longitudinal Direction</u>			
.231	-.133 ± .025	-.142 ± .026	1.259 ± .091
.315	-.092 ± .016	-.100 ± .021	1.083 ± .007
.363	-.061 ± .017	-.068 ± .014	1.089 ± .014
.448	-.023 ± .015	-.034 ± .021	1.055 ± .012
.507	+.003 ± .014	+.012 ± .020	1.055 ± .009
.577	+.053 ± .021	+.061 ± .030	1.060 ± .019
.638	+.105 ± .015	+.115 ± .021	1.104 ± .036
.721	+.060 ± .018	+.063 ± .017	1.071 ± .021
<u>Tangential Direction</u>			
.236	+.154 ± .026	+.130 ± .020	1.140 ± .026
.326	+.103 ± .026	+.113 ± .019	1.064 ± .024
.374	+.110 ± .014	+.118 ± .013	1.090 ± .021
.459	+.109 ± .009	+.111 ± .025	1.106 ± .063
.518	+.081 ± .021	+.073 ± .018	1.089 ± .026
.588	+.037 ± .024	+.045 ± .020	1.027 ± .015
.649	+.067 ± .031	+.072 ± .016	1.054 ± .009
.707	+.020 ± .006	+.036 ± .024	1.079 ± .030

TABLE 6.2 Preferred Orientation Data for
Core from Lower Middle of Ingot

Radius	G ₃	G ₂	J
<u>Radial Direction</u>			
.252	-.033 ± .013	-.034 ± .024	1.015 ± .000
.262	-.011 ± .015	-.013 ± .017	1.008 ± .002
.283	-.020 ± .016	-.015 ± .013	1.010 ± .004
.313	-.011 ± .011	-.010 ± .013	1.009 ± .003
.343	-.020 ± .007	-.020 ± .010	1.009 ± .004
.372	-.031 ± .015	-.031 ± .012	1.016 ± .005
.403	-.033 ± .007	-.041 ± .005	1.024 ± .003
.433	-.020 ± .009	-.020 ± .007	1.021 ± .005
.464	-.006 ± .012	-.005 ± .012	1.027 ± .009
.494	-.029 ± .009	-.033 ± .009	1.049 ± .006
.524	-.021 ± .016	-.015 ± .016	1.098 ± .015
.554	-.052 ± .014	-.056 ± .018	1.088 ± .014
.584	-.053 ± .015	-.055 ± .012	1.097 ± .017
.615	-.065 ± .004	-.080 ± .004	1.085 ± .011
.645	-.174 ± .022	-.171 ± .019	1.136 ± .031
.676	-.127 ± .013	-.128 ± .013	1.098 ± .014
.705	-.146 ± .009	-.160 ± .009	1.126 ± .016
.715	-.126 ± .012	-.134 ± .013	1.140 ± .018
.725	-.131 ± .012	-.138 ± .013	1.158 ± .026
.730	-.127 ± .013	-.134 ± .015	1.188 ± .009
.735	-.097 ± .006	-.098 ± .006	1.084 ± .008
.740	-.148 ± .013	-.147 ± .014	1.204 ± .036
<u>Longitudinal Direction</u>			
.231	-.126 ± .026	-.130 ± .021	1.162 ± .035
.315	-.046 ± .019	-.052 ± .023	1.047 ± .010
.363	-.036 ± .024	-.036 ± .021	1.035 ± .011
.448	+.040 ± .013	+.033 ± .012	1.041 ± .011
.507	+.036 ± .014	+.042 ± .016	1.053 ± .022
.577	+.046 ± .016	+.057 ± .015	1.036 ± .007
.638	+.073 ± .015	+.080 ± .016	1.055 ± .008
.721	+.095 ± .024	+.092 ± .025	1.089 ± .030
<u>Tangential Direction</u>			
.261	+.105 ± .017	+.087 ± .019	1.095 ± .019
.307	+.103 ± .008	+.096 ± .011	1.060 ± .014
.390	+.127 ± .019	+.104 ± .017	1.084 ± .014
.440	+.103 ± .030	+.076 ± .030	1.057 ± .022
.534	+.067 ± .030	+.052 ± .043	1.035 ± .023
.584	+.065 ± .023	+.046 ± .020	1.042 ± .024
.670	+.115 ± .015	+.106 ± .016	1.057 ± .013
.723	+.101 ± .021	+.105 ± .033	1.069 ± .030

TABLE 6.3 Preferred Orientation Data for
Core from Upper Middle of Ingot

Radius	G ₃	G ₂	J
Radial Direction			
.262	+0.005 ± .019	+0.003 ± .023	1.018 ± .017
.277	-0.009 ± .013	-0.008 ± .011	1.018 ± .006
.306	-0.017 ± .010	-0.027 ± .008	1.021 ± .011
.339	-0.003 ± .008	-0.007 ± .007	1.005 ± .002
.369	-0.033 ± .008	-0.035 ± .009	1.014 ± .004
.401	-0.027 ± .003	-0.023 ± .010	1.008 ± .002
.431	-0.009 ± .013	-0.013 ± .012	1.010 ± .003
.462	-0.053 ± .015	-0.056 ± .015	1.059 ± .003
.493	-0.048 ± .006	-0.048 ± .004	1.098 ± .008
.523	+0.007 ± .009	-0.030 ± .017	1.099 ± .005
.553	-0.054 ± .014	-0.059 ± .012	1.090 ± .014
.583	-0.063 ± .007	-0.059 ± .003	1.218 ± .016
.613	-0.074 ± .011	-0.079 ± .017	1.161 ± .024
.643	-0.125 ± .008	-0.129 ± .008	1.197 ± .018
.673	-0.160 ± .017	-0.167 ± .015	1.159 ± .030
.703	-0.192 ± .005	-0.178 ± .003	1.155 ± .005
.713	-0.143 ± .009	-0.156 ± .006	1.152 ± .024
.724	-0.133 ± .015	-0.137 ± .006	1.164 ± .010
.729	-0.131 ± .006	-0.135 ± .007	1.171 ± .010
.734	-0.104 ± .019	-0.110 ± .022	1.122 ± .019
.739	-0.107 ± .012	-0.109 ± .011	1.181 ± .010
Longitudinal Direction			
.231	-0.056 ± .029	-0.068 ± .026	1.101 ± .034
.315	-0.069 ± .017	-0.052 ± .026	1.056 ± .019
.363	-0.030 ± .031	-0.039 ± .020	1.029 ± .018
.448	.000 ± .014	+0.007 ± .011	1.033 ± .010
.507	+0.061 ± .026	+0.042 ± .022	1.055 ± .019
.577	+0.068 ± .016	+0.068 ± .013	1.060 ± .008
.638	+0.094 ± .019	+0.098 ± .019	1.077 ± .020
.721	+0.116 ± .016	+0.133 ± .014	1.116 ± .041
Tangential Direction			
.230	+0.062 ± .022	+0.072 ± .032	1.105 ± .034
.320	+0.097 ± .018	+0.091 ± .034	1.108 ± .034
.368	+0.115 ± .020	+0.114 ± .023	1.078 ± .024
.453	+0.083 ± .016	+0.080 ± .018	1.049 ± .020
.512	+0.052 ± .026	+0.050 ± .014	1.031 ± .015
.582	+0.067 ± .018	+0.061 ± .013	1.054 ± .015
.643	+0.080 ± .016	+0.069 ± .014	1.051 ± .017
.718	+0.094 ± .017	+0.089 ± .019	1.067 ± .028

TABLE 6.4 Preferred Orientation Data for
Core from Top of Ingot

Radius	G ₃	G ₂	J
Radial Direction			
.257	+0.019 ± .008	+0.012 ± .012	1.046 ± .018
.271	+0.015 ± .020	+0.010 ± .016	1.018 ± .005
.302	+0.041 ± .006	+0.027 ± .013	1.015 ± .002
.336	+0.043 ± .007	+0.039 ± .012	1.017 ± .011
.366	-0.002 ± .008	-0.015 ± .007	1.012 ± .005
.396	-0.008 ± .004	+0.002 ± .007	1.021 ± .005
.426	-0.039 ± .010	-0.041 ± .015	1.037 ± .014
.456	-0.052 ± .019	-0.051 ± .013	1.025 ± .006
.487	-0.052 ± .017	-0.050 ± .016	1.029 ± .010
.518	-0.047 ± .014	-0.049 ± .012	1.091 ± .006
.548	-0.069 ± .015	-0.074 ± .020	1.073 ± .022
.578	-0.027 ± .012	-0.060 ± .009	1.104 ± .016
.608	-0.104 ± .016	-0.111 ± .016	1.159 ± .046
.638	-0.107 ± .011	-0.107 ± .011	1.122 ± .020
.668	-0.166 ± .015	-0.171 ± .013	1.149 ± .027
.703	-0.136 ± .012	-0.144 ± .009	1.121 ± .011
.715	-0.181 ± .014	-0.178 ± .017	1.172 ± .019
.724	-0.170 ± .016	-0.174 ± .017	1.200 ± .033
.730	-0.171 ± .004	-0.159 ± .007	1.163 ± .009
.735	-0.144 ± .008	-0.151 ± .007	1.137 ± .022
.740	-0.164 ± .009	-0.171 ± .015	1.221 ± .015
Longitudinal Direction			
.231	-0.179 ± .029	-0.177 ± .038	1.327 ± .095
.315	-0.123 ± .028	-0.125 ± .032	1.126 ± .046
.363	-0.083 ± .016	-0.082 ± .022	1.065 ± .016
.448	+0.022 ± .027	.000 ± .034	1.061 ± .010
.507	+0.070 ± .015	+0.065 ± .019	1.096 ± .034
.577	+0.069 ± .013	+0.074 ± .010	1.071 ± .007
.638	+0.091 ± .029	+0.093 ± .027	1.069 ± .016
.721	+0.065 ± .029	+0.065 ± .027	1.073 ± .021
Tangential Direction			
.230	+0.062 ± .022	+0.072 ± .032	1.105 ± .034
.320	+0.097 ± .018	+0.091 ± .034	1.108 ± .030
.368	+0.115 ± .020	+0.114 ± .023	1.077 ± .024
.453	+0.083 ± .016	+0.080 ± .018	1.049 ± .020
.512	+0.052 ± .026	+0.050 ± .014	1.031 ± .015
.582	+0.067 ± .018	+0.061 ± .013	1.054 ± .015
.643	+0.080 ± .016	+0.070 ± .014	1.051 ± .017
.718	+0.094 ± .017	+0.089 ± .019	1.067 ± .028

FIGURE 6.2 Polynomial Curve of Best Fit for Combined G_3 Data in Longitudinal Direction

From moderately negative at the ID, the growth index values rose to near zero at about $\frac{1}{4}$ of the distance from the inner to the outer wall and then fell to severely negative values at the OD.

Experimental Equipment

Preferred orientation data were obtained with a General Electric XRD-V Diffractometer. A 1° divergence slit with a 0.063-inch wide curved slit was used to confine the X-ray beam to the increment of interest. Curved confining slits of 0.067-inch, 0.092-inch, and 0.119-inch radii were used to cause the X-ray beam to impinge upon the increments of interest and to minimize the error at low 2θ angles.

An LGP-30 digital computer was used to calculate the tabulated G_2 , G_3 , and J values and to evaluate the statistical curves from the G_3 data.

FIGURE 6.3 Polynomial Curve of Best Fit for Combined G_3 Data in Radial Direction

Experimental Procedure

The four HAPO I and E cores were heat-treated in Ecco Grade A salt (50% NaCl, 50% KCl) for 12 minutes at 1319°F to 1364°F , delayed in air for 43 seconds, and quenched in water at 130°F . All cores were heat-treated in HAPO blank size (1.437 inches OD) prior to drilling.

Each core was taken from a different ingot, and from a different location in that particular ingot, to obtain a normal range of impurities, fabrication, and heat treating variables. The first core was obtained from the bottom of the ingot, the second core from the lower middle, the third core from the upper middle, and the fourth core from the top. The chemical analyses of the four cores examined are given in Table 6.5.

The cores were machined to obtain longitudinal, tangential, and radial specimens.^{1,2,3} The specimens were incremented and each increment was scanned a sufficient number of times to bring the

TABLE 6.5 Chemical Analysis of the Four Cores Examined

Location in Ingot	Density (g/cm ³)	Isotopic (% U ²³⁵)	Element (ppm)													
			N ₂	B	Cr	Fe	Mg	Mn	Ni	Si	H	Al	Cd	Cu	Zr	C
Bottom	18.96	0.712	10	<.15	11	107	04	09	28	29	—	12	<20	05	<05	—
Lower Middle	18.94	0.712	12	<.15	10	109	04	08	27	30	1.0	7	<20	05	<05	502
Upper Middle	18.95	0.712	10	<.15	12	127	05	08	30	34	—	8	<20	05	<05	433
Top	18.96	0.712	8	.15	08	86	<04	07	28	30	—	6	<20	04	<05	—

95% confidence limits on the mean of the G_2 and G_3 values to within approximately $\pm .03$.

Future Work

Studies of texture gradients in uranium cores after various stages of processing will be continued.

References

- ¹V. Morton and R. N. Thudium. "Texture Gradients in Uranium Fuel Cores," Summary Tech. Rpt. for the Period July 1, 1961 to September 30, 1961, USAEC Report NLCO-840, p. 67. October 20, 1961. (Classified)
- ²V. Morton, R. N. Thudium, N. Crank, Jr., and C. A. Powell. "Texture Gradients in Oil Quenched, Mark V-B Outer Fuel Cores," Summary Tech. Rpt. for the Period January 1, 1962 to March 31, 1962, USAEC Report NLCO-850, p. 61. April 16, 1962. (Classified)
- ³N. Crank, Jr. and C. A. Powell. "Texture Gradients in Uranium Fuel Cores," Summary Tech. Rpt. for the Period July 1, 1962 to September 30, 1962, USAEC Report NLCO-860, p. 49. October 31, 1962.
- ⁴C. A. Powell and N. K. Smith. "Texture Gradients in Oil-Quenched HAPO I and E Fuel Cores," Summary Tech. Rpt. for the Period October 1, 1962 to December 31, 1962, USAEC Report NLCO-865, p. 31. February 1, 1963.
- ⁵E. F. Sturcken. "A Generalized Growth Index Formalism," Papers Presented at the X-ray Preferred Orientation Meeting Held at National Lead Company of Ohio, November 9 and 10, 1959, USAEC Report NLCO-804, p. 9. July 15, 1960.
- ⁶P. R. Morris. Comparative Measurements of the Velocity of Propagation of an Ultrasonic Pulse in Uranium Fuel Elements, USAEC Report NLCO-764, p. 13. November 24, 1958.
- ⁷R. N. Thudium and P. R. Morris. "Brief Description of the 'Area-Weight' Treatment for the 18 Plane Set," Papers and Discussion from the X-Ray Preferred Orientation Meeting Held at Argonne National Laboratory December 15 and 16, 1960, USAEC Report ANL-6359, p. 55. May, 1961.

7. ELECTRON MICROPROBE EXAMINATION OF PHOSPHIDES IN URANIUM

J. W. Colby

Abstract

Samples of production-grade derby metal containing approximately 400 ppm of phosphorous were examined in an electron microprobe X-ray analyzer recently installed in the Laboratory of the National Lead Company of Ohio. Uranium phosphides were identified and two different modes of precipitation were observed.

Introduction

Uranium ingots are produced at National Lead Company of Ohio by melting a combination of derbies and various other uranium feed materials. "Derby" is the name given to the high-purity uranium regulus produced by the direct reduction of UF_4 to metal.

Recently it was discovered that several uranium ingots contained phosphorous in quantities larger than usual. The increase in phosphorous content was traced to the derbies, and two samples were obtained from a derby containing approximately 400 ppm phosphorous.

A recently acquired electron microprobe was employed to locate and identify the second-phase uranium phosphide precipitates, and to characterize them insofar as possible.

From previous work on the uranium-phosphorous system,¹ it was presumed that the phosphorous would be present as the monophosphide, UP. A sample of UP obtained from Argonne National Laboratory was used as a standard for the microprobe study.

Objectives for This Quarter

The objectives for this quarter were to locate and identify any phosphorous inclusions present in uranium, and to characterize them if possible.

Summary of Results

Uranium phosphides were identified in each of the two derby samples. The mode of precipitation, however, was different in each. In one of the samples (obtained from the center of the derby) the precipitate occurred as a fine network structure. In the other sample (obtained from the edge of the derby) the uranium phosphide occurred both as large angular and as large irregular inclusions. The angular inclusions have the same appearance as UC and UN precipitates. In some instances, the uranium phosphides were associated with uranium carbides and nitrides.

Equipment

The equipment employed for this investigation was an Applied Research Laboratories EMX electron microprobe X-ray analyzer, shown in Figure 7.1. Briefly, a finely focused beam of high energy electrons is caused to impinge on the area of the sample to be analyzed. Upon impact, the electrons ionize atoms in the sample causing them to emit X rays characteristic of the material being bombarded. The wavelength of the X rays is indicative of the element emitting them, and the intensities of the X rays are related to the mass concentration of the elements present.

Three crystal spectrometers and detectors analyze the emitted X rays, and the outputs of the detectors can be utilized in various types of readout systems.

Another useful feature of the microprobe (the mode used in this report) is the scanning presentation. A set of four electrostatic deflection plates located at the electron optical objective lens position is synchronized with a similar set of deflection plates in an oscilloscope. A portion of the electrons striking the sample surface are scattered back. The number of electrons scattered

1309-1

FIGURE 7.1 Applied Research Laboratories EMX Electron Microprobe X-Ray Analyzer. 1-Scaler, 2-Timer; 3-Flow Gas Regulator; 4-Spectrometer Vacuum Tank; 5-Electron Gun; 6-Optical Microscope; 7-Lens Power Supplies; 8-Vacuum Control System; 9-Strip Chart Recorder; 10-Readout Mode Selector Controls; 11-Sample Current Meter; 12-Detector Power Supply; 13-Electron Beam Scanning System Console; 14-Pulse Height Analyzer; 15-Oscilloscope; 16-Sample Chamber; 17-Filament Power Supply; 18-High Voltage Power Supply

back is a function of surface topography and of the atomic number of the element causing the scattering. In using this mode of analysis, the electron beam is caused to scan the surface of the sample, the beam in the oscilloscope being swept in synchronization with the beam in the microanalyzer. The back-scattered electrons are detected, and the output of the detector is used to modulate the

intensity of the oscilloscope. Hence, an image is obtained which is analogous to an optical image. Magnifications up to 1770X are obtainable.

Alternately, the output of the X-ray detectors may be used to modulate the intensity of the oscilloscope. Hence, the distribution of one or more elements in an inclusion, grain boundary, or other

area of interest, may be obtained and visually displayed on the oscilloscope. Since the number of electrons back-scattered is a function of atomic number, the portion entering the sample is also a function of atomic number, and this sample current may also be used to modulate the intensity of the oscilloscope.

These latter two types of presentation, the X-ray image and the sample-current image, are used throughout this report.

A more complete description of the equipment and its theory of operation may be found in the literature.^{2, 3}

The operating conditions for this study were: accelerating voltage, 30 kilovolts; emission current, 120 microamperes; average sample current, 0.05 microamperes. The spectrometer used for the detection of phosphorous employed a 4-inch ADP crystal with an FPC Minित्रon using P-10 gas (90% argon — 10% methane). Photographic exposure times were 4 minutes for the X-ray images, and 22 seconds for the sample-current images. The

samples were mounted in Wood's metal (1-inch diameter by $\frac{3}{16}$ -inch thick) and were polished.

Results

Figure 7.2 is an optical micrograph of the UP sample obtained from Argonne National Laboratory. The sample had a reported composition of 90% UP and 10% U metal. Figure 7.3a is a sample-current image of a similar area; and Figure 7.3b is a phosphorous K_{α} X-ray image of the same field as Figure 7.3a, showing the distribution of phosphorous in the sample. The dark areas in Figures 7.3a and 7.3b are platelets of uranium.

The sample-current image (Figure 7.3a) is analogous to an optical image with one important difference: the brightness of the sample-current image is related to the atomic number of the elements present. The darker the area, the higher the atomic number. Hence, the dark areas in Figure 7.3a are uranium, the intermediate areas are UP, and the small bright areas are probably oxides.

Figure 7.4 is an optical micrograph showing UP inclusions in one of the derby samples containing 400 ppm phosphorous. These were subsequently identified in the electron microprobe as phosphides. It was not possible to perform a quantitative analysis for phosphorous in any of the inclusions discussed in this article. To perform such an analysis, a pure phosphorous standard (or some other phosphorous standard for which the composition was accurately known on a micron scale) would be needed. The phosphorous content in these inclusions is the same as the phosphorous content in the UP sample obtained from Argonne National Laboratory. The uranium content in these inclusions was determined to be 88 w/o (theoretical uranium content of UP is 88.5 w/o). The spectrum was scanned from 0.6 angstroms to 10.0 angstroms, and no other element was detected.

Figures 7.5, 7.6, 7.7 and 7.8 are images of different types of phosphide inclusions found in the same derby sample as in Figure 7.4. Figure 7.5b is an image formed by back-scattered electrons

946-1

FIGURE 7.2 Optical Micrograph of Uranium Phosphide Sample Obtained from Argonne National Laboratory Showing Platelets of Uranium in a UP Matrix (500X)

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FIGURE 7.3a Sample-Current Image of Same Sample as Figure 7.2 (1770X)

946-3

FIGURE 7.3b Phosphorous K_{α} X-Ray Image of Same Field as Figure 7.3a (1770X)

and is somewhat analogous to a sample-current image. No further information may be obtained from such an image than is obtained from a sample-current image. They merely complement one another, and Figure 7.5b is included only to illustrate this mode of presentation. In such an image, the dark areas correspond to light elements or holes, while the whiter areas correspond to heavier elements, exactly opposite of the sample-current image.

Figure 7.6 is interesting in that it shows three inclusions together, only one of which is a phosphide. The two remaining inclusions were unidentified. The spectrum was scanned and no elements other than uranium were detected. The uranium content was determined to be approximately 90 w/o. From the sample-current image, one can infer that the mean atomic number⁴ of these two inclusions is greater than the mean atomic number of UP. These two conditions would be satisfied if the two inclusions were UC_2 .

Figures 7.7 and 7.8 were included because, in addition of being images of typical phosphide

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FIGURE 7.4 Optical Micrograph of Uranium Phosphide Inclusions in Uranium Derbies Containing 400 ppm Phosphorous (500X)

FIGURE 7.5 Uranium Phosphide Inclusion in Same Sample as in Figure 7.4. (a) Sample-Current Image, (b) Back-Scattered Electron Image; (c) Phosphorous K_{α} X-Ray Image. (1770X)

FIGURE 7.6 Uranium Phosphide Inclusion Associated With Two Other Unknown Inclusions. Same Sample as Figures 7.4 and 7.5. (a) Sample-Current Image, (b) Phosphorous K_{α} X-Ray Image. (1770X)

FIGURE 7.7 Uranium Phosphide Inclusion in Same Sample as in Figures 7.4, 7.5, and 7.6. (a) Sample-Current Image, (b) Phosphorous K_{α} X-Ray Image. (1770X)

946-12

(a)

946-13

(b)

FIGURE 7.8 Uranium Phosphide Inclusion From Same Sample as in Figures 7.4, 7.5, 7.6, and 7.7. (a) Sample-Current Image Showing Growth Steps of Polygonal Symmetry; (b) Phosphorous K_{α} X-Ray Image. (1770X)

946-14

inclusions, they illustrate the resolution that may be obtained in a sample-current image. In Figure 7.8a, the inclusion is sufficiently well resolved that the growth steps may be seen to be of polygonal symmetry.⁵ The large size of this inclusion (approximately 20 by 30 microns) indicates that the diffusion rate of phosphorous must be quite high.

Figure 7.9 is an optical micrograph of the second sample from the same derby containing approximately 400 ppm of phosphorous. The phosphide precipitate in this sample is in the form of a fine network phase. Figures 7.10a and 7.10b are sample-current images of this phase taken at 440X and 880X respectively. Figure 7.10c is a phosphorous K_{α} X-ray image of the same field as 7.10b showing that this network phase is also uranium phosphide.

FIGURE 7.9 Optical Micrograph of Uranium Phosphide Network Phase in Second Sample from Uranium Derby Containing 400 ppm Phosphorous (500X)

946-15

(a)

946-16

(b)

946-17

(c)

FIGURE 7.10 Uranium Phosphide Network Structure From Same Sample as in Figure 7.9. (a) Sample-Current Image (440X); (b) Sample-Current Image (880X); (c) Phosphorous K_{α} X-Ray Image, Same Field as 7.10b. (880X)

Conclusions

Uranium phosphide inclusions were identified and shown to exist in several different forms and so cannot be characterized. The form assumed is most certainly dependent on the cooling rate. Although a complete quantitative analysis could not be performed on the inclusions examined, no elements other than U and P could be found, and the uranium content is quite close to stoichiometric. Hence, it is believed that the inclusions were UP.

Future Work

Finished uranium fuel cores having a high phosphorous content will be examined in the electron microprobe to determine in what form the phosphides are present.

References

- ¹F. A. Rough and A. A. Bauer. "Uranium-Phosphorous," Constitution of Uranium and Thorium Alloys, USAEC Report BMI-1300, p. 54. June 2, 1958.
- ²D. B. Wittry and R. Fitzgerald. "Equipment for Beam Scanning and Step Scanning in Electron-Probe Analysis," Proceedings of the annual conference on industrial applications of X-ray analysis, 10th, Vol. 5, pp. 538-553. New York: Plenum Press, 1962.
- ³R. Castaing. "Electron Probe Microanalysis," Advances in Electronics and Electron Physics, Vol. XIII, pp. 317-386. New York: Academic Press, 1960.
- ⁴D. M. Poole and P. M. Thomas. Quantitative Electron-Probe Microanalysis, UKAEA Report AERE-R-3815. August, 1961.
- ⁵W. T. Read, Jr. Dislocations in Crystals, pp. 147-152, New York: McGraw-Hill, 1953.