NLCO-860
General, Miscellaneous,
and Progress Reports
(TID-4500, 18th ed.)

SUMMARY TECHNICAL REPORT
FOR THE PERIOD
JULY 1, 1962 TO SEPTEMBER 30, 1962

S. MARSHALL, DIRECTOR
TECHNICAL DIVISION

R. BURGETT
TECHNICAL EDITOR

Date of issuance: October 31, 1962

NATIONAL LEAD COMPANY OF OHIO
Box 39158, Cincinnati 39, Ohio
Contract No. AT(30-1)-1156

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NLCO - 860
General, Miscellaneous,
and Progress Reports
(TID - 4500, 18th ed.)

DISTRIBUTION

	No. of Copies
Internal	24
Special	15
Cincinnati Area Office, USAEC	
C. L. Karl	1
duPont Company, Aiken	
T. C. Evans	1
V. I. Montenyohl	1
General Electric Company, Richland	
S. M. Gill	1
J. E. Minor	1
K. W. Norwood	1
J. T. Stringer	1
Mallinckrodt Chemical Works	
J. A. Fellows	1
A. E. Ruehle	1
J. H. Yeager	1
National Lead Company	
G. W. Wunder	1
Nelco Metals, Inc	1
Oak Ridge Operations Office, USAEC	
J. W. Ruch	1
David Zachry, Patent Branch	1
St. Louis Area Office, USAEC	
F. H. Belcher	1
External distribution as shown in TID - 4500, 18th ed., category UC - 2	591

CONTENTS

	Page No.
SUMMARY	9
1. Improvement of Green Salt Quality	11
Reduction of UO_3 by Ammonia	11
Reaction Rates for the Hydrofluorination of UO_2 Derived from Hanford UO_3	17
Development of Equipment for the R-O-R Process	20
2. Reduction Evaluation of Large UF_4 -Mg Briquettes	25
3. Magnesium-Lithium Alloy Reductant for Reducing Green Salt to Metal	35
4. Evaluation of Pickled Drip Crops as Remelt Feed	41
5. An Electron Bombardment Furnace for the Bendix Time-of-Flight Mass Spectrometer	45
6. Texture Gradients in Uranium Fuel Cores	49
7. Yield Criteria for Alpha-Uranium Single Crystals	53
8. Atmospheric Corrosion of Uranium	61
9. Prevention of Chloride Pitting of Uranium Fuel Cores	65
10. The Determination of Chloride by the Coulometric Method	69

TECHNICAL PROJECT SUPERVISION

NATURE OF ACTIVITY (Projects)	PERFORMED UNDER SUPERVISION OF
<u>Chemical</u> Projects Relating to Feed Evaluation, Refining and Chemical Processing.	M. A. DeSesa, Head, Chemical Department.
<u>Metallurgical</u> Projects Relating to Fabrication, Foundry Technology and Physical Metallurgy.	C. E. Polson, Head, Metallurgical Department.
<u>Pilot Plant</u> Metals Development, Pilot Production, Process Engineering and Refinery Operations.	J. O. Davis, Head, Pilot Plant.
<u>Analytical Chemistry</u> Investigations in Wet Chemical and Instrumental Analysis.	J. W. Robinson, Head, Analytical Department.
<u>Statistical Studies and Technical Illustration Services.</u>	P. N. McCreery, Head, Quality Control Department

SUMMARY

	Page No.
Laboratory tests have indicated that undissociated ammonia can be used advantageously to reduce UO_3 to UO_2	11
Kinetic data are given for the hydrofluorination of UO_2 from Hanford-source UO_3 under various operating conditions.	17
A seal was developed to prevent the mixing of dissociated ammonia and air in the R-O-R process equipment.	20
Large UF_4 -Mg briquettes were made having good physical strength and good reduction characteristics.	25
Magnesium alloyed with lithium was used as the reductant for green salt in small scale reductions.	35
Drip crops pickled in HNO_3 were evaluated as remelt feed and were found deleterious to quality.	41
An electron bombardment furnace was constructed for use with the Bendix time-of-flight mass spectrometer.	45
Fuel cores were examined by X-ray diffraction techniques in the radial, tangential, and longitudinal directions as functions of radial position.	49
Stereographic projections have been prepared of the fraction of an arbitrarily directed tensile stress resolved as shear stress on the various modes of a number of twinning systems.. . . .	53
The stable corrosion product formed when uranium metal is exposed to moist atmosphere was identified as $\text{UO}_3 \cdot 2\text{H}_2\text{O}$	61
Electrochemical studies have shown that chloride pitting of uranium fuel cores in aqueous solutions can be eliminated by the addition of sodium nitrite.	65
An automatic coulometric titrator has been constructed that permits accurate and rapid determination of chloride ions.	69

1. IMPROVEMENT OF GREEN SALT QUALITY

W. Burkhardt

Abstract

The use of undissociated ammonia for the reduction of UO_3 is a promising approach to effecting economies in the Green Salt Plant and improving green salt quality. The only foreseeable source of difficulty found in a laboratory study of the reaction is that the reduction rate might limit reactor throughputs. Thermobalance tests indicate that the use of undissociated ammonia for reduction may be beneficial to hydrofluorination conversion and that very little dissociation of excess ammonia occurs. Kinetics and the mechanism of the reduction reaction are discussed.

Kinetic data for the hydrofluorination of UO_2 from Hanford — source UO_3 to UF_4 have been obtained for various HF concentrations and temperatures.

Equipment modifications are being developed that will enable existing plant reactors to be used as a production facility for the R-O-R* process. The development reported herein is a seal to prevent the mixing of dissociated ammonia and air, two of the gaseous reactants used in the R-O-R process.

REDUCTION OF UO_3 BY AMMONIA

C. W. Huntington M. G. Mendel
R. P. Linfert

Introduction

The use of undissociated ammonia as a reductant for orange oxide has been considered in the past as an alternative to additional dissociator capacity or as a means of controlling reduction temperatures. Recently, increasing costs of main-

* *The R-O-R process is used to convert a relatively inert UO_3 to a reactive UO_2 by successive reduction to UO_2 , oxidation to U_3O_8 , and reduction to UO_2 .*

tenance on the ammonia dissociators and hydrogen off-gas system have resulted in renewed interest in this reduction technique. It is reasoned that if the excess ammonia in the fluid bed reactors does not dissociate appreciably, it would be possible to use wet scrubbing, a relatively trouble-free process, in the off-gas system. In addition to reducing maintenance costs, such a change could reduce direct materials costs, since excess reductant could be recovered and recycled as aqueous ammonia to the Scrap Recovery Plant. Plans for a plant test of this reduction technique were terminated several years ago when the possibility of serious corrosion originating from nitridization of reactor components was suggested; however, it is felt that the successful use of undissociated ammonia at LeBouchet, France, has shown that corrosion would not be a problem.

Another possible advantage of ammonia reduction is suggested in work reported by Hanford^{1,2} in 1956. In this work, thermobalance tests indicated that UO_2 produced by ammonia reduction from both pot UO_3 and continuous-calciner UO_3 hydrofluorinated more rapidly than did hydrogen-reduced samples.

A possible disadvantage is that the reduction rate with ammonia is likely to be slower than with hydrogen, as indicated by laboratory work at Mallinckrodt Chemical Works³ and by tests in a three-stage fluidized bed reactor at Argonne National Laboratory.⁴

Objective for This Quarter

To determine by laboratory tests the feasibility of using undissociated ammonia for the reduction of the oxides currently being processed in the Green Salt Plant (Port Hope pot-calcined UO_3 , Mallinckrodt pot-calcined UO_3 , and Hanford continuous-calcined UO_3).

Summary of Results

All three oxides currently being processed in the Green Salt Plant can be reduced by undissociated ammonia. Reduction rates are slower than with hydrogen; however, the subsequent hydrofluorination conversion appears somewhat faster. Essentially no dissociation of ammonia gas occurs in the thermobalance chambers.

The reduction of batch-produced UO_3 by ammonia was found to take place in two distinct steps, with an abrupt change in rate occurring at about $\text{UO}_{2.56}$. The first part of the reaction is faster with ammonia than with hydrogen; the second part is slower. It is postulated that the ammonia is catalytically decomposed on the surface of the oxide and that the reduction is effected by atomic hydrogen. A phase change near $\text{UO}_{2.56}$ evidently retards the dissociation process throughout the remainder of the reaction.

Experimental Data

Reduction of Batch-Produced UO_3

The first reduction of Port Hope UO_3 was made in a thermobalance at 932°F with 1 liter per minute NH_3 . The time required for 97% conversion to UO_2 was 2200 seconds, approximately twice as long as the hydrogen reduction time. As shown in Figure 1.1, the reduction pattern with ammonia was quite different from that observed with hydrogen. Initial reaction to about 40% conversion was more rapid than with hydrogen and occurred in 200 seconds; reduction 97% UO_2 required an additional period of 2000 seconds. The reaction of MCW UO_3 with ammonia followed a similar pattern (Figure 1.1). Reduction of Port Hope oxide at other temperatures revealed similar breaks in the reduction curves (Figure 1.2). At 842°F only the first part of the reaction occurred.

FIGURE 1.1 Reduction of UO_3 with Hydrogen and Ammonia at 932°F

Reduction of Various Uranium Oxides

The results of the tests with batch-produced UO_3 prompted investigation of the reduction characteristics of different kinds of oxides. Various samples of laboratory and production oxides with surface areas ranging from 0.2 to $12.3 \text{ m}^2/\text{g}$, were reduced with ammonia at 932°F . The results of these tests are summarized in Table 1.1, and examples of different types of reduction curves are shown in Figure 1.3. All the powder samples exhibited the same reaction pattern: the initial 40% of the reaction was rapid in comparison with the remaining 60%. As shown by curve B in Figure 1.3, the difference was less pronounced with the milled continuous oxides. The reduction of unground (spheroidal) continuous -pot oxide, curve A, Figure 1.3, did not follow this sequence; instead, the rate was extremely slow throughout the reaction.

FIGURE 1.2 Reduction of Port Hope UO_3 with NH_3 at Various Temperatures

TABLE 1.1 Reduction of Various Uranium Oxide Powders by Ammonia

Temperature: 932°F
Sample Weight: 1.5 g
 NH_3 Flow Rate: 1 liter/min,
except as noted otherwise

Oxide	Surface Area (m^2/g)	Reduction Times* (sec)		
		40%	97%	100%
Port Hope UO_3	4.97	80	2220	2650
MCW UO_3	5.26	80	2050	2500
Non-sulfated UO_3 (lab)	2.6	170	2750	3150
High-Th UO_3 (lab)	0.6	140	2650	3100
Calcined ADU ($UO_{2.73}$)	12.3	40	1400	1650
Hanford UO_3	2.36	280	2100	2450
Continuous-pot UO_3 ground**	1.0	370	3300	3800
Continuous-pot UO_3 , as-produced	0.2	1800	7500	8500

* Time required for indicated conversions.

** NH_3 flow rate, 2 liters/min.

Comparison with Hydrogen-Helium Mixture

In order to compare the reductant properties of ammonia and hydrogen under conditions more close-

ly approximating those used in the plant, another series of tests was made at 1050°F. Samples of UO_3 from Port Hope, Mallinckrodt, and Hanford were reduced with ammonia and with 3-to-1 mixtures of hydrogen and helium. The total gas flow for all tests was 2 liters per minute. The results of these tests, which are summarized in Table 1.2, indicated that ammonia reduction rates in the plant would be slower than those occurring with cracked ammonia by a factor of approximately 1.5.

TABLE 1.2 Comparison of Reduction Rates Obtained with Ammonia and with a 3:1 Mixture of H_2 and He

Oxide	Time Required for 97% Reduction at 1050°F (sec)	
	NH_3	H_2 -He
Port Hope UO_3	410	280
MCW UO_3	400	280
Hanford UO_3	410	225

NOTE: Total gas flow was 2 liters per minute.

FIGURE 1.3 Reduction of Various Oxides with Ammonia at 932°F

Dependence of Reduction Rates on Ammonia Excess

In early tests with MCW oxide, it was observed that the reduction time at 932°F was reduced by about 25% by increasing the ammonia flow rate

from 1 to 2 liters/minute. A more comprehensive investigation with Port Hope UO_3 showed that the reduction rate increases with increasing NH_3 flow rate up to 2.35 liters/minute, the maximum flow possible with the equipment used. Relationships at 932°F are represented in Figure 1.4.

FIGURE 1.4 Reduction of Port Hope UO_3 with Various Flow Rates of NH_3 at 932°F

Ammonia Content of Off-Gas from Thermobalance Tests

The approximate percentage of undissociated ammonia in the off-gas from the thermobalance tests was determined by comparing the volumes of a sample before and after scrubbing with nitric acid. All measurements made at temperatures up to 1100°F indicated that 94% to 97% of the off-gas streams was undissociated ammonia. It is believed that leakage of air into the thermobalance system was at least partially responsible for the unrecovered portion.

Hydrofluorination Tests

Results of several hydrofluorination tests were in agreement with Hanford data^{1,2} that hydrofluorination of oxides reduced with ammonia is more rapid than the reaction of oxides reduced with hydrogen. Results obtained with Port Hope and MCW UO_3 are summarized in Figures 1.5 and 1.6. In the series with MCW oxides, undissociated ammonia proved to be a more desirable reductant, from the standpoint of hydrofluorination conver-

FIGURE 1.5 Hydrofluorination of UO_2 Prepared from Port Hope UO_3

FIGURE 1.6 Hydrofluorination of UO_2 Prepared from MCW UO_3

sion, than either undiluted hydrogen or simulated cracked ammonia (3 volumes hydrogen to 1 volume nitrogen). Additional tests with Port Hope UO_3 showed that, when ammonia was the reductant, increasing the reduction temperature from 1000°F to 1200°F caused the early part of the hydrofluorination reaction to be somewhat slower; however, as shown in Table 1.3, the over-all rate of conversion was not appreciably affected.

In tests with two samples of Hanford UO_3 , activation by the R-O-R technique (described in a subsequent subsection by Geers) was shown to be as effective when ammonia is used as the reduc-

TABLE 1.3 Hydrofluorination of UO_2 Prepared from Port Hope UO_3 by Ammonia Reduction

Reduction Temperature (°F)	1000	1100	1200
Hydrofluorination Temperature (°F)	1000	1000	1000
% UF_4 at 2 minutes	86.1	81.2	79.5
4	94.6	91.7	90.2
6	96.1	95.4	94.1
10	97.3	97.6	97.3
14	97.3	98.3	97.8

tant as when hydrogen is used. Results of these tests are summarized in Table 1.4.

TABLE 1.4 Hydrofluorination of Hanford Oxides Prepared by R-O-R Activation

Sample No.	1		2	
Reductant	H ₂	NH ₃	H ₂	NH ₃
% UF ₄ at 1 minute	44.6	48.2	50.8	52.2
2	82.5	88.1	86.0	90.2
3	93.4	96.5	95.2	96.8
4	97.7	97.2	97.2	97.2
5	97.9	97.5	98.2	97.8
6	98.4		98.5	
8	98.9			

Conditions for all tests:

Flow rate of reductant: 2 liters per minute

Reduction temperature: 1100°F

Oxidation temperature: 750°F

Rereduction temperature: 1000°F

Hydrofluorination temperature: 1000°F

Discussion

Use of Undissociated Ammonia in the Green Salt Plant

The laboratory data indicate that undissociated ammonia could be successfully used to reduce the three different oxides now being processed in the Green Salt Plant.

The reduction rate would be slower than with hydrogen, perhaps by a factor of 1.5; however, it will be necessary to conduct tests in the plant equipment to determine whether this factor would significantly affect productivity. If it does, it might be possible to increase reduction rates by using higher excesses of ammonia than are used with dissociated ammonia; or it might be possible to use a slightly higher reduction temperature without seriously affecting the hydrofluorination process. With ammonia, the initial part of the reaction is faster and the final part is slower than with hydrogen; some adjustment of set temperatures might therefore be required.

Very little, if any, dissociation of ammonia occurred in the thermobalances. It does not appear likely that appreciable dissociation would occur in the plant equipment; however, the decomposition of ammonia is a complicated process which is catalyzed by a variety of conditions, and plant tests will be needed to determine the degree of recovery possible. If satisfactory recovery of unreacted ammonia is accomplished, it will be feasible to use larger excesses of ammonia in reduction.

It seems certain that a change to the use of ammonia for reduction would have no adverse effect on the hydrofluorination process. On the contrary, the thermobalance data indicate that improved conversion to green salt may result.

Kinetics and Mechanism of Ammonia Reduction

That the kinetics and mechanism of ammonia reduction are quite different from those of hydrogen reduction is graphically depicted in Figure 1.1. As shown by the reduction curves and by analysis of the off-gas, the reaction involves the ammonia molecule itself, not simply the hydrogen resulting from a prereaction dissociation process. Thus, the reaction apparently proceeds via catalytic decomposition of ammonia on the surface of the oxide.

There are two very interesting features of the reaction:

1. The initial part is more rapid than with hydrogen.
2. The rate abruptly decreases at about 40% conversion, and the ensuing reaction proceeds more slowly than with hydrogen.

With the assumption that the process is essentially one of catalytic decomposition of ammonia, followed by reduction by the hydrogen formed, plausible reasons for both features can be postulated.

In the catalytic decomposition of ammonia, it is believed that the rate-limiting step is the desorption of nitrogen from the surface of the catalyst. In reduction by hydrogen gas, chemisorption of hydrogen is considered to be the rate-determining step^{5,6} probably because the hydrogen molecule must be distorted before reaction with active oxygen sites can occur⁶. With ammonia, adsorption and dissociation are both rapid, and atomic hydrogen is the reductant. Since it is not necessary to provide the energy to distort molecular hydrogen, reaction with ammonia is the faster. If this explanation is correct, it follows that the rate of desorption of nitrogen in the reaction with ammonia must be faster than the chemisorption of hydrogen in the reaction with hydrogen gas.

The change in rate coincides with the phase change, U_3O_8 -(orthorhombic) $\rightarrow$ UO_2 +(cubic) which occurs near the composition $UO_{2.56}$.⁷ Since the ensuing reaction is much slower than with hydrogen, it appears that the change in crystal habit at this point adversely affects the decomposition of ammonia. Possible reasons for this effect include reduction in the availability of active sites for adsorption and hindrance of the desorption of nitrogen. That some geometric factor is operative is indicated by the fact that the rate change occurs at nearly the same composition with all powder samples, regardless of the original oxygen-to-uranium ratios or surface areas.

The reduction of UO_3 by ammonia has been studied by Kuhlman.³ He did not observe the two-step sequence, probably because bed-depth effects obscured the characteristics of the reaction. Kuhlman used larger samples (4.236 g) which resulted in bed depths of approximately 5 mm; whereas in reduction by hydrogen, it has been found that observed rates are affected by samples larger than 4 g and deeper than 1 mm.⁵ Velocity constants about 1/10 of those observed in hydrogen reduction and an activation energy of 31.5 kcal per mole were reported in this early work.

Interpretation of the reduction data obtained to date in the present study is complicated by several factors, chief of which is that reduction rates were dependent upon the flow rate of ammonia throughout the range of flows used. Additional work is in progress to define quantitatively the kinetics of the reaction and to determine whether the mechanism suggested above is tenable. Since the over-all process appears to be the result of two reactions — dissociation of ammonia and reaction between hydrogen and the oxide — the mechanics are undoubtedly complex.

Future Work

Plant tests will be designed to determine the following data:

1. Productivity of the reduction step.
2. Consumption of ammonia and degree of recovery of the excess.
3. Hydrofluorination characteristics of ammonia-reduced oxides.

The kinetics and mechanism of ammonia reduction will be studied further, and an attempt will be made to determine reasons for the beneficial effects observed in the hydrofluorination of ammonia-reduced oxides.

REACTION RATES FOR THE HYDROFLUORINATION OF UO_2 DERIVED FROM HANFORD UO_3

D. C. Bonfer

Introduction

Hanford continuous-calciner UO_3 is presently being processed by National Lead Company of Ohio. As part of a program to characterize this material, a laboratory thermobalance study of the hydrofluorination reaction was conducted.

Objective for This Quarter

To develop reaction rate data for the hydrofluorination of UO_2 derived from Hanford continuous-calciner UO_3 .

Summary of Results

The temperature at which Hanford UO_3 is reduced to UO_2 was found to have an effect upon the subsequent hydrofluorination reaction rates. A faster hydrofluorination rate is realized following reduction at 1175°F than following reduction at 935°F .

The maximum hydrofluorination rates using 35, 49, and 100% hydrogen fluoride for Hanford UO_3 reduced at a temperature of 1175°F were obtained at 840, 860, and 920°F , respectively. Changing the reduction temperature to 935°F yielded maximum hydrofluorination rates at 825, 850, and 875°F , respectively.

Metal-grade UF_4 can be prepared from Hanford UO_3 in the laboratory thermobalance by using a reduction temperature of 1175°F and a hydrofluorination temperature programmed to rise from 600°F to 1000°F during the reaction. Under the above conditions, final conversions to UF_4 were obtained that were equivalent to NLO batch UO_3 .

The laboratory data indicate that it may be possible to select plant processing conditions for the direct conversion of Hanford UO_3 to metal-grade UF_4 without resort to the oxidation-reduction activation procedure.

Experimental Procedure

The sample used in this study was Hanford continuous-calciner UO_3 . Spectrochemical, chemical, and screen analyses for this sample are presented in Table 1.5.

Laboratory equipment and experimental procedure used in obtaining the reaction rates are described in a previous report.⁸

TABLE 1.5 Spectrochemical, Chemical, and Screen Analyses of Hanford Continuous-Calciner UO_3 Used in Test

Spectrochemical Analysis (ppm)		Chemical Analysis	
Al	< 6	SO_4 (ppm)	11,400
B	< 0.2	Fe (ppm)	50
Cd	< 0.2	Ni (ppm)	6.9
Cr	15	Na (ppm)	32
Cu	< 1	Th (ppm)	< 10
Fe	53	U (%)	81.63
Mg	7	UO_3 (%)	98.08
Mn	5	NO_3 (%)	1.36
Mo	< 6	HCL Insol (%)	< 0.01
Ni	6	H_2O (%)	0.56
P	< 20	Wet Screen (% Retained)	
Pb	3	+ 40	0.4
Si	21	+ 80	2.8
Sn	2	+ 100	2.8
V	< 40	+ 150	4.2
Zn	< 20	+ 250	11.9
Zr	< 5	+ 325	11.6
		- 325	66.4

Discussion

The initial hydrofluorination study using a 1000°F reduction temperature and anhydrous hydrogen fluoride gave poor reproducibility of the rate data. The cause of this poor reproducibility was suspected to lie in the preceding reduction step. It appeared that occasionally the temperature of the particles exceeded the desired 1000°F , thus resulting in a beneficial effect on the hydrofluorination reaction. This observation, together with data reported in a recent Oak Ridge Gaseous Diffusion Plant quarterly report,⁹ indicated that additional consideration of reduction conditions was required before continuing the hydrofluorination rate study. Therefore, it was decided to study the effect of reduction temperatures of 935°F and 1175°F on the subsequent hydrofluorination reaction. Hydrofluorination was performed at 850°F and 900°F . These data are presented in Table 1.6.

The data in Table 1.6 indicates that a faster hydrofluorination rate is realized following reduction

TABLE 1.6 Thermobalance Conversion of
Hanford UO_3 to UF_4

Reduction Temp ($^{\circ}\text{F}$)	935	1175	935	1175
Hydrofluorination Temp ($^{\circ}\text{F}$)	850	850	900	900
Time (min)	Conversion to UF_4 (%)			
1.0	35.8	38.2	42.2	35.7
2.0	63.0	62.7	64.1	62.0
3.0	68.6	70.1	69.8	70.6
4.0	71.8	74.1	73.3	74.9
5.0	74.7	76.9	75.7	77.7
10.0	82.4	85.7	82.8	85.7
16.0	86.9	90.4	87.3	90.4
20.0	88.9	92.3	89.3	92.4
25.0	90.6	93.8	90.9	94.0
30.0	91.8	94.8	92.4	95.1

at 1175°F than following reduction at 935°F . This may be explained by the fact that the inherent activity is preserved during reduction in hydrogen at 935°F and the UO_2 produced may react initially with hydrogen fluoride with such vigor that the particle temperature will approach sintering conditions. If this occurs, it will require a longer period of time for the reaction to approach completion.

Since the Hanford UO_3 was found to be sensitive toward reduction temperature, a few additional tests were made using anhydrous hydrogen fluoride and programmed temperatures. The purpose of these tests was to determine if conditions could be found to convert the oxide to metal-grade UF_4 at favorable reaction rates without the use of the oxidation-reduction activation process. These data are presented in Table 1.7.

It is shown that metal-grade UF_4 can be prepared from Hanford UO_3 in the thermobalance by using a reduction temperature of 1175°F and a hydrofluorination temperature programmed from 600°F to 1000°F . It is also shown, that under these conditions, final conversion to UF_4 equivalent to that of NLO batch UO_3 can be obtained in the laboratory thermobalance. Hence, it may be possible to choose production plant reduction and hydrofluorination conditions to permit manufacture of metal-

TABLE 1.7
Thermobalance Hydrofluorination Rates

	NLO UO_3	Hanford UO_3					
Reduction Temp ($^{\circ}\text{F}$)	1000	1175	1175	1000	1000	1175	
Hydrofluorination Temp ($^{\circ}\text{F}$)	600- 1000	600- 1000	500- 1000	1000	850	850	
Time (min)	Conversion to UF_4 (%)						
5	74.3	68.7	60.4	70.9	77.9	76.9	
10	85.8	84.5	76.6	77.8	84.2	85.7	
16	91.5	93.8	90.0	82.5	87.8	90.4	
20	95.4	97.0	94.6	84.7	89.4	92.3	
25	96.6	98.0	97.6	86.7	90.6	93.8	
30	97.2	98.3	98.3	88.4	91.5	94.8	

grade UF_4 from Hanford UO_3 without resort to the R-O-R activation process.

The reaction rate data for the $\text{HF}-\text{H}_2\text{O}$ (steam) mixtures are presented in Figures 1.7 and 1.8. The inverse of time (hours) to reach a conversion of 90 mole % is plotted against the temperature at which the reaction is carried out. The experimental data define a set of curves, each curve corresponding

FIGURE 1.7 Hydrofluorination of UO_2 Derived from Hanford UO_3 Reduced at 1175°F Showing the Effect of HF Concentration and Temperature on the Reaction Rate

FIGURE 1.8 Hydrofluorination of UO_2 Derived from Hanford UO_3 Reduced at 935°F Showing the Effect of HF Concentration and Temperature on the Reaction Rate

to a particular composition of the gas phase. Each of the curves intersects the temperature axis at the equilibrium temperature. Figure 1.7 represents the reaction rates obtained for UO_2 derived from Hanford UO_3 using a reduction temperature of 1175°F . The maximum hydrofluorination reaction rate with 35, 49, and 100% hydrogen fluoride occurred at 840, 860, and 920°F , respectively. Figure 1.8 shows the reaction rate data for UO_2 derived from Hanford UO_3 using a reduction temperature of 935°F . The maximum hydrofluorination rate with 35, 49, and 100% hydrogen fluoride occurred at 825, 850, and 875°F , respectively.

DEVELOPMENT OF EQUIPMENT FOR THE R-O-R PROCESS

J. F. Geers

Introduction

Previous tests^{10,11} in Green Salt Plant equipment have demonstrated the feasibility of a reduction-oxidation-reduction (R-O-R) process. This process is used for converting a UO_3 feed

that exhibits low reactivity in reduction and hydrofluorination into a reactive UO_2 which may be hydrofluorinated to UF_4 at relatively high feed rates.

In order to place the R-O-R process on-stream as a production operation, several plans were considered for utilizing existing plant equipment.¹² In one plan, of low capital cost, two reduction-hydrofluorination reactor banks are used. Each bank consists of a pair of fluid bed reactors followed by screw reactors in series. In one bank, the UO_3 of low reactivity is reduced with dissociated ammonia to UO_2 in the fluid beds and one screw reactor. The resulting UO_2 is oxidized with air to U_3O_8 in three screw reactors in series. The other reactor bank is used for the reduction of U_3O_8 to UO_2 in the fluid beds and one screw reactor. Hydrofluorination of the UO_2 to UF_4 occurs in the remaining three screw reactors.

To prevent a possibly hazardous condition from developing in the reactor bank to be used for the reduction-oxidation steps, a safe means of sealing between the two gaseous reactants, dissociated ammonia (DA), and air is required. To meet this need, a prototype seal incorporating a nitrogen lift has been constructed and tested.

Objective for This Quarter

1. To design, construct, and test a sealing system for the R-O-R process equipment that will assure that dissociated ammonia and air do not come into contact with one another.

Summary of Results

1. The prototype seal, incorporating a nitrogen lift and seal hopper, provides an adequate and safe means of sealing between the first screw reactor and the remaining screw reactors.
2. The nitrogen lift alone is capable of providing a seal between the two sets of reactors.
3. Analysis of the nitrogen gas stream discharging from the lift indicates that it has essentially the same hydrogen concentration as the entering

plant nitrogen. It is concluded, therefore, that the hydrogen carryover is negligible.

Experimental Procedure

The prototype sealing system that was installed and tested is shown in Figure 1.9.

FIGURE 1.9 Sealing System for Reduction-Oxidation-Reduction Process

This seal was evaluated under conditions of keeping dissociated ammonia (DA) and HF separate; i.e., DA was on the fluid bed — first screw reactor side of the seal, and HF was on the other. These are the gases that are used in the normal operation of a reactor bank producing UF_4 .¹² Thus, the equipment was tested under actual plant conditions with little or no interference to regular production of UF_4 . Testing the seal with DA and HF was also less hazardous than using dissociated ammonia and air as the reactants.

Discussion

The system tested is a double-seal system. The primary seal is existing and consists of a level of UO_2 powder in a hopper. The secondary seal is maintained by a bed of powder (also UO_2) that is fluidized by a flow of nitrogen. This latter piece of equipment, called a nitrogen lift, provided a second seal in case of a loss of powder level in the seal hopper.

Since the sealing characteristics of a height of powder in a seal hopper are known, the test program was primarily centered on the nitrogen lift portion of the sealing system. In this evaluation, the following items were considered to be of prime importance:

1. The flow of nitrogen required for operation of the lift.
2. The amount of powder held up in the lift.
3. The performance of the lift as the only means of sealing.
4. The general operating characteristics of the lift system.

These items are discussed in the following paragraphs.

Nitrogen Flow Required for the Operation of the Lift

The nitrogen flow must be high enough to maintain the powder in the lift in a fluidized state, thereby preventing the lift feed screw from jamming, and yet low enough to prevent excessive carryover of fines into the HF off-gas system. To determine the minimum nitrogen flow required, the flow rate was started at a high level of 12 scfm (standard cubic feet per minute) and lowered until the lift feed screw started to jam. This lower flow limit was found to be 5.5 to 6 scfm. The amount of fines carried over from the lift was estimated from the frequency with which it was necessary to blow back the carbon tube filter in the off-gas line. This action removed the accumulation of fines that was carried over by the gas stream. At both the

6 scfm flow rate and the 12 scfm flow rate, this filter had to be blown back approximately once per shift.

On the basis of these tests, the optimum nitrogen flow to the lift is approximately 8 to 10 scfm.

Amount of Powder Held Up in the Gas Lift

The amount of powder retained in the lift is an important consideration in the sealing ability of the lift. If there is insufficient powder in the lift, or if all the powder is blown from the lift by the fluidizing nitrogen, a nitrogen failure coupled with an empty seal hopper would allow the gaseous reactants to mix.

To determine the amount of powder held up in the lift, the solids flow to the lift was stopped, while the nitrogen was allowed to continue to flow through the lift for a period of time. The nitrogen was then turned off, and the flange on top of the lift was removed. The level of powder above the top of the feed screw was then measured. The results of a series of these tests are summarized in Table 1.8.

TABLE 1.8 Results of Nitrogen Flow Test

Nitrogen Flow (scfm)	Time Without Feed (min)	Level of Settled Powder Above Top of Screw (in.)
8.1	10	11
6.2	15	12
8.7	60	11
8.7	180	8.5

From these data, it is concluded that, at a normal nitrogen flow to the lift, sufficient powder is retained in the lift to provide a satisfactory seal even though the solids flow to the lift is stopped for a 2 to 3-hour period.

Performance of the Lift as the Only Means of Sealing

To evaluate the effectiveness of the gas lift as the only means of sealing, the seal hopper was purposely emptied of powder by stopping the UO_2 feed to the seal hopper and allowing the lift feed screw (hopper discharge screw) to run. The dissociated ammonia flow to the fluid bed—first screw reactors was replaced with nitrogen, while HF continued to flow through the other two screw reactors.

After the seal hopper was emptied, the lift feed screw was allowed to run for approximately one hour. During this period, the nitrogen to the fluid bed—screw reactor was turned off, and the following observations were made:

1. There was no significant drop in the HF pressure in the hydrofluorination reactors.
2. There was no increase in the fluid bed pressure.
3. There was no evidence of HF discharging from the hydrogen off-gas line.
4. The lift feed screw did not jam.
5. The lift fluidizing nitrogen pressure did not suddenly drop.

All these observations indicate that the lift was capable of maintaining a seal even with an empty seal hopper. If the seal had not held, the HF would have flowed back through the reduction reactors causing the hydrofluorination reactor pressure to drop, the DA pressure to rise, and HF to discharge from the hydrogen off-gas line. It also would have been possible for the gas lift nitrogen to flow back through the screw, thereby collapsing the powder bed in the lift. This, in turn, would have jammed the screw and the pressure of the lift nitrogen would have dropped.

To further confirm these observations, the HF was turned off and, after the hydrofluorination screw reactors were purged with nitrogen, the powder remaining inside the gas lift and the inside walls of the empty seal hopper were inspected. These inspections did not reveal any evidence of attack by

HF on the residual UO_2 in the gas lift or on the walls of the seal hopper.

To determine if there were any flow of gas from the fluid bed — screw reactor through the lift into the hydrofluorination reactors, a system for detecting hydrogen in the nitrogen discharging from the lift was installed and put into operation. The seal hopper was emptied while the dissociated ammonia and the HF were kept flowing; therefore, if any dissociated ammonia leaked from the fluid bed — screw reactor to the hydrofluorination reactors, the hydrogen content of the nitrogen discharging from the lift would increase.

The results of this monitoring indicated that the hydrogen content of the discharge nitrogen from the lift was essentially the same as the hydrogen content of the entering plant nitrogen (approximately 0.6% hydrogen).

This test was performed three times and, in each test, the seal hopper was empty for approximately 1 hour. In two of the tests, the hydrofluorination reactors were vented to the HF recovery system with a resultant high pressure inside the reactors. In the other test, the hydrofluorination reactors were vented to the scrubber system. This results in a low pressure inside the reactors.

From these tests, it is concluded that the lift is adequate for preventing leakage of hydrogen from the reduction-reactor side of the seal to the hydrofluorination-reactor side of the seal.

General Operating Characteristics of the Lift System

Throughout the test period (approximately 4 weeks), the lift operated without any major difficulty.

Table 1.9 presents selected values of nitrogen flow to the lift and estimated pressure drops across the lift. As expected, these data indicate that the pressure drop across the lift is related to the flow through the lift.

TABLE 1.9 Typical Nitrogen Flow and Pressure Drop Data for the Nitrogen Lift

N_2 Flow (scfm)	N_2 Supply Pressure (psig)	Lift Inlet Pressure	Estimated Lift Exit Pressure	ΔP Across Lift
11.4	11	4.5	0.4	4.1
11.4	11	4.3	0.4	3.9
11.4	11	4.3	0.5	3.8
11.4	11	4.3	0.7	3.6
8.7	12	6.2	2.7	3.5
8.7	12	5.8	2.5	3.3
7.7	11	5.8	2.6	3.2
6.8	11	5.0	1.8	3.2
6.2	11.5	6.2	3.4	2.8

The data in Table 1.9 were used to estimate the interlock pressure between the dissociated ammonia supply system and the lift nitrogen.

References

- ¹General Electric Company. Separations Technology Section Monthly Report for July, 1956, USAEC Report HW-44580 H, p. 25. August 8, 1956 (Classified).
- ²General Electric Company. Separations Technology Section Monthly Report for August, 1956, USAEC Report HW-45115 H, p. 45. September 11, 1956 (Classified).
- ³C. W. Kuhlman, Jr. Reduction of Uranium Trioxide to Uranium Dioxide with Anhydrous Ammonia, USAEC Report MCW-217. September 8, 1949.
- ⁴E. Petkus, N. Levitz, M. Jones, and M. Deerwester. "Green Salt Process," Chemical Engineering Division Summary Report for January, February, and March, 1956, USAEC Report ANL-5560, pp. 113-116. May 2, 1956.
- ⁵K. J. Notz and M. G. Mendel. "X-ray and Kinetic Study of the Hydrogen Reduction of $\gamma\text{-UO}_3$," J. Inorg. Nucl. Chem., 14:55. 1960.
- ⁶W. R. DeHollander. A Kinetic Study of the Reduction of Uranium Oxides with Hydrogen, USAEC Report HW-46685. November 8, 1956.
- ⁷K. J. Notz, C. W. Huntington, and W. Burkhardt. "Hydrogen Reduction of Uranium Oxides," Ind. Eng. Chem. Proc. Design and Devel., 1:213. 1962.
- ⁸G. G. Briggs. Chemical Equilibria and Reaction Rates for Hydrofluorination of UO_2 from "Ammonium Diuranate" and From UO_3 , USAEC Report NLCO-720. March 12, 1958.

⁹Uranium Hexafluoride Technology of Process Development. ORGDP Quarterly Report for First Fiscal Quarter, July 1, 1961, to September 30, 1961, USAEC Report KC-643, Pt. 1. January 30, 1962.

¹⁰W. Burkhardt, L. P. Trimberger, J. F. Geers, J. E. Flinn, D. J. Loudin, and D. C. Bonfer. "The Activation of Continuous-Pot UO_3 by Reduction-Oxidation-Reduction," Summary Tech. Rpt., USAEC Report NLCO-830, pp. 23-27. August 4, 1961 (Classified).

¹¹W. Burkhardt, J. F. Geers, L. P. Trimberger, D. J. Loudin, and J. E. Flinn. "Plant-Scale Tests of Reduction-Oxidation-Reduction Activation of Continuous-Pot UO_3 ," Summary Tech. Rpt., USAEC Report NLCO-850, pp. 17-24. April 16, 1962 (Classified).

¹²C. D. Harrington and A. E. Ruehle, eds. Uranium Production Technology, pp. 195-236. Princeton, New Jersey: Van Nostrand, 1959.

2. REDUCTION EVALUATION OF LARGE UF_4 - Mg BRIQUETTES

H. A. Kraus

S. O. Samoriga

Abstract

A test was made to find the minimum pressure required to press UF_4 -Mg briquettes, 11 $\frac{1}{2}$ -inches in diameter, having good physical strength. The test included green salt from two sources - dry-process UF_4 hydrofluorinated from UO_2 and wet-process (Winlo) UF_4 . Briquettes were made with three magnesium excesses: 3.6%, 2.1% and 0.6%. The test included the reduction of the briquettes to metal.

Introduction

Massive uranium metal is produced at the National Lead Company of Ohio by a thermite-type reaction in which green salt (UF_4) is reduced by granular magnesium in a closed steel vessel (furnace pot) lined with ground magnesium fluoride slag. The loose blend of green salt and magnesium is packed into the vessel, capped, and heated inside an electric resistance furnace until the reaction occurs. A uranium regulus (derby) forms at the bottom of the furnace pot. After cooling, the derby is separated from the by-product magnesium fluoride slag.

Briquetting of the loose blend of UF_4 and Mg offers several theoretical advantages. It provides a method to increase the mass of the charge per unit volume which, in turn, increases the total heat of reaction in the fixed volume of the reaction in the fixed volume of the reaction vessel. This greater heat of reaction should raise the temperature of the liquid reaction products and should increase the time available for the molten uranium to separate from the liquid magnesium fluoride slag. As a result, a higher yield of better quality metal should be produced. In addition, prior work indicated that this process is less sensitive to production and material variables.

To distinguish between the two types of green salt that were briquetted, the dry-process UF_4 produced from hydrofluorinated UO_2 will be called NLO UF_4 ; and the wet-process UF_4 will be called Winlo UF_4 . All of the Winlo UF_4 used in this test was in the dehydrated form.

Previous Work On Project

The present work is the continuation of several previous briquetting tests.^{1,2} The briquetting portion of the tests was carried out at the Oliver Corporation, Battle Creek, Mich. The 1961 test demonstrated that good quality UF_4 -Mg briquettes could be made in production quantities (approximately 1000 briquettes were produced) at a press pressure of 16 tons per sq in. Lower pressures were not tried during this test because of the number of variables already being evaluated and because the briquettes were at the maximum height that would permit charging four briquettes into a reduction pot. In the earliest test, the mold and punch used in the present test were developed; and the most suitable die lubricants were determined.

The large number of briquettes in the 1961 test were reduced to metal in a statistically designed reduction program. The briquetted charges showed significantly increased derby yields (an average increase of 2% as compared with the control reductions), improved derby quality (95% of the derbies were Grade I, or virtually slag-free), and less sensitivity to processing and feed material variables than the unbriquetted charges. Nearly 90% of the briquettes were made with both 3.6% excess magnesium and NLO UF_4 . A limited test was also made with 2% excess magnesium and with dehydrated Winlo UF_4 -Mg blends. Results were generally good.

Objectives for This Quarter

The principal objective of this test was to determine the minimum press pressure required to produce good quality UF_4 -Mg briquettes.

Secondary objectives were: (1) to reduce the UF_4 -Mg briquettes formed at the different pressures to metal and to compare the results with those of the 1961 production-scale test and with control charges composed of a loose blend of UF_4 and Mg; (2) to determine the effect of a lower magnesium excess on derby yield and quality; and (3) to test briquettes made from Winlo UF_4 more fully.

Summary of Results

Briquetting

Both the dehydrated Winlo and NLO UF_4 -Mg blends formed briquettes with good physical strength at 8 tons per sq in. or higher.

On the average, holding the briquettes under pressure in the press for 10 seconds increased the density of the briquettes by an amount equivalent to that obtained by increasing the pressure 2 tons per sq in. without such a dwell period. A two-fold increase of the briquetting pressure from 8 to 16 tons per sq in. increased the briquette density less than 5%. A briquetting pressure of 6 tons per sq in. was submarginal for Winlo UF_4 -Mg blends, and only marginal for NLO UF_4 -Mg blends. When, in addition to physical strength, the reduction characteristics of the briquettes were taken into consideration, the optimum briquetting pressure was indicated to be 10 tons per sq in. with a 10-second dwell time in the press at that pressure.

Reduction

Since the 83 test reductions were divided among two types of green salt, three magnesium excess levels, and five formation pressure levels, only one to four reductions were made of each type of briquette. Hence the reduction results can only be regarded as indicative of the results that might

be expected of a production operation. To give added significance to the reduction results, they are compared with the results of the 1961 production-scale test.

In general, the briquettes containing 3.6% excess magnesium gave better results with both types of green salt tested — NLO and Winlo. The NLO UF_4 derby yields average 99.6%. This yield compares favorably with those obtained in the 1961 production-scale test (99.3%). Exceptionally clean derbies (100% Grade I) were produced with both types of green salt at the 3.6% level of excess magnesium. In the 1961 test, 95% Grade I derbies were produced at this level of excess magnesium.

Equipment and Procedure

Blending and Packaging

The results of the UF_4 -Mg blending studies made during the 1961 test indicated that the materials segregate. It was therefore decided to weigh and blend each briquette charge in individual cans instead of blending in large batches. However, the Winlo green salt was blended in a rotary double-cone blender to insure homogeneity before it was packaged and blended with magnesium. Two blender loads of green salt were required for each lot. A total of 56 cans was packaged for each lot. Samples were taken from the first, middle, and last can of each blender load of green salt.

Nearly the same procedure was followed for both types of UF_4 used, except that the NLO UF_4 was taken from blended lots and was therefore not rebled. Each can of Winlo UF_4 -Mg weighed 107 pounds. The cans of NLO UF_4 -Mg weighed 120 pounds.

Briquetting

Description of Equipment

The same mold (Figure 2.1) was used as in the previous briquetting tests.^{1,2} The briquetting, as

1088-1

FIGURE 2 1 Briquetting Mold and UF_4 -Mg Briquette

before, took place at the Oliver Corporation, Battle Creek, Michigan. The mold was designed to operate in a single-action, moving-down-type hydraulic press. By having the 11½-inch-diameter forming cylinder float on the bottom punch as the top punch moved down, the effect of a double-action press was obtained. The forming press was a Farquhar 3,000-ton, vertical, four-column, hydraulic type, as shown in Figure 2.2.

Operating Procedure

The Winlo UF₄-Mg blends were briquetted first. The operating procedure was nearly the same as

the previous production-scale test except for the following changes: (1) varying the press pressure from 6 to 16 tons per sq in. in two-ton increments; (2) allowing the press to dwell for 10 seconds at maximum pressure, at the lower test pressures and (3) shipping the briquettes unprotected (in the earlier tests the briquettes were packed in vermiculite for shipment). The lack of protective packaging materials supplied one measure of the physical strength of the briquettes. The two other measures were (1) breakage during stripping from the mold and (2) breakage during handling in the subsequent reduction test.

FIGURE 2.2 Briquetting Press with Auxiliary Equipment

TABLE 2.1 Average Densities of UF₄-Mg Briquettes Formed at Varied Pressures

UF ₄	Magnesium Excess (%)	Pressure (tons per sq in.) and Dwell Time								
		6	8		10		12		14	16
		10 sec	0	10 sec	0	10 sec	0	10 sec	0	0
Normal	0.6	3.52	3.54	3.61	3.60	3.63	3.65	3.70	3.70	3.73
	2.1	3.56	3.56	3.59	3.61	3.66	3.64	3.69	3.70	3.73
	3.6	3.58	3.53	3.58	3.60	3.65	3.65	3.69	3.70	3.74
Winlo	0.6	3.18	—	3.36	3.33	3.40	—	3.47	3.45	3.51
	2.1	3.24	—	3.37	3.37	3.42	3.48	3.50	3.48	3.55
	3.6	3.27	3.29	3.38	3.37	3.46	3.44	3.50	3.49	3.54

Results

All of the briquettes made at 8 tons per sq in. were hard and exhibited no tendency to break. The 10-second dwell time increased their density to the equivalent of those made at 10 tons per sq in. without a dwell. A summary of the briquette densities for the two types of green salt at the various pressures and magnesium excess are shown in Table 2.1. Typical briquettes are shown in Figures 2.3 and 2.4.

A total of 336 briquettes (168 briquettes of each type of green salt) were produced during this test. Six Winlo UF₄-Mg briquettes and two NLO UF₄-Mg briquettes were broken when stripped from the mold. All of the broken briquettes were made at 14 and 16 tons per sq in. except one that was made at 10 tons per sq in. with a 10-second dwell time. No briquettes were broken in shipment to Fernald. A probable reason for the somewhat greater breakage of the Winlo UF₄-Mg blends is that these blends segregated while being hauled

1220-6

FIGURE 2.3 Winlo UF₄-Mg (3.6% Excess) Briquettes Pressed at 8 Tons Per Sq In. With and Without Dwell

1220-5

FIGURE 2.4 NLO UF₄-Mg (3.6% Excess) Briquettes Pressed at 8 and 10 Tons Per Sq In. With Dwell

to Battle Creek. Magnesium-rich areas were visible in these briquettes. Winlo UF₄ is known to be free-flowing and more uniform in particle size than NLO UF₄. This could account for its tendency to segregate from the magnesium.

Surprisingly, after completion of the Winlo UF₄-Mg briquetting campaign, the mold wall was comparatively clean with only small areas of adhering magnesium. During the NLO UF₄-Mg briquetting, an adhering layer of magnesium gradually spread over the entire surface of the mold area, that was subjected to the briquetting pressure.

Reduction

Description of Equipment and Procedure

The special equipment that was fabricated for the 1961 production-scale test was used to load the briquettes into the reduction pot and to hold them in position while the liner was jolt-formed around them.

The reduction procedure began with the assembling of the briquettes that were made at like formation pressures and press dwell times in groups of four. A standard, 15-inch, tapered steel reduction pot was prepared for charging by first jolt-packing a 1½-inch bottom liner of magnesium fluoride. Next, four centering spacers were placed in the reduction pot. The four briquettes were lowered into the pot by using specially designed tongs, and a hold-down clamp was installed to keep the briquettes in place. Magnesium fluoride was introduced into the annular cavity formed by the spacers between the reduction pot and briquettes.

After approximately 1½ minutes of jolt-packing, the four centering spacers were removed. The holes left by the removal of the spacers were filled with magnesium fluoride, and jolting was resumed for 15 minutes. Then the hold-down clamp was removed, the charge was capped with magnesium fluoride, and the lid was bolted to the reduction pot.

The charged reduction pots were heated in one of three Rockwell electric resistance furnaces. For the Winlo UF_4 -Mg briquette reductions, 15 kva was applied to all three furnace elements. For the NLO UF_4 -Mg briquette reductions, 15 kva was applied to the top and center elements only. This procedure followed present production practice. The initial furnace control temperature was 1300°F for the NLO UF_4 reductions and 1200°F for the Winlo UF_4 reductions. Sixteen control reductions were made with loose blends of each type of green salt with 3.6% excess magnesium. The two furnace control temperatures selected simulated present production practices. As the derbies were broken out they were cleaned, weighed and identified. The derbies were graded visually as I, II, or III, depending upon the amount of slag adhering, to their top surfaces. Grade I derbies are practically slag-free; Grade II derbies have a thin layer of slag covering not over half of the top surface; derbies with larger amounts of slag are classified as Grade III.

Results

The reduction evaluation of the UF_4 -Mg briquettes was secondary to the main purpose of this test which was to investigate lower briquetting pressures. However, in addition to having good physical strength, the briquettes must ultimately prove satisfactory in reduction. Since the number of briquettes made at each pressure and magnesium excess was very limited, the reduction results cannot be considered conclusive but, rather, only indicative of the results that might be expected in a production operation. The results of this test, however, have been given added weight by comparison with the statistically designed test of 1961.² A summary of the results for both the briquette and control reductions is in Table 2.2.

NLO UF_4 -Mg Briquettes — The briquettes having 3.6% excess Mg gave better yields (99.6%, average) than those having 2.1% excess Mg (99.1% average yield) or those having 0.6% excess Mg (97.0%

average yield). Yields from briquettes having 3.6% excess Mg were better at 8 to 12 tons per sq in. than at 14 to 16 tons per sq in. The optimum briquetting pressure appears to be approximately 10 tons per sq in. with a 10-second dwell time. Results at 16 tons per sq in. were near those of the previous production test.

Derbies made from briquettes having 3.6% excess Mg were uniformly and exceptionally clean and free of adhering MgF_2 slag. (See Figure 2.5.) All were Grade I. Slaggy derbies were encountered only at the lower magnesium excess levels, when only the top two of the three furnace heating elements were used. Using the bottom heater element of the reduction furnaces on all seven of the reductions at 0.6% excess Mg eliminated the slag, but produced derbies of enlarged diameter. On the previous test, 95% of the derbies made from briquettes having 3.6% excess Mg were Grade I. Firing times were slightly longer than in the 1961 production test (325 min vs 290 min), except that when the bottom heater element was used, the firing time dropped to 260 min.

No differences were noted among furnaces, either in the control or in the briquette reductions. The average yield on control (loose-blend) reductions averaged 95.6% versus 97.3% for the previous test. Ninety-two percent of the control derbies were Grade I, as compared with 77% on the previous test. Average firing time of control reductions was 235 minutes versus 260 minutes in the previous test.

The higher yields from the control charges in this test can be attributed to the fact that all green salt used was of good quality; whereas, in the 1961 test, the green salt quality ranged from poor to good.

Winlo UF_4 -Mg Briquettes — As with the NLO UF_4 -Mg briquettes, those with 3.6% excess Mg gave much better results than the briquettes with the lower Mg excesses. Derby yields were good, 98.6% at 3.6% excess Mg and 8 to 12 tons per sq

TABLE 2.2 Summary of UF₄-Mg Briquette and Control Reduction Data

Magnesium Excess (%)	Briquette Pressure (tsi)	NLO UF ₄ -Mg Briquettes				Winlo UF ₄ -Mg Briquettes			
		Number Reductions	Average Yield (%)	Average Derby Grade	Average Firing Time (min)	Number Reductions	Average Yield (%)	Average Derby Grade	Average Firing Time (min)
3.6	16	56*	99.3	1.05	290	—	—	—	—
	16	2	99.4	1.0	345	2	98.3	1.0	315
	14	2	99.7	1.0	310	2	97.5	1.0	330
	12	3	99.8	1.0	320	2	98.6	1.0	320
	10	3	99.9	1.0	345	2	98.6	1.0	370
	8	3	99.7	1.0	325	3	98.6	1.0	370
	6	1	99.2	1.0	300	—	—	—	—
	Average		99.6	1.0	325	—	98.3	1.0	345
2.1	Control	14	95.6	1.1	235	16	96.3	1.1	295
	16	4*	99.4	1.25	285	—	—	—	—
	16	2	98.9	1.5	310	1	97.5	1.0	325
	14	2	99.9	2.0	290	2	97.5	1.3	435
	12	3	99.3	1.7	350	3	98.1	1.3	365
	10	2	99.0	1.0	310	3	96.8	1.7	375
	8	2	98.8	1.0	330	3	97.1	1.3	420
	6	1	98.8	1.0	320	—	—	—	—
0.6	Average		99.1	1.4	320	—	97.4	1.4	390
	16	1	97.1	1.0	275	1	98.7	1.0	360
	14	2	97.0	1.0	255	2	100††	2.2	480
	12	1	97.9	1.0	245	2	99.5	1.5	445
	10	1	93.9	1.0	245	3	98.7	1.7	405
	8	1	98.2	1.0	275	4	99.3	2.5	430
	6	1	98.1	1.0	265	—	—	—	—
	Average		97.0	1.0	260	7**	100††	2.7	475
						5†	98.7	1.1	360

* 1961 test reductions

** Average of 7 derbies at a furnace control of 1200°F.

† Average of 5 derbies at a furnace control of 1250°F.

†† Yield over 100% because of adhering slag.

in. versus 96.3% for the control charges, but not nearly so good as the yields of the NLO UF₄-Mg briquettes. The cause of the difference is probably the uniform-sized, rounded particles of the Winlo UF₄, which blend poorly with the Mg particles and reduce the packing density. No effect of formation pressure on reduction results was noted over the range 8 to 16 tons per sq in. One reduction of briquettes at 6 tons per sq in. gave inferior results.

This was the first reduction test of Winlo UF₄-Mg briquettes in slag liner; therefore, no comparison can be made with earlier results.

Very clean derbies were produced at 3.6% excess Mg. Slag-free derbies were also obtained at 0.6% excess Mg when the furnace control temperature was increased from 1200°F to 1250°F. Of the 16 control (loose-blend) derbies, 15 were Grade I and one was Grade II.

Firing times were slightly longer than for the NLO UF₄-Mg briquettes (345 min versus 325 min at 3.6% excess Mg). Increasing the firing control temperature from 1200°F to 1250°F reduced the firing time for the 0.6% excess Mg briquettes from 475 minutes to 360 minutes and, also, reduced the

1243-7

LOT 3 10 SEC
NORMAL

FIGURE 2.5 Derbies Produced From NLO UF_4 -Mg Briquettes That Were Pressed at 10 Tons Per Sq In. With a 10 Second Dwell Time

enlarged derby diameter obtained at the longer firing time.

Several differences were noted among the furnaces used. Furnace No. 1 gave slightly lower average yield (95.3%) than furnaces 2 and 3 (97.2% and 96.9%, respectively) on the control reductions. Also, in the 2.1% excess Mg reductions, four out of five derbies from Furnace No. 1 were Grade II, averaging 97.0% yield; and 5 derbies from Furnace No. 3 were all Grade I, averaging 97.8% yield.

Conclusions

This test indicated that UF_4 -Mg briquettes having good physical strength and reduction characteristics can be pressed at approximately 10 tons per square inch with a dwell at that pressure of 10 seconds. Briquettes made under these conditions were reduced consistently to exceptionally clean, high-yield derbies.

This test and the 1961 production-scale test have established the optimum conditions for briquetting and reducing NLO UF_4 . Further development work on the reduction of Winlo UF_4 briquettes is needed to achieve optimum results. Higher firing temperatures and milled Winlo UF_4 should be investigated.

The adoption of UF_4 -Mg briquetting as a production practice would have several advantages in addition to the production of clean derbies at high yields: (1) Elimination of chemical processing of reduction residues would provide a marked reduction in costs; (2) elimination of magnesium fluoride slag from the recasting operation would improve ingot quality; (3) incidental benefits would be realized, such as closer determination of optical melt temperatures with a slag-free melt, and better accountability of materials resulting from the more uniform reduction results.

References

¹G. E. Wuller, Jr. Briquetted Uranium Tetrafluoride - Magnesium Blend for Batch Reduction Charges, USAEC Report NLCO-672. December 21, 1956.

²W. E. Shaw. Production Test and Evaluation of Large UF₄-Mg Briquettes, USAEC Report NLCO-841. October 11, 1961.

3. MAGNESIUM-LITHIUM ALLOY REDUCTANT FOR REDUCING GREEN SALT TO METAL

J. H. Trapp

Abstract

Magnesium alloyed with as much as 5.4 w/o lithium was used as the reductant for green salt in small-scale bomb reductions. Although there was no improvement in derby yield, preheat times were shorter. The effects on slag-metal separation were variable.

Introduction

Uranium is produced at this site by the reduction of green salt with magnesium in closed steel vessels lined with magnesium fluoride slag. The equipment and methods for performing the reduction on a small scale are similar to these used in the production plant and are described in detail in an earlier report.¹

When the reaction takes place, a uranium regulus or "derby" forms at the bottom of the reaction vessel. The degree to which this derby separates from the by-product MgF_2 slag is an important consideration in the reduction process for at least two reasons:

1. The yield of derby metal from the reduction increases with better slag-metal separation.
2. The yield of ingot metal from subsequent vacuum remelting is sharply dependent upon the amount of slag adhering to, and entrapped in, the derbies that are used as remelt feed.

One way to improve slag-metal separation is to produce a slag with a lower melting point. Adding lithium to the magnesium reductant will produce a slag of MgF_2 and LiF having a lower melting point than that of MgF_2 alone. For example, although the melting point of pure MgF_2 is $2305^\circ F$, a reductant containing 5 w/o lithium produces a slag with a liquidus of $2228^\circ F$ and a solidus of $2066^\circ F$.²

In previous work, the use of small amounts of lithium (1 w/o and 2 w/o of the magnesium reductant) was shown to be effective as a means of initiating the reaction.³ It was also shown that the reaction initiation temperature is related to the reductant melting point. Since no study had been made of the effects of using Mg-Li alloys or of using lithium in amounts greater than 2 w/o of the reductant, it was decided to evaluate Mg-Li alloys containing as much as 5 w/o lithium as reductants for green salt.

Objectives for This Quarter

The objective of this work was to determine the effect on crude derby yield, preheat times, and quality of slag-metal separation of using Mg-Li alloys containing as much as 5 w/o lithium as reductants in the bomb reduction of green salt to uranium.

Summary of Results

In small-scale bomb reductions, the use of Mg-Li alloy reductants containing 0.077 w/o, 0.85 w/o, 1.76 w/o or 4.6 w/o gave the following results:

1. Derby metal yields were not significantly different from those obtained with magnesium only as the reductant.
2. The best slag-metal separation was obtained when 0.077 w/o lithium alloy was the reductant.
3. Shorter preheat times were obtained than when magnesium alone was used as the reductant. When 0.85 w/o or more lithium was alloyed with magnesium and used as the reductant, the average firing time was 65.4 minutes. When 0.077 w/o lithium was alloyed with magnesium and used as the reductant, the average firing time was 86.2 minutes. When Nelco magnesium only was used as the reductant, the average firing time was 102.8 minutes.

Materials

The Mg-Li alloys were furnished by the Dow Chemical Company. A supply of unalloyed Dow 5 magnesium was also furnished for use as a secondary control reductant. (The primary control reductant was regular Nelco magnesium obtained from current production.) However, the Dow 5 magnesium was analyzed and was found to contain small pellets containing as much as 1.2 w/o lithium. The average lithium content was 0.077 w/o. The small particles of Mg-Li alloy contaminating the Dow 5 magnesium probably come originally from the other Mg-Li alloys and were picked up in the grinding and packaging operations.

A minimum of five reductions of each Mg-Li alloy and control was planned. However, since the Mg-Li alloy samples supplied by the Dow Chemical Company were not large enough for five reductions each, some of the samples were combined to achieve a range of Mg-Li alloys. Table 3.1 shows the analyses of the blends used and the number of reductions made from each.

A sieve analysis of the reductants is given in Table 3.2.

All reductions were made from one lot of green salt. Chemical and physical properties of this material were as follows:

UF₄ 97.60 w/o
 AOI 0.94 w/o
 UO₂F₂ 1.40 w/o

TABLE 3.2 Reductant Sieve Analysis

USBS Sieve No.	Reductant*			
	NELCO	0.077 w/o Li	0.85 w/o Li	1.76 w/o Li
+10	0.1	0.9	0.8	0.6
-10 +20	56.4	64.2	58.7	60.5
-20 +30	33.4	27.6	26.5	27.3
-30 +40	6.7	4.8	7.1	6.0
-40 +50	1.9	1.5	2.3	4.1
Pan	1.5	0.9	4.7	1.9

* No sieve analysis was made on the Mg-4.6 w/o lithium alloy.

H₂O 0.06 w/o
 Tap Density. . 3.91 g/cc
 Surface Area . 0.36 m²/g

Procedure

The liner for the reduction pot was ground MgF₂ slag jolt-packed into place. Forty pounds of green salt and the correct weight of reductant (adjusted to account for the lithium content so that a reductant excess of 4 w/o of the stoichiometric requirement was used) were blended for 10 minutes in a twin-shell blender. The blend was carefully charged by hand into the lined pot and capped with slag. The steel lid was bolted to the pot, and the charged pot was placed in a furnace held at 1250°F. The time interval from the placing of the pot in the furnace to the initiation of the reduction reaction is called the preheat time. Initiation of the re-

TABLE 3.1 Lithium Analysis of Reductants

Reductant	Lithium (w/o)	Blends	No. of Reductions
Nelco Primary Control	—	—	5
Dow 5 Secondary Control	0.077	Lithium as contaminant in particles containing 1.2 w/o Li	5
Dow -1 w/o Li	0.85	Blend of 5 w/o alloy with Dow 5 magnesium, as received	5
Dow -2 w/o Li	1.76	Blend of 2 w/o alloy with Dow 5 magnesium	3
Dow -5 w/o Li	4.6	50-50 Blend of 5.4 w/o alloy with 3.2 w/o alloy	5

duction reaction was detected by noting sonic and subsonic vibrations of the furnace. After cooling, the derbies were broken out, cleaned by chipping with a hammer, and weighed.

At a later date, the derbies were cleaned more thoroughly by blasting with a stream of MgF_2 slag and compressed air, and then reweighed.

Results

None of the alloys used as reductants was effective in increasing metal yields (see Table 3.3). An apparent exception is the Mg-4.6 w/o lithium alloy, for which the average derby yield before cleaning was significantly different from the average derby yield of the controls. However, after all derbies were blast cleaned, the average derby yield obtained with this alloy was the same as that of the control (see Table 3.4). Visual examination of the derbies before cleaning revealed a greater amount of slag on the derbies made with Mg-4.6 w/o Li, and blast cleaning results confirmed this observation.

One explanation of the higher slag content is that slags containing appreciable amounts of LiF wet the uranium surface better than slags of MgF_2

TABLE 3.4 Derby Yields Before and After Blast Cleaning

Reductant	Before Blasting Average Yield (w/o)	After Blasting Average Yield (w/o)
Nelco (Control)	97.2	95.6
Dow -0.077 w/o Li	96.6	96.0
Dow -0.85 w/o Li	96.1	95.6
Dow -1.76 w/o Li	97.2	95.1
Dow -4.6 w/o Li	99.2*	95.6

* Only this yield is significantly different from the control reduction yield (see Table 3.3).

alone. No interfacial tension data are available for mixtures of LiF and MgF_2 against uranium; however, liquid LiF is known to have excellent wetting ability for several different surfaces. Further confirmation of this supposition comes from the fact that all derbies made with Mg-4.6 w/o alloy were Grade III.

A second explanation for the high slag content is that the shorter firing time resulted in a lower peak reaction temperature and that this lower temperature offset the beneficial effect of the decrease in slag melting point. In support of this view are

TABLE 3.3 Summary of Reduction Results

Reductant	Average Crude Yield (w/o)	Average Preheat Time (min)	Average Derby Grade
NELCO			
Control Results	97.2	102.8	2.6
Dow 5 (0.077 w/o Li)			
Experimental Results	96.0	86.2	1.4
Magnitude of Effect with 95% Confidence	-1.2 ± 1.4	-16.6 ± 13.7	-1.2 ± 0.7
Dow 5 (0.85 w/o Li)			
Experimental Results	96.1	64.0	2.6
Magnitude of Effect with 95% Confidence	-1.1 ± 2.0	-38.8 ± 10.2	0 ± 1.3
Dow 5 (1.76 w/o Li)			
Experimental Results	97.2	67.0	2.7
Magnitude of Effect with 95% Confidence	0 ± 6.3	-35.8 ± 12.9	$+0.1 \pm 1.3$
Dow 5 (4.6 w/o Li)			
Experimental Results	99.2	65.2	3
Magnitude of Effect with 95% Confidence	2.0 ± 1.8	-37.6 ± 11.1	0.4 ± 0.9

NOTE: Significant effects are the bolder numbers

the following calculated adiabatic reaction temperatures:⁴

Slag Melting Point (°F)	Preheat Time (min)	Average Charge Temperature (°F)	Adiabatic Reaction Temperature (°F)
2066-2228 (5 w/o alloy)	65	711	2630
2305	102.8	893	2780

The average decrease in slag melting temperature is 158°F, and the decrease in adiabatic reaction temperature is 150°F. Thus the advantage of lower slag melting point is canceled by the lower adiabatic reaction temperature.

No explanation can be given for the good slag-metal separation obtained with the Dow Mg-0.077 w/o lithium reductant. The amount of lithium is too small to lower the slag melting point appreciably.

Preheat times for reductions made with Mg-Li alloys were all significantly shorter than those for the controls. However, the correlation of preheat time with lithium content is poor as may be seen by examining the data in Table 3.3. If the charge-liner interface temperature is calculated for the different preheat times, and alloy compositions are calculated from solidus temperature, the following results are obtained:

Reductant	Preheat Time (min)	Calculated Interface Temperature (°F)	Mg-Li Alloy* (w/o Li)
Dow Mg-1.76, 0.85, or 4.6 w/o Li	65	1068	5.7 (Eutectic at 1090°F)
Dow Mg-0.077 w/o Li	86.2	1198	0.18
Nelco Mg	102.8	1214	0 (Mg Melting Point, 1205°F)

* Which melts at interface temperature.

Examination of the Mg-Li equilibrium diagram (Figure 3.1) reveals a two-phase region extending from about 5.7 w/o lithium to about 10 w/o lithium. Since the alloys used in this study were prepared by blending a molten stream of lithium with a molten stream of magnesium, it is felt that a certain portion of this alloy could have fallen within this two-phase region. Subsequent shredding and sampling, moreover, would mask this effect so that it would appear from analyses that the alloys all fell within the solid solution region. Thus, as has previously been pointed out, since initiation of the

FIGURE 3.1 Magnesium-Lithium Equilibrium Diagram

reaction will occur upon melting of the reductant, the alloys having average lithium contents of 0.85 w/o, 1.76 w/o, and 4.6 w/o, would all cause initiation at the same temperature due to the heterogeneous nature of the alloy and, therefore, would all have the same firing time.

The heterogeneous nature of the Mg-Li alloys was confirmed by metallographic examination.

References

- ¹O. R. Magoteaux and C. C. Smitherman. Factors Affecting Yield and Metal Quality in the Reduction of UF₄ to Metal, USAEC Report NLCO-794, pp. 13-16. February 18, 1959.
- ²E. M. Levin, H. F. McMurdie and F. P. Hall. Phase Diagrams for Ceramists, p. 225. Columbus, Ohio: American Ceramic Society, 1956.

³J. H. Trapp. "Effect of Lithium Addition on Bomb Reduction," Summary Tech. Rpt. for the Period October 1, 1961 to December 31, 1961, USAEC Report NLCO-845, pp. 31-36. January 24, 1962 (Classified).

⁴K. O. Beatty, Jr. and O. R. Magoteaux. Thermal Conditions in the Bomb Reduction of UF₄ to Metal, USAEC Report NLCO-771, p. 14. November 28, 1958.

4. EVALUATION OF PICKLED DRIP CROPS AS REMELT FEED

H. M. Eikenberry

J. C. Straub

Abstract

Drip crops pickled in nitric acid were evaluated as feed for the remelt operation. They were shown to be deleterious to the quality of uranium fuel cores.

Objective for This Quarter

The objective for this quarter was to determine the effects of using drip crops pickled to either a 5% or a 10% loss of weight as remelt feed for the production of reactor-grade metal.

Introduction

In the current practice for producing fuel cores at the National Lead Company of Ohio, uranium feed material is melted in an uncoated graphite crucible in a vacuum furnace. The melt is poured at about 2550°F into refractory-coated, heated graphite molds. The uranium ingots are then fabricated into rods in a rolling mill, the rods are machined to cores, and the cores are cleaned by pickling and are inspected for surface defects. Rejection or acceptance of cores is based, in part, on their surface condition.

The quality of cores is dependent upon many factors. Previous investigations have shown that remelt feed material,^{1,2} crucible coating,^{3,4} furnace operating pressure,⁵ the remelt cycle,⁶ and mold heating,⁷ all can affect the core-to-good-core yield.

In the studies that were made of the effects of remelt feed² on ingot chemical purity and yields with heated molds, it was found that drip crops, untreated except for degreasing, were deleterious to core-to-good-core yield. However, no significant difference was detected between the yields of cores produced from ingots processed from the control charges and charges consisting of one Grade I derby and drip crops (pickled to a 5% weight loss). This suggested that additional work should be done to determine the effect of pickled drip crops on metal quality.

Summary of Results

A series of 36 charges was vacuum induction melted and cast into ingots in the Pilot Plant Annex. Three types of charges were used: (A) control; (B) drip crops pickled to a target weight loss of 5%; and (C) drip crops pickled to a target weight loss of 10%. All controllable variables were held constant except the type of feed material.

A statistical analysis was made of the resulting data and is summarized below:

1. The ingot casting yield obtained from charges containing drip crops was significantly lower than that obtained from the control charges.
2. The core-to-good-core yield obtained from ingots containing drip crops in the charge was lower than that obtained from the control charges.

Procedures

The compositions of the three types of feed material were as follows:

Charge A — Control charges; two Grade I derbies (best grade) and pickled rolling mill scrap.

Charge B — One Grade I derby and drip crops pickled to an average target weight loss of 5%.

Charge C — One Grade I derby and drip crops pickled to an average target weight loss of 10%. The pickling procedures were as follows:

1. Target of 5% weight loss
 - a. Bath composition — 6N HNO₃

- b. Temperature — 200°F
- c. Time in bath — $\frac{3}{4}$ to 1 hour
- 2. Target of 10% weight loss
 - a. Bath composition — 6N HNO₃
 - b. Temperature — 200°F
 - c. Time in bath — 2 to 2½ hours

Acid was added at the rate of 20 gallons per hour after the temperature reached 180°F to maintain the bath at 6N.

The procedure used to produce the ingots was as follows:

- 1. Uncoated crucibles were used.
- 2. The charge weight was 1270 pounds.
- 3. The furnace pressure was less than 3×10^{-2} Torr (mm Hg).
- 4. The remelt cycle was as follows:
 - a. 165 kw for 55 minutes
 - b. 100 kw for 55 minutes
 - c. 0 kw for 5 minutes and pour
- 5. An induction coil was used to heat the one-piece graphite molds wash-coated with MgZrO₃.
- 6. Samples were taken from all ingots for chemical analysis. The top and bottom samples consisted of $\frac{1}{8}$ -inch wafers for all chemical determinations except hydrogen. A press was used to punch sample buttons of metal from the wafers for chemical analyses. The samples for hydrogen were $\frac{1}{2}$ -inch by 2-inch by 1-inch pieces taken from the top of the ingots only, since it was shown in previous work⁵ that no significant difference exists between hydrogen values at tops and bottoms of ingots.
- 7. The ingots were then processed to fuel cores for Hanford. Ingot identity was maintained on all cores.
- 8. Three cores from seven ingots produced from each of the three charge types were selected for metallographic evaluation.

Results

The procedure for pickling the drip crops was designed to dissolve 5% and 10% of the material

by weight. In practice, the actual weight losses exceeded these target values. For example, four batches of drip crops scheduled for a 5% weight loss actually lost an average of 6.5%. Similar results were obtained when seven batches of drip crops were pickled to a target of 10% weight loss. Here, an average weight loss of 15% occurred. The variation in weight loss was attributed to the wide range of impurity levels found in the drip crops.

Thirty-six ingots were produced, 12 from each charge type. The average chemical analyses, casting yield before cropping, and core-to-good-core yield are shown in Table 4.1. The 95% confidence limits on the mean are included.

The average ingot yields obtained from the charges containing drip crops were significantly lower than those from the control charges. The ingot yields from drip crops pickled for a target of 5% weight loss and 10% weight loss were lower by $2.0 \pm 0.5\%$ and $0.8 \pm 0.5\%$ respectively.

The average core-to-good-core yield of cores processed from the drip crops pickled for a target weight loss of 5% was significantly lower ($29.9 \pm 16.8\%$) than the control yields. No significant difference was detected between the yield of cores processed from the drip crops pickled for a target weight loss of 10% and the control yields. Even though the difference was not significant, a $15.7 \pm 16.8\%$ lower yield was obtained with the drip crop charge. With a larger number of samples, this difference might well have proved significant.

Chemical analyses of the ingots produced from the three charge types indicated that the average impurity levels were all within the chemical specifications. Although some of the differences in impurities between the control and test ingots were statistically significant, the differences were small and were deemed not important.

A metallographic examination of fuel core samples from both the test and control charges reveal-

TABLE 4.1 Summary of Average Yields and Chemical Analyses with 95% Confidence Limits

	Charge Type A	Charge Type B	Charge Type C
Ingot Casting Yield (%)	98.0 $\pm$ 0.3	96.0 $\pm$ 0.3	97.2 $\pm$ 0.3
Core -to-good - core Yield (%)	99.8 $\pm$ 0.2 - 11.9	69.9 $\pm$ 11.9	84.1 $\pm$ 11.9
Density (g/cc)	18.9204 $\pm$ 0.0069	18.9108 $\pm$ 0.0069	18.9121 $\pm$ 0.0069
Chemical Impurities (ppm)			
Carbon	508 $\pm$ 22	599 $\pm$ 22	572 $\pm$ 22
Nitrogen	38 $\pm$ 5	32 $\pm$ 5	32 $\pm$ 5
Hydrogen	1.35 $\pm$ 0.33	1.52 $\pm$ 0.33	1.38 $\pm$ 0.33
Chromium	15.4 $\pm$ 0.7	17.0 $\pm$ 0.7	17.0 $\pm$ 0.7
Iron	92 $\pm$ 4	114 $\pm$ 4	123 $\pm$ 4
Magnesium	6.3 $\pm$ 0.5	6.7 $\pm$ 0.5	6.5 $\pm$ 0.5
Manganese	10.4 $\pm$ 0.3	11.1 $\pm$ 0.3	11.1 $\pm$ 0.3
Nickel	26.5 $\pm$ 0.9	34.9 $\pm$ 0.9	35.8 $\pm$ 0.9
Silicon	38 $\pm$ 0.6	46 $\pm$ 0.6	47 $\pm$ 0.6

ed no differences in grain size or in the size and quantity of inclusions.

It is concluded from the above results that drip crops should not be used as remelt feed in the production of reactor-grade uranium ingots.

References

¹H. M. Eikenberry, G. F. Jennings, D. DeTrou and J. Chick. "Studies of the Casting of Uranium Metal," Summary Tech. Rpt., USAEC report NLCO-690, p. 97. October 21, 1957.

²H. M. Eikenberry. "Effects of Feed Material on Ingot Chemical Purity and Yields," Summary Tech. Rpt., USAEC report NLCO-826, p. 51. May 5, 1961.

³O. R. Magoteaux, H. M. Eikenberry and D. L. Elston. "Evaluation of Refractory Coatings for Graphite Crucibles and Molds Used in the Vacuum Melting of Uranium," Summary Tech. Rpt., USAEC report NLCO-760, p. 85. October 24, 1958.

⁴H. M. Eikenberry, J. W. Mahaffey and R. B. Steck. "New Development in the Vacuum Melting and Casting of Uranium in Tonnage Quantities," Vacuum Metallurgy Conference, Transactions, 4th, edited by R. F. Bunshah, pp. 101-117. New York: Interscience, 1960.

⁵H. M. Eikenberry, R. B. Steck and D. DeTrou. "The Effect of Furnace Pressure on Uranium Ingot Chemistry and Metal Quality," Summary Tech. Rpt., USAEC report NLCO-810, p. 81. August 11, 1960 (Classified).

⁶H. M. Eikenberry. "Metal Casting Process (Uranium). 1. Improvement in Ingot Metal Quality," Summary Tech. Rpt., USAEC report NLCO-600, p. 91. January 16, 1956 (Classified).

⁷E. B. Blasch, G. F. Jennings and G. E. Wuller, Jr. Ingot Mold Heating as a Method of Controlling Metal Quality, USAEC report NLCO-697. September 16, 1957.

5. AN ELECTRON BOMBARDMENT FURNACE FOR THE BENDIX TIME-OF-FLIGHT MASS SPECTROMETER

P. R. Morris

R. W. Bonham

Abstract

An electron bombardment furnace was constructed for use with the Bendix time-of-flight mass spectrometer. A 0.75-inch OD by 0.5-inch deep graphite crucible was maintained at a temperature of 1800°C and a pressure of 5×10^{-6} Torr (mm Hg) with this unit. This temperature was achieved with 575 watts of bombardment power and 190 watts of filament power. The furnace design permits removal and replacement of crucibles through a vacuum lock.

Introduction

There are a number of problems in the uranium remelt process that have made it necessary for the National Lead Company of Ohio to give some attention to gas-metal reactions. To implement the study of such reactions, it was necessary to obtain instrumentation that would provide rapid analysis of the environmental atmosphere encountered in the melting of uranium metal. It was decided that the Bendix time-of-flight mass spectrometer could be used to monitor the products of an effusion cell and thus provide the necessary data to determine the nature of the reaction of interest. The general design of the mass spectrometer¹ and the specific unit at the National Lead Company of Ohio² have been described previously.

Previous Work on Project

Some work in this area was performed under an off-site contract with Battelle Memorial Institute four years ago.³ These experiments met with only limited success, because of qualifications imposed by the experimental procedure. Sufficient moisture was retained by the furnace assembly to react with the crucible and mask out the uranium reaction

products. Further, the quantity of data that could be obtained for each experiment was greatly restricted in that an equilibrium had to be assumed to exist, a sample collected, and this sample taken to another building for analysis.

Under a second off-site contract at Bendix Corporation, Detroit, Michigan, examination of the problem continued. A Knudsen cell furnace was constructed, and feasibility studies centering around the applicability of the Bendix instrument were carried out. The Bendix instrument performed satisfactorily in this study.⁴

The original furnace design employed a spiral filament wound on a ceramic form. Reaction with the ceramic form at elevated temperatures caused premature filament failure, necessitating frequent replacement. In addition, insufficient clearance between the high voltage lead and the furnace shell produced arcing at moderate voltages.

Description of Equipment

Furnace

A pictorial representation of the electron bombardment furnace is shown in Figure 5.1. The furnace was designed to mount directly beneath the spectrometer ion source in a $3\frac{7}{16}$ -inch-diameter chamber. The self-supporting filament consists of a single turn of 0.040-inch tungsten wire bent to form a $1\frac{1}{8}$ -inch-diameter circle. Filament power and high voltage are supplied by means of two special feed-throughs, secured from the Alite Division of U. S. Stoneware Company. These feed-throughs employ an OFHC copper conductor capable of carrying 40 amperes at 3 kv. The feed-throughs are threaded into the furnace base and are sealed with Parker Viton-A Lock-O-Seals.

FIGURE 5.1 Electron Bombardment Furnace

Attempts to silver-solder the feed-throughs to the furnace base failed to produce vacuum-tight seals because of inadequate clearance. In operation, the feed-throughs are cooled externally with forced air. The selection and installation of suitable feed-throughs proved to be the most difficult design problem encountered.

The graphite crucible is supported by a 0.040-inch tungsten rod mounted on a feed-through which, in turn, is affixed to the end of a movable piston. The crucible is coaxial with, and encircled by, the filament. The piston passes through a 2-inch, high-vacuum gate valve, permitting crucible removal and replacement without loss of vacuum. An O-ring vacuum seal permits piston travel. Evacuation of the chamber below the gate valve prior to re-entry is achieved through the illustrated pump-out line by means of a mechanical pump. When the chamber pressure is 5×10^{-3} Torr (mm Hg), the gate valve is opened to allow the instrument diffusion pump to complete the evacuation.

Spectrometer pressure rises to 10^{-4} Torr when the valve is opened, but returns to less than 10^{-6} Torr within a few minutes.

Tantalum radiation shields are employed to reduce heat loss from the crucible. The upper radiation shield is positioned and supported by fused quartz rings. The shield, electrically insulated from the furnace shell, assumes a potential close to that of the filament, due to space charge effects, reducing electron bombardment of the shield. The upper of the two disk-type shields is electrically insulated from the crucible.

The furnace is water-cooled by means of a coil of $\frac{1}{8}$ -inch copper tubing silver-soldered to the furnace shell. The tubing enters the vacuum chamber through Swagelok threaded thermocouple fittings. Viton-A O-rings are used to seal the thermocouple fittings to the base.

Power Supply

Filament power is supplied by four transformers (P5002 Stancor 10v, 10 amp). One-half of each secondary is used to provide a 5-volt, 40-amp maximum output. Manual regulation of filament power is accomplished by a variable autotransformer. An ammeter (0 to 5 amp) in the primary circuit serves to indicate filament current.

Bombardment power is supplied by a UTC CG-308 transformer. This transformer, used in conjunction with two, Type 866-A, mercury vapor rectifiers, is capable of delivering 3000 vdc at 500 ma. Attempts to use solid state replacements for these rectifiers were unsuccessful because of damage sustained by the solid state devices during transient arcing. A 0.006-henry, 40-amp choke (Triad C-80V) in the primary circuit limits transient short-circuit current in the secondary to 1.6 amp. A 15 amp circuit breaker of the instantaneous, magnetic, trip-free type is located in the primary circuit to protect against sustained overloading. Manual regulation of bombardment voltage is accomplished by a variable autotransformer.

Bombardment voltage and current are indicated by 0 to 4000 vdc and 0 to 500 ma dc meters.

The furnace design permits the application of negative high voltage to the filament with the crucible grounded or, if desired, grounding one side (or the center) of the filament and applying positive high voltage to the crucible. At present, the filament is operated at negative high voltage with the crucible grounded, in accord with the recommendation of Panish and Reif.⁵

Results

Crucible temperature as a function of bombardment power is shown in Figure 5.2. Temperatures were measured with a Leeds and Northrup optical pyrometer. Temperatures have been corrected for the effect of absorption caused by the viewing port.

At lower temperatures (below 1200°C) radiant heating by the filament produces a temperature gradient in the crucible, as evidenced by crucible

lid temperatures as much as 100°C above the temperature of the crucible floor at 1000°C. The importance of this effect is reduced at 1350°C, where only a 4°C differential was noted. Above 1650°C, lid temperatures 30°C below those of the crucible floor were observed.

Recommendations

Stability of the present power supply could be improved by automatically controlling filament emission. The addition of a diffusion pump to the pump-out line would speed piston chamber evacuation and eliminate the pressure surge that now accompanies the opening of the gate valve. A diffusion pump so located could also be used to assist in the evacuation of the furnace chamber, thus providing lower operating pressures and reducing the background that results from outgassing of the graphite crucible.

Acknowledgments

The writers are indebted to Jerome May, who fabricated the furnace and suggested modifications in design.

References

- ¹D. B. Harrington. "Time-of-Flight Spectrometry," *Encyclopedia of Spectroscopy*, edited by Dr. G. L. Clark, pp. 628-647. New York: Reinhold, 1960.
- ²A. D. Cavett and R. W. Bonham. "Installation and Calibration of the Time-of-Flight Mass Spectrometer for Use in Remelt Reaction Studies," *Summary Technical Report for the Period April 1, 1960 to June 30, 1960*, USAEC Report NLCO-810, p. 95. August 11, 1960 (Classified).
- ³R. W. Endebrock, E. L. Foster, Jr., and R. F. Dickerson. *Examination of Factors Affecting the Quality of Vacuum Induction-Melted Uranium*, USAEC Report BMI-1275. July 3, 1958 (Classified).
- ⁴G. J. O'Halloran. *Knudsen Cell Sample System and Uranium Analysis Feasibility Study*, Research Laboratories Division Report 1439. Detroit: The Bendix Corporation, March 31, 1960.
- ⁵M. B. Panish and L. Reif. "High Temperature Knudsen Effusion Sampling System," *Rev. Sci. Instr.*, **32**: 831. 1961.

FIGURE 5.2 Correlation of Total Furnace Power Versus Crucible Temperature

6. TEXTURE GRADIENTS IN URANIUM FUEL CORES

N. Crank, Jr. C. A. Powell

Abstract

Two fuel cores were examined by X-ray diffraction techniques in the radial, tangential, and longitudinal directions as functions of radial position. G_3 , G_2 , and J data are tabulated. G_3 values are plotted as a function of radial position in the radial, longitudinal, and tangential directions for both beta heat-treated and alpha-rolled cores.

Introduction

In an effort to predict more accurately the behavior of uranium fuel cores during thermal neutron irradiation, techniques for texture gradient evaluation^{1,2,3} in the radial, tangential, and longitudinal directions have been developed. Fuel cores from the various processes at this site and 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 Past and present examination of uranium fuel cores in three mutually perpendicular directions continues to demonstrate the shortcomings of the midwall technique.^{1,2,3,4,5,6}

Objectives for This Quarter

1. To devise sampling plans for three mutually perpendicular directions in HAPO fuel core blanks.
2. To collect X-ray preferred orientation data on two cores having the same dimensions; one in the alpha-rolled condition, the other beta heat-treated and quenched in oil.
3. To improve sampling techniques.

Summary of Results

Sampling plans were devised to permit examination of surfaces normal to the three mutually per-

pendicular directions of interest in HAPO fuel cores. Specimens were machined from the sample cores, the preferred orientation data were collected, and growth indices were calculated.

The alpha-rolled core, when examined in the radial direction, displayed a positive growth tendency at midwall with decreasing growth values at both ID and OD. In the tangential direction, a steady positive growth level was shown throughout the wall. In the longitudinal direction, a tendency toward negative growth was revealed at the inner and outer surfaces, rising to positive growth at about one-fourth of the distance from inner to outer surfaces and decreasing to a greater negative growth at about three-fourths of this distance.

The beta heat-treated core, when examined in the radial direction, displayed large negative predicted growth values on the ID and OD rising to large positive growth at midwall. In the tangential direction, the data reveal a somewhat inverse growth tendency to that displayed in the radial direction. These data do not verify the calculated growth values in the tangential direction of previously examined, beta heat-treated fuel cores. In the longitudinal direction, a slightly positive growth tendency was revealed at the ID, increasing to larger positive growth at the OD.

Experimental Equipment

Preferred orientation data were obtained with a General Electric XRD-V diffractometer. A 1-degree 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.

Experimental Procedures

Both cores were machined from a uranium rod which had been rolled at 600°C. One core was examined in the as-rolled condition. The second core was heat-treated in molten NuSal (50 w/o NaCl, 50 w/o KCl) for 12 minutes at 1370°F, delayed in air for 10 seconds, and quenched in Houghto K oil at 132°F to 157°F.

Data collected on longitudinal and tangential specimens were obtained as previously reported^{1,2} with the exception of the use of a corrected beam confining slit.²

Revisions of sampling techniques have been made in cutting specimens for radial direction studies. To obtain specimens for the radial direction, 1 $\frac{3}{4}$ -inch-long cylinders were taken from the core. The cylinders were then mounted in an angular dividing head attachment of a milling machine with the long axis of the cylinders in a vertical plane. Dual milling cutters with spacers were employed to make simultaneous cuts, equally distributed about a radius, through the longitudinal axis of the cylinder to the desired depth (Figure 6.1). One complete pass through the cylinder resulted in the cutting of two radial specimens (Figure 6.2). After each pass, the angular dividing

head was rotated the desired number of degrees to make succeeding cuts. The radial cuts were filled with epoxy resin to support the specimens while being held in a lathe spindle and chuck assembly. The excess stock used to hold specimens for milling was removed to within $\frac{1}{64}$ inch of the bottom of the radial cuts in the lathe. The remaining $\frac{1}{64}$ -inch of excess stock at the bottom of the radial cuts was then removed by hand grinding on rotating grinding wheels with 60 grit silicon carbide paper. The radial specimens were then mounted, and data were collected as previously reported.^{1,2}

Each increment was scanned a sufficient number of times to bring the 95% confidence limits on the means of the G_2 and G_3 values to within approximately ± 0.03 . The growth indices were calculated by using a digital computer.

1182-11

FIGURE 6.2 Radial Specimens as They Appear After Removal From Milling Machine

1182-10

FIGURE 6.1 Cutting Radial Sample Along the Longitudinal Axis With Dual Milling Cutters

Table 6.1 and 6.2 list the G_2 , G_3 , and J values. Plots of G_3 in the radial, tangential, and longitudinal directions as functions of radial position are presented in Figures 6.3 and 6.4.

TABLE 6.1 Values of G_3 , G_2 , and J with 95% Confidence Limits; HAPO Fuel Core Blank, Alpha-Rolled and Machined to Finished Size

Radius	G_3	G_2	J	Radius	G_3	G_2	J
Radial				Radial			
.241	.047 ± .015	.051 ± .014	1.246 ± .032	.618	.066 ± .009	.079 ± .016	1.089 ± .009
.246	.079 ± .019	.092 ± .016	1.102 ± .015	.648	.062 ± .018	.073 ± .016	1.104 ± .037
.251	.061 ± .010	.075 ± .012	1.105 ± .007	.683	.040 ± .014	.063 ± .010	1.054 ± .008
.256	.080 ± .027	.101 ± .025	1.122 ± .025	.702	.045 ± .022	.065 ± .020	1.063 ± .022
.261	.082 ± .016	.092 ± .013	1.117 ± .017	.712	.026 ± .024	.041 ± .023	1.048 ± .004
.266	.072 ± .021	.083 ± .010	1.132 ± .055	.718	.018 ± .019	.030 ± .022	1.053 ± .016
.271	.057 ± .017	.077 ± .021	1.108 ± .050	.726	-.003 ± .028	.020 ± .018	1.061 ± .016
.291	.065 ± .016	.075 ± .013	1.090 ± .037	Longitudinal			
.311	.078 ± .030	.088 ± .020	1.109 ± .052	.270	-.066 ± .028	-.075 ± .023	2.183 ± .227
.332	.089 ± .012	.107 ± .010	1.108 ± .023	.363	.043 ± .012	.061 ± .015	1.172 ± .028
.352	.101 ± .030	.105 ± .024	1.106 ± .038	.466	-.002 ± .029	.009 ± .021	1.484 ± .063
.372	.074 ± .016	.089 ± .024	1.088 ± .003	.542	-.061 ± .019	-.054 ± .034	1.821 ± .253
.402	.092 ± .021	.106 ± .030	1.104 ± .048	.610	-.116 ± .019	-.097 ± .029	1.991 ± .145
.424	.092 ± .012	.106 ± .004	1.096 ± .010	.686	-.070 ± .018	-.047 ± .015	1.945 ± .015
.445	.080 ± .019	.094 ± .014	1.100 ± .014	Tangential			
.464	.094 ± .018	.107 ± .013	1.112 ± .019	.283	.053 ± .026	.051 ± .024	1.206 ± .080
.484	.068 ± .019	.084 ± .020	1.091 ± .006	.377	.062 ± .030	.092 ± .029	1.173 ± .012
.510	.089 ± .009	.106 ± .009	1.115 ± .012	.463	.120 ± .027	.123 ± .024	1.623 ± .012
.530	.087 ± .014	.098 ± .006	1.105 ± .003	.522	.056 ± .018	.091 ± .017	1.174 ± .042
.559	.104 ± .022	.093 ± .024	1.228 ± .035	.641	.088 ± .021	.080 ± .020	1.576 ± .049
.588	.093 ± .016	.098 ± .020	1.130 ± .042	.700	.078 ± .028	.063 ± .024	1.584 ± .087

TABLE 6.2 Values of G_3 , G_2 , and J with 95% Confidence Limits; HAPO Fuel Core Blank, Beta Heat-Treated at Finished Size

Radius	G_3	G_2	J	Radius	G_3	G_2	J
Radial				Radial			
.241	-.156 ± .017	-.146 ± .014	1.183 ± .044	.614	-.017 ± .023	.001 ± .029	1.032 ± .012
.246	-.079 ± .012	-.077 ± .012	1.043 ± .005	.636	-.059 ± .019	-.047 ± .030	1.029 ± .009
.251	-.052 ± .007	-.040 ± .007	1.030 ± .009	.666	-.036 ± .009	-.023 ± .004	1.036 ± .009
.255	-.048 ± .024	-.031 ± .025	1.026 ± .000	.676	-.066 ± .012	-.042 ± .006	1.033 ± .005
.260	-.027 ± .021	-.008 ± .021	1.007 ± .000	.690	-.055 ± .013	-.036 ± .014	1.039 ± .013
.265	-.002 ± .008	.008 ± .011	1.020 ± .023	.707	-.073 ± .024	-.059 ± .028	1.040 ± .012
.270	.007 ± .012	.026 ± .009	1.022 ± .002	.714	-.093 ± .016	-.074 ± .018	1.077 ± .005
.290	.019 ± .009	.028 ± .009	1.029 ± .009	.721	-.126 ± .004	-.112 ± .012	1.109 ± .019
.318	.026 ± .013	.044 ± .010	1.020 ± .007	Longitudinal			
.338	.057 ± .016	.051 ± .014	1.031 ± .004	.270	.013 ± .029	.008 ± .020	1.045 ± .030
.359	.052 ± .023	.060 ± .020	1.022 ± .006	.363	.021 ± .010	.042 ± .021	1.026 ± .011
.379	.086 ± .016	.096 ± .007	1.042 ± .003	.459	.014 ± .021	.024 ± .020	1.022 ± .006
.399	.060 ± .018	.079 ± .016	1.039 ± .006	.542	.003 ± .020	.013 ± .025	1.045 ± .030
.418	.091 ± .010	.098 ± .007	1.042 ± .006	.603	.039 ± .011	.059 ± .020	1.031 ± .010
.439	.086 ± .027	.099 ± .026	1.046 ± .021	.686	.046 ± .011	.079 ± .025	1.048 ± .005
.461	.096 ± .019	.102 ± .018	1.046 ± .012	Tangential			
.481	.025 ± .013	.039 ± .006	1.020 ± .009	.268	.001 ± .015	-.002 ± .011	1.026 ± .014
.503	.049 ± .014	.055 ± .005	1.016 ± .004	.362	-.008 ± .012	.021 ± .020	1.022 ± .003
.522	.024 ± .013	.035 ± .005	1.014 ± .003	.447	-.044 ± .014	.044 ± .010	1.034 ± .010
.541	.017 ± .014	.044 ± .012	1.019 ± .005	.541	.030 ± .013	.023 ± .017	1.018 ± .005
.562	-.026 ± .027	-.014 ± .026	1.025 ± .005	.627	.038 ± .026	.057 ± .019	1.034 ± .007
.581	-.028 ± .023	-.019 ± .028	1.030 ± .016	.685	.056 ± .025	.058 ± .020	1.070 ± .032

FIGURE 6.3 Mean Values of G_3 (With 95% Confidence Limits) as a Function of Radial Position in the Three Directions Investigated; HAPO Fuel Core Blank, Alpha-Rolled and Machined to Finished Size.

Future Work

Studies of texture gradients in uranium cores after various stages of processing at this site 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).
- ³B. G. LeFevre and E. F. Sturcken. Sampling Techniques for Measuring Texture Gradients in Thick-Walled Uranium Fuel Elements, paper Presented at the X-Ray

FIGURE 6.4 Mean Values of G_3 (With 95% Confidence Limits) as a Function of Radial Position in the Three Directions Investigated; HAPO Fuel Core Blank, Beta Heat-Treated at Finished Size.

Preferred Orientation Meeting Held at Savannah River Laboratory, June 7 and 8, 1962.

⁴R. B. Russell and L. R. Aronin. "Balanced Texture in Uranium," Fundamental and Applied Research and Development in Metallurgy, Progress Report for February, 1959, USAEC Report NMI-2075, pp. 17-25. March 30, 1959.

⁵R. B. Russell and L. R. Aronin. "Balanced Texture in Uranium," Fundamental and Applied Research and Development in Metallurgy, Progress Report for March, 1959, USAEC Report NMI-2076, pp. 15-25, May 13, 1959.

⁶J. W. Starbuck and H. C. Kloepper, Jr. "Preferred Orientation Studies of End-Quenched Jominy Bars," Process Development Quarterly Report, Part 1 - Laboratory Work, USAEC Report MCW-1430, pp. 89-104. July 1, 1959.

7. YIELD CRITERIA FOR ALPHA-URANIUM SINGLE CRYSTALS

P. R. Morris

Abstract

Stereographic projections have been prepared of the fraction of an arbitrarily directed tensile stress resolved as shear stress on the various modes of the $\{130\}$ - $\langle 310 \rangle$, $\{\sim 172\}$ - $\langle 312 \rangle$, and $\{\sim 176\}$ - $\langle 512 \rangle$ twinning systems. These projections, together with similar projections previously prepared for an arbitrarily directed compressive stress and estimates of critical resolved shear stresses previously drawn from the work of Lloyd and Chiswick, have been used to prepare yield criteria for alpha-uranium single crystals for arbitrarily directed tensile and compressive stresses. The results are presented in the form of stereographic projections.

Introduction

Uranium fuel elements undergo dimensional changes during neutron irradiation. These dimensional changes, if excessive, can seriously impair reactor operation. For this reason, considerable effort is being devoted to the development of theories for the prediction of dimensional changes. These theories seek to combine the directional dependence of certain physical processes in an alpha-uranium single crystal according to the frequency of crystals in each orientation.

Objective

The objective of this work is the development of a satisfactory theory for the prediction of dimensional changes which uranium fuel elements undergo during irradiation.

Discussion

Yield Criteria

In a previously proposed¹ form of solution for the prediction of dimensional changes of uranium

fuel cores during irradiation, the following were assumed:

1. Anisotropic irradiation growth experienced by individual crystallites is unaffected by stresses of the magnitude which can be occasioned by mechanical constraints.

2. In general, the strains produced in neighboring crystallites by anisotropic irradiation growth will be incompatible due to differences in spatial orientation. The preservation of a continuous medium requires compatibility of strain between neighboring crystallites. This compatibility is achieved initially by an elastic adjustment resulting in the creation of stresses which vary from point to point within an individual crystallite. As irradiation proceeds, these stresses increase.

3. Stress relief is provided by the mechanisms of creep and plastic flow. As in all crystalline materials, the applied stress necessary to cause plastic deformation in an alpha-uranium single crystal displays a pronounced dependence on the crystallographic direction in which the stress is applied. The dependence of strain rate on stress and temperature (creep) is also expected to be a function of crystallographic direction.

A mathematical description of the proposed solution incorporating plastic flow requires the definition of yield criteria for the various deformation mechanisms which are expected to be active in the temperature range of interest. Deformation mechanisms reported by Lloyd and Chiswick,² which are operative at room temperature are listed below, arranged in order of frequency of occurrence and ease of operation: (1) (010) - $[100]$ slip, (2) $\{130\}$ twinning, (3) $\{\sim 172\}$ twinning, and (4) kinking, cross-slip, $\{\sim 176\}$ twinning, and $\{011\}$ slip. The resolved critical shear stress for slip on the (010) - $[100]$ slip system is reported as 0.34 kg/mm^2 . In subsequent work,³ the authors report a value of 0.29 kg/mm^2 for the initiation of (010) - $[100]$ slip

at 600°C. Butcher⁴ has observed (010) - [100] slip, {130}, and $\{\sim 172\}$ twinning at 450°C and observes that operative deformation mechanisms at this temperature are similar to those at room temperature.

We may conclude from this evidence that if satisfactory yield criteria can be obtained for room temperature deformations, these same criteria should suffice between room temperature and 450°C. Strain hardening (which accompanies finite deformation) and stress, strain-rate relationships show definite temperature dependence, and must be considered separately.

In an effort to define yield criteria for alpha-uranium single crystals subjected to tensile loading in the temperature range $\sim 26^\circ\text{C}$ to 450°C, stereographic projections were prepared of the fraction of a tensile stress resolved on the various modes of the {130} (Figures 7.1a and b), $\{\sim 172\}$ (Figures 7.2a, b, c, and d), and $\{\sim 176\}$ (Figures 7.3a, b, c, d, and e) twinning systems. The last projection (Figures 7.1b, 7.2d, and 7.3e) for each system illustrates the favored mode (or modes). In the {130} system, the (130) - $[\bar{3}\bar{1}0]$ mode (Figure 7.1b) is favored, except along the [001] - [100] boundary, where the (130) - [310] mode is equally probable.

FIGURE 7.1a Stereographic Projection of Resolved Shear Stress on (130)-[310] Twin System for Tensile Loading

FIGURE 7.1b Stereographic Projection of Resolved Shear Stress on (130)- $[\bar{3}\bar{1}0]$ Twin System for Tensile Loading

FIGURE 7.2a Stereographic Projection of Resolved Shear Stress on $(\bar{1}72)$ - $[\bar{3}12]$ Twin System for Tensile Loading

In the $\{\sim 172\}$ system, the (172) - $[\bar{3}\bar{1}2]$ mode is favored, except on the octant boundaries. Along the [100] - [010] boundary, the $(\bar{1}72)$ - $[\bar{3}12]$ mode is equally probable. Along the [010] - [100] boundary, the $(\bar{1}72)$ - $[\bar{3}\bar{1}2]$ mode is equally probable. Along the [001] - [100] boundary, the (172) - $[\bar{3}12]$ mode is equally probable. In the $\{\sim 176\}$ system, a composite projection indicating regions favoring the (176) - $[\bar{5}1\bar{2}]$ and $(17\bar{6})$ - $[\bar{5}12]$ modes has been prepared (Figure 7.3e). Values of 0.34 kg/mm²,

FIGURE 7.2b Stereographic Projection of Resolved Shear Stress on $(\bar{1}72)$ - $[3\bar{1}2]$ Twin System for Tensile Loading

FIGURE 7.2d Stereographic Projection of Resolved Shear Stress on (172) - $[3\bar{1}2]$ Twin System for Tensile Loading

FIGURE 7.2c Stereographic Projection of Resolved Shear Stress on $(\bar{1}72)$ - $[312]$ Twin System for Tensile Loading

criteria for arbitrarily directed tensile (Figure 7.4) and compressive (Figure 7.5) stresses.

Effect of Irradiation on Mechanical Properties

Buckley⁷ has irradiated single crystal uranium foils, 15 to 20 μ in thickness. The foils were oriented with the $[010]$ axis parallel to the length of the foil. The foils were irradiated on one sur-

0.74 kg/mm², 0.89 kg/mm², and 10 kg/mm² were taken for the critical resolved shear stresses for (010) - $[100]$ slip, and for $\{130\}$ - $\langle 310 \rangle$, $\{\sim 172\}$ - $\langle 312 \rangle$, and $\{\sim 176\}$ - $\langle 512 \rangle$ twinning respectively.^{3,5} These values were used in conjunction with the stereographic projections of Figures 7.1b, 7.2d, 7.3e, and others presented in a previous report,⁶ to prepare stereographic projections of the yield

FIGURE 7.3a Stereographic Projection of Resolved Shear Stress on $(\bar{1}76)$ - $[5\bar{1}2]$ Twin System for Tensile Loading

FIGURE 7.3b Stereographic Projection of Resolved Shear Stress on $(1\bar{7}6)$ - $[5\bar{1}2]$ Twin System for Tensile Loading

FIGURE 7.3d Stereographic Projection of Resolved Shear Stress on (176) - $[5\bar{1}2]$ Twin System for Tensile Loading

FIGURE 7.3c Stereographic Projection of Resolved Shear Stress on (176) - $[5\bar{1}2]$ Twin System for Tensile Loading

FIGURE 7.3e Stereographic Projection of Resolved Shear Stress on $\{176\}$ - $\langle 512 \rangle$ Twin System for Tensile Loading

face by recoiling fission fragments having an average penetration depth of $\sim 3 \mu$. The irradiated layer is restrained by the bulk of the specimen, and required to deform plastically because of irradiation growth. The irradiated portion was observed to deform primarily by $\{110\}$ - $\langle 110 \rangle$ slip in preference to $\{130\}$ twinning. The author concludes that slip is favored by the slow strain rates. This conclusion is in keeping with present knowl-

edge of the creep process,⁸ in which crystallographic slip generally plays a prominent part, but twinning is relatively unimportant, except at low temperatures and high stresses. Frequent slip and twin traces were observed on the irradiated surface of the foil, while the unirradiated surface was devoid of deformation marks.

FIGURE 7.4 Stereographic Projection of Yield Stress for Alpha-Uranium Single Crystal Subject to Tension (Values are in kg/mm²)

On first inspection, we might be led to conclude that irradiation results in lowering the yield or creep strength of the irradiated portion of the single crystal. Since the unirradiated portion was some 5 to 7 times the thickness of the irradiated portion, however, the observed result is to be expected, even if the strength of the irradiated portion equals, or in fact exceeds, that of the unirradiated portion. It would be of interest to conduct this experiment under conditions such that the average penetration of fission fragments was half the thickness of the foil, in order to resolve the question of whether the strength of single crystals is altered during irradiation. Some light has been shed on this question by creep tests conducted on alpha-uranium samples during irradiation by Roberts and Cottrell,⁹ and by Rose.¹⁰ Roberts and Cottrell observed steady state creep in polycrystalline uranium

FIGURE 7.5 Stereographic Projection of Yield Stress for Alpha-Uranium Single Crystal Subject to Compression (Values are in kg/mm²)

specimens subjected to stresses of 190 to 1,900 lb/in.² during irradiation at 100°C. No such effect was observed in a control specimen subjected to a stress of 1940 lb/in.² at 100°C without irradiation. The increase in creep rate during irradiation is attributable to intergranular stresses arising from anisotropic irradiation growth. Rose observed no significant differences in creep rate due to irradiation for uranium specimens subjected to a stress of 4500 lb/in.² at 450°C. At this temperature, anisotropic irradiation growth is not observed; hence it is reasonable to assume that the mechanical properties of alpha-uranium single crystals are not appreciably altered during irradiation.

The Deformation of Polycrystalline Uranium During Irradiation

The problem of deformation of a polycrystalline aggregate has been considered by Taylor,^{11,12} Bishop and Hill,^{13,14} and Lin.¹⁵ Taylor¹¹ showed

that five independent deformation mechanisms are required to accomplish a plastic strain in which volume is conserved, but which is otherwise arbitrary. He considered the problem of determining the combination of five operating shears for face-centered cubic materials, which have four $\{111\}$ slip planes, each containing three $\langle 110 \rangle$ slip directions, or a total of 12 possible modes. Bishop and Hill¹⁴ deduced that of the $\binom{12}{5} = 792$ sets of five shears, only 384 are independent, and employed the principle of maximum plastic work to deduce the five operative systems from the 384 possible. Bishop¹⁶ has also attempted, by this approach, to predict tensile and compressive textures in face-centered cubic metals.

Blackburn, Harnby, and Stobo,¹⁷ Blackburn,¹⁸ and Anderson and Bishop¹⁹ have considered the effect of thermal cycling and irradiation growth on the creep of uranium. All have assumed either uniform deformation or uniform stress. Boas and Hargreaves,²⁰ Urie and Wain,²¹ and Boas and Ogilvie²² have observed variations in plastic deformation from grain to grain, and within a grain during the deformation of polycrystalline aluminum and alpha-brass. If plastic deformation is inhomogeneous in face-centered cubic materials, which have 12 possible slip modes, it is likely that uranium, with a much more limited number of possible slip modes, will deform in an extremely inhomogeneous manner during irradiation. It does not seem reasonable, therefore, to require uniform deformation in the development of a theory for the prediction of dimensional changes which a polycrystalline uranium specimen undergoes during irradiation.

Conclusions

In forming conclusions based on Figures 7.4 and 7.5, the following reservations should be kept in mind:

1. The yield criteria are valid for infinitesimal strains only; strain hardening and recovery processes, which influence the relationship between stress and strain rate, and which have a pronounced temperature dependence, have not been considered.

2. The yield criteria are based in part on previous estimates⁵ of critical resolved shear stress for $\{130\}$, $\{\sim 172\}$, and $\{\sim 176\}$ twinning.

Bearing in mind the limitations imposed by these conditions, we consider qualitatively the anticipated effects of strength anisotropy during irradiation of polycrystalline uranium. The prime textures which we observe in beta heat-treated uranium fuel cores include a higher than normal incidence of (200) poles parallel to the thermal gradient which exists during quenching. There is a considerable spread in this texture, so that a higher than normal incidence of (110) and (312) poles is also observed in this direction. In the direction of the core axis, there is a higher than normal incidence of (020) and (200) poles. In the tangential (circumferential) direction, there is a higher than normal incidence of (020) poles. Again there is considerable spread in these textures. The textures are most severe near the surface, and nearly random near midwall.

Where a (200) texture exists, we expect a higher than normal incidence of crystallites to be subjected to compressive loading, since an alpha-uranium crystal becomes shorter in the direction of the (200) pole during irradiation. Those crystals which are compressed in a direction near the pole of the (120) may be expected (see Figure 7.5) to yield first. During yielding, they may be expected to rotate so that the (010) pole is brought closer to the direction of compression. Where a (200) texture exists, we thus expect a migration of material from orientations in the vicinity of the (120) pole toward the (020) pole.

Where a (020) texture exists, we expect a higher than normal incidence of crystallites to be subjected to tensile loading, since an alpha-uranium

single crystal lengthens in the directions of the (020) pole during irradiation. Again, those crystals near the pole of the (120) may be expected (see Figure 7.4) to yield first. During yielding, they may be expected to rotate so that the [100] direction is brought closer to the direction of extension. Where a (020) texture exists, we thus expect a migration of material from orientations in the vicinity of the (120) pole toward the [100] direction. The effect of these migrations should be to reduce the instantaneous growth (or shrinkage) rate of polycrystalline uranium specimens with increasing exposure.

References

- ¹P. R. Morris. "The Form of a Solution for the Prediction of Dimensional Changes of Uranium Fuel Cores During Irradiation," Summary Tech. Rpt. for the Period January 1, 1962 to March 31, 1962, USAEC Report NLCO-850, p. 69. April 16, 1962 (Classified).
- ²L. T. Lloyd and H. H. Chiswik. Deformation Mechanisms of Alpha-Uranium Single Crystals, USAEC Report ANL-5367. December 14, 1954.
- ³H. H. Chiswik, A. E. Dwight, L. T. Lloyd, M. V. Nevitt, and S. T. Ziegler. "Advances in the Physical Metallurgy of Uranium and Its Alloys," International Conference on the Peaceful Uses of Atomic Energy Proceedings, 2nd, Geneva, 1958, Vol. 6, pp. 394 - 412. New York: United Nations Press, 1958.
- ⁴B. R. Butcher. The Deformation of Alpha-Uranium at 450°C and 500°C, UKAEA Report AERE-R-2898. April, 1959.
- ⁵P. R. Morris. "Slip and Twinning in Alpha-Uranium Single Crystals Subjected to Compressive Loading," Summary Tech. Rpt. for the Period April 1, 1962 to June 30, 1962, USAEC Report NLCO-855, p. 69. July 25, 1962.
- ⁶*Ibid*, Figures 9.1, 9.2b, 9.3e, and 9.4d.
- ⁷S. N. Buckley. "The Relationship Between Irradiation Growth in Mono- and Polycrystalline Alpha-Uranium," Paper Presented at the Institute of Metals Symposium on Uranium and Graphite on March 20 and 21, 1962, London.
- ⁸Gunther Schoeck. "Theories of Creep," Mechanical Behavior of Materials at Elevated Temperatures, Chapter 5, edited by John E. Dorn. New York: McGraw-Hill, 1961.
- ⁹A. C. Roberts and A. H. Cottrell. Creep of Alpha Uranium During Irradiation with Neutrons, UKAEA Report AERE-M/R-1969. May, 1956.
- ¹⁰H. C. Rose. A Compressive Creep Test of Alpha Uranium Under Neutron Irradiation, UKAEA Report AERE-M/R-2068. September 25, 1956.
- ¹¹G. I. Taylor. "Analysis of Plastic Strain in a Cubic Crystal," Stephen Timoshenko 60th Anniversary Volume, pp. 218-224. New York: MacMillan, 1938.
- ¹²G. I. Taylor. "Strains in Crystalline Aggregates," Proceedings of the Colloquium on Deformation and Flow of Solids (Madrid, 1955), pp. 3-12. Berlin: Springer, 1956.
- ¹³J. F. W. Bishop and R. Hill. "A Theory of the Plastic Distortion of a Polycrystalline Aggregate Under Combined Stresses," Phil. Mag., 42: 414. 1951.
- ¹⁴J. F. W. Bishop and R. Hill. "A Theoretical Derivation of the Plastic Properties of a Polycrystalline Face-Centered Metal," Phil. Mag., 42: 1298. 1951.
- ¹⁵T. H. Lin. "Analysis of Elastic and Plastic Strains of a Face-Centered Cubic Crystal," J. Mech. Phys. of Solids, 5: 143. 1957.
- ¹⁶J. F. W. Bishop. "A Theory of the Tensile and Compressive Textures of Face-Centered Cubic Metals," J. Mech. Phys. Solids, 3: 130. 1955.
- ¹⁷W. S. Blackburn, G. Harnby, and J. J. Stobo. "The Effect of Thermal Cycling on the Creep of Uranium," Reactor Science, 12: 162. 1960.
- ¹⁸W. S. Blackburn. "The Effect of Internal Stresses Due to Irradiation Growth and Thermal Cycling on the Creep of Uranium in the Cases of Both Elastic and Plastic Behaviour," Reactor Science and Technology, 14: 107. 1961.
- ¹⁹R. G. Anderson and J. F. W. Bishop. "The Effect of Neutron Irradiation and Thermal Cycling on Permanent Deformations in Uranium under Load," Paper Presented at the Institute of Metals Symposium on Uranium and Graphite on March 20 and 21, 1962, London.
- ²⁰W. Boas and M. E. Hargreaves. "On the Inhomogeneity of Plastic Deformation in the Crystals of an Aggregate," Proc. Royal Soc. (London), A193: 89, 1948.
- ²¹V. M. Urie and H. L. Wain. "Plastic Deformation of Coarse-Grained Aluminum," J. Inst. Met., 81: 1953. 1952-3.
- ²²W. Boas and Ogilvie. "The Plastic Deformation of a Crystal in a Polycrystalline Aggregate," Acta Met., 2: 655. 1954.

8. ATMOSPHERIC CORROSION OF URANIUM

T. R. Kato

E. T. Vonderbrink

Abstract

The stable corrosion product formed when uranium metal is exposed to moist atmosphere was identified as $\text{UO}_3 \cdot 2\text{H}_2\text{O}$. A possible mechanism of the formation of $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ is explained.

Introduction

Atmospheric corrosion of uranium metal can be the cause for rejection of finished fuel cores or can cause difficulties in subsequent plating and cladding operations. Uranium is known to react with water to form hydrogen and uranium dioxide. Waber^{1,2} has noted the formation of yellow corrosion products, which he has identified as $\text{UO}_3 \cdot x\text{H}_2\text{O}$, and $\text{UO}_3 \cdot 2\text{H}_2\text{O}$, under different experimental conditions. Such yellow corrosion products have been observed on uranium ingots, rods, and cores at the National Lead Company of Ohio.

Objectives for This Quarter

1. To identify the yellow corrosion product which is formed on uranium metal exposed to the atmosphere.
2. To obtain insight into the mechanism of formation of this corrosion product.

Summary of Results

1. The yellow product formed in the atmospheric corrosion of uranium is $\text{UO}_3 \cdot 2\text{H}_2\text{O}$.
2. A mechanism of oxidation of U^{4+} to U^{6+} in atmospheric corrosion by hydrogen peroxide is suggested.

Identification of Yellow Corrosion Product

Uranium metal samples were placed in a high-humidity atmosphere. A yellow corrosion product soon became evident. However, to obtain a good, homogeneous sample of the material in a sufficient

quantity for laboratory analysis, the metal specimens were allowed to continue to corrode for more than a year. The corrosion product was subjected to X-ray analysis, differential thermal analysis, thermogravimetric analysis, and various optical analyses. The results of these tests are given below.

X-Ray Analysis

A powder diffraction pattern (Table 8.1) of the yellow corrosion product was taken at 25°C with a Norelco Diffractometer. This diffraction pattern agrees with ASTM data obtained by Dawson³ for $\text{UO}_3 \cdot 2\text{H}_2\text{O}$.

TABLE 8.1 X-Ray Data for Yellow Corrosion Product

Interplanar Spacing, d (Å)	Normalized Intensities, I/I_0
7.37	100
5.05	3
4.46	4
3.68	19
3.59	43
3.50	31
3.33	4
3.22	50
3.16	28
2.97	4
2.89	6
2.739	3
2.571	15
2.536	9
2.154	4
2.034	9
2.014	9
1.961	12
1.781	7
1.615	6

Differential Thermal Analysis (DTA)

Figure 8.1 is a differential thermogram of the yellow corrosion product. This thermogram had

FIGURE 8.1 Differential Thermal Analysis Plot for Corrosion Product ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$)

the three endothermic peaks and one exothermic peak similar to DTA peaks obtained by Dell and Wheeler⁴ when they added water to uranium trioxide ($\text{UO}_3 + 2 \text{H}_2\text{O} \rightarrow \alpha \text{UO}_3 \cdot 2 \text{H}_2\text{O}$) at 20°C . These DTA data identify the corrosion product as $\text{UO}_3 \cdot 2\text{H}_2\text{O}$.

Thermogravimetric Analysis (TGA)

Figure 8.2 is a thermogram, obtained in atmosphere, of the corrosion product. A weighed amount of the corrosion product (step 1 on graph), which was assumed to be $\text{UO}_3 \cdot 2\text{H}_2\text{O}$, was subjected to TGA. The experimental weight loss at step 2 corresponds to the theoretical weight loss if one molecule of water of hydration were lost from $\text{UO}_3 \cdot 2\text{H}_2\text{O}$. The weight loss in step 3 corresponds to the loss of the second molecule of water of hydration resulting in the formation of UO_3 . Subsequent heating of the UO_3 results in the formation of U_3O_8 (step 4). This thermogram is typical of $\text{UO}_3 \cdot 2\text{H}_2\text{O}$; and, hence, identifies the corrosion product.

Optical Analysis

Optical analysis of the corrosion product revealed a mean refraction index of 1.697 ± 0.002 ,

FIGURE 8.2 Thermogravimetric Analysis of Corrosion Product ($\text{UO}_3 \cdot 2\text{H}_2\text{O}$)

which is in agreement with $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ produced from the reaction of UO_3 and H_2O at room temperature.

Study of the Mechanism of the Formation of $\text{UO}_3 \cdot 2\text{H}_2\text{O}$

The yellow corrosion product identified as $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ can be observed on uranium metal exposed to the atmosphere. These observations show invariably that the anodic area is surrounded by yellow corrosion product as Figure 8.3 indicates.

The corrosion product formed at the anode appears black, while at the cathode the corrosion product is yellow with specks of green-black particles. Positive identification was made of the yellow cathodic corrosion product as $\text{UO}_3 \cdot 2\text{H}_2\text{O}$, but the black anodic corrosion product was not identified.

FIGURE 8.3 Formation Site of Yellow Product on Uranium Metal

It is well known that electropositive uranium reacts with water, displacing hydrogen with the formation of U^{4+} oxides. According to Waber,^{1,2} since the corrosion product formed in aqueous solution appears gelatinous, the U^{4+} ion could be in the form of $U(OH)_4$ or $UO_2 \cdot 2H_2O$. Compounds with appreciable amounts of U^{6+} have been reported by Waber,¹ when uranium was exposed to water vapor.

The initial uranium corrosion product was assumed to be U^{4+} , and the following experiments were conducted to acquire insight into the mechanism of formation of the U^{6+} material identified as $UO_3 \cdot 2H_2O$.

Experiment 1 — This experiment was undertaken to determine whether $UO_3 \cdot 2H_2O$ could be formed by the following reaction:

UO_2 was ground, thoroughly washed with distilled water, and placed in a large test tube with a constant flow of air (see Figure 8.4).

After the experiment had continued for 4 weeks, the UO_2 was examined optically for $UO_3 \cdot 2H_2O$. None was formed under these experimental conditions.

FIGURE 8.4 Apparatus for Experiment 1

Experiment 2 — This experiment was undertaken to determine whether $UO_3 \cdot 2H_2O$ could be formed by the following reaction:

An apparatus similar to that used in Experiment 1 was employed. The pH of the distilled water was adjusted to 9 by adding NaOH. After 4 weeks, no $UO_3 \cdot 2H_2O$ could be observed.

Experiment 3 — The purpose of this experiment was to determine whether $UO_3 \cdot 2H_2O$ could be formed electrolytically by the following reaction:

UO_2 was placed in a glass container, and sufficient distilled water was added to form a slurry. Two platinum electrodes were immersed in the slurry and a potential of 16 volts was applied to the system.

After 2 weeks, a yellow product identified by X-ray diffraction as $UO_3 \cdot 2H_2O$ was obtained at the cathode. No change could be observed in the UO_2 at the anode.

Experiment 4 — This experiment was performed to determine whether $UO_3 \cdot 2H_2O$ could be formed electrolytically between two uranium electrodes

in distilled water. Figure 8.5 shows the apparatus constructed for the test. A potential of 16 volts was applied to the system.

FIGURE 8.5 Apparatus for Experiment 4

A yellow corrosion product identified as $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ was formed at the cathode within 1 week, while a black corrosion product formed at the anode.

Discussion of the Experiments

As Figure 8.3 indicates, the yellow corrosion product forms at the cathodic site. Experiments 1 and 2 show that oxygen alone, in the presence of water vapor at room temperature, cannot cause the formation of $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ from UO_2 . Experiments 3 and 4 show that $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ forms at the cathodic site upon application of a direct current. This may be explained by the formation of H_2O_2 at the

cathode, which oxidizes the U^{4+} to U^{6+} with the formation of stable $\text{UO}_3 \cdot 2\text{H}_2\text{O}$. The presence of H_2O_2 was proved: an aliquot of a solution in which uranium corrosion had occurred, and yellow corrosion products had been observed, gave a positive qualitative test⁵ for H_2O_2 .

Conclusion

Observations and experimental data show that the atmospheric corrosion of uranium is electrochemical in nature and that the formation of $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ can be explained by the oxidation of U^{4+} to U^{6+} by H_2O_2 .

References

- ¹J. T. Waber. A Review of the Corrosion Behavior of Uranium, USAEC Report LA-2035. April, 1956.
- ²J. T. Waber. "The Corrosion of Plutonium and Uranium," Chapter 6, Metallurgy and Fuels, edited by H. M. Finniston and J. P. Howe, Series V, Volume 4. New York: Pergamon, 1961.
- ³J. K. Dawson, E. Wait, K. Alcock, and D. R. Chilton. "Some Aspects of the System Uranium Trioxide-Water," J. Chem. Soc. (London) 3531. 1956.
- ⁴R. M. Dell and V. J. Wheeler. The Reactivity of Fluidized-Bed Uranium Trioxide, UKAEA Report AERE-R-3466. October, 1960.
- ⁵F. Feigl. Spot Tests in Inorganic Analysis, 5th ed., p. 354. New York: Elsevier, 1958.

9. PREVENTION OF CHLORIDE PITTING OF URANIUM FUEL CORES

E. T. Vonderbrink

T. R. Kato

Abstract

Electrochemical studies have shown that chloride pitting of uranium fuel cores in aqueous solutions can be eliminated by the addition of sodium nitrite to the solutions.

Introduction

Uranium is known to exhibit active-passive corrosion behavior similar to that of stainless steel. Some of the worst cases of pitting have been observed in metals and alloys that depend on passivity or a protective film for their corrosion resistance. The most common pitting agent is the chloride ion.

In processing uranium fuel cores, the metal is immersed in aqueous solutions containing chloride ions during quenching and washing operations, and consequently is subject to conditions favorable to pitting. Since pitting of fuel cores can be a cause for their rejection, measures to eliminate pitting are desirable.

Sodium nitrite is well known as an anodic corrosion inhibitor. Laboratory studies were conducted to determine the amount of sodium nitrite required to eliminate the chloride pitting of uranium. The employment of electrochemical techniques in laboratory studies of pitting corrosion afforded accurate, rapid, and reproducible data which were not readily available by weight-loss methods and visual observations.

Objectives for This Quarter

1. To determine the amount of sodium nitrite inhibitor that would prevent chloride pitting of uranium fuel cores.
2. To determine the effect of oxygen on the corrosion inhibition of uranium in sodium nitrite-sodium chloride solutions.

Summary of Results

The results of laboratory tests have shown:

1. A sodium chloride/sodium nitrite ratio of 1:35, or higher, will eliminate pitting corrosion of uranium in solutions containing up to 500 ppm chloride ion.
2. The presence of oxygen is required, since its absence will cause sodium nitrite to lose its inhibitive effects on uranium corrosion in chloride solutions.

Electrochemical Corrosion

The electrochemical theory of corrosion states that in aqueous solutions metals corrode by the formation of cells on the metal surface. These cells consist of anodes, the region of metal oxidation and chemical attack, and cathodes, the region of reduction and no chemical attack. The electrolytic circuit joining anode to cathode is completed by conduction of current through the solution. With the formation of a complete circuit, a potential is established. Measurement of this potential can be used to study the corrosion reaction.

When measuring the potential of the corrosion cell, it is imperative that no current be drawn from the circuit. This would lead to polarization and result in inaccurate readings. A change in the corrosion potential in the noble direction (a more positive potential indicates film buildup and corrosion protection, and a change in the corrosion potential in the less noble direction (a less positive potential) indicates film breakdown and chemical attack of the metal.

Apparatus and Procedure

The experimental corrosion cell (Figure 9.1) was composed of a 500 cc glass reaction vessel covered with a ground glass cap with openings in

FIGURE 9.1 Experimental Corrosion Cell

the cap for 2 electrodes and 2 gas tubes. A Leeds and Northrup saturated calomel electrode was used as a reference electrode. The potential of the latter on the hydrogen scale is 0.244V at 25°C. The working electrode was a 1/4-inch-diameter uranium rod which was coated with paraffin wax at the metal-liquid interface to avoid interface corrosion. Prior to immersion in the test solution, the uranium electrode was pickled in nitric acid solution and thoroughly washed with distilled water. Potentials were measured using a Keithley Electrometer (Model 610A) which had a very high input impedance. Steady state potentials were normally reached within 12 hours, as shown by a continuous strip chart recorder. The temperature of the corrosion cell was maintained at 25°C. No mechanical stirring was used in the experiment. Distilled water was used for all experiments. The chemicals were dried at 100°C prior to use. Sodium chloride was used in amounts up to 500 ppm.

Test Data

Figure 9.2 shows how various sodium chloride:sodium nitrite ratios affected the uranium corrosion potential. Changes in potential (ΔE) were calculated by subtracting the steady state potential of uranium in NaCl-NaNO₂ solutions from the steady state potential of uranium in NaCl solutions containing no NaNO₂. The point of interest is not the value of the potential itself, but the effect of some variable (in this case, the NaCl:NaNO₂ ratio) in changing the potential to a more noble value.

FIGURE 9.2 Effect of Sodium Nitrite on Corrosion Potential of Uranium in Chloride Solutions

As shown in Table 9.1, no pitting was observed when ΔE was approximately 0.50V. The ΔE value of approximately 0.50V was the maximum potential change reached during the studies. At NaCl/NaNO₂ ratios from 1/35 to 1/90 inclusive, ΔE was very small, indicating passivity of the metal.

Figure 9.3 shows the effect of oxygen (air) on the corrosion potential of uranium in solutions containing 1/35 NaCl/NaNO₂. Curve 1 was obtained when the cell was purged with argon in order to eliminate oxygen in the system. The argon purging resulted in an increase in the cor-

TABLE 9.1 Effect of Sodium Nitrite on Corrosion Potential of Uranium in Chloride Solutions

Ratio NaCl/NaNO ₂	ΔE (Volts)	Observations
100/0	—	Pitting
1/10	0.03	
1/20	0.13	
1/25	0.18	
1/30	0.32	
1/35	0.48	No Pitting
1/40	0.52	
1/50	0.52	
1/60	0.52	
1/70	0.54	
1/80	0.54	
1/90	0.54	

rosion potential in the less noble direction indicating chemical attack of the working electrode. Curve 2 was obtained when the system was purged with air. This curve is very similar to curve 3 which was obtained when nothing was added to the system.

FIGURE 9.3 Effect of Oxygen on Corrosion Potential of Uranium in Solutions Containing 1/35 NaCl/NaNO₂

10. THE DETERMINATION OF CHLORIDE BY THE COULOMETRIC METHOD

J. R. Proll

Abstract

Chloride ions can be titrated with silver ions generated electrolytically by a constant current. The end point is detected potentiometrically with a silver wire electrode. The required instrumentation is described, and procedures for the analysis of several types of samples are presented. The samples normally encountered in this laboratory may be analyzed without prior separations. Results obtained by the proposed procedures are shown to be comparable to those obtained, more laboriously, by conventional methods.

Introduction

In the past, routine determinations of microgram concentrations of chloride ions have been made by the turbidimetric method.¹ A volumetric procedure in which the end point was detected potentiometrically with a silver indicating electrode² was developed here but was never used extensively due to difficulties experienced in detecting the apparent equivalence potential. A volumetric procedure using polarized gold electrodes for end point detection³ has also been used, but it requires the use of a recording titrator which is not available for routine use. Macro concentrations of chloride have been determined by both the gravimetric and the Mohr volumetric method. All of these methods are rather slow and time consuming. A rapid, automatic procedure was desired which could be applied to all ranges of chloride ion concentration. An automatic coulometric procedure for the determination of 0.2 to 10 mg of chloride in 50 ml of solution has been described by Lingane.⁴ It was decided to attempt to adapt this procedure to both microgram and higher concentrations of chloride ion.

Objectives

1. To set up the required instrumentation.
2. To develop methods applicable to the various types of samples received.

Summary of Results

An automatic coulometric titrator has been constructed for the determination of chloride ions. Methods have been developed for use on aqueous feeds, aqueous raffinates, nitric acid, quench water, coolant, 40% caustic soda, 40% caustic potash, and acid filtrates. The major interferences are Fe^{+3} and NO_2^- ions. When these ions are present their effects are eliminated by reduction with ascorbic acid. The precision of a single determination at the 95% confidence level was found to be ± 9.07 $\mu\text{g/ml}$ at a concentration of 100 $\mu\text{g/ml}$.

Instrumentation

Electronic Equipment

A power supply, milliammeter, electric timer, resistors, and relay are built into a cabinet which can be placed on top of a Beckman Model K Automatic Titrator. A simplified circuit diagram of the automatic coulometric titrator is given in Figure 10.1. The power supply is a conventional electronic rectifier which operates on regulated 110 v ac. The coarse cell current adjustment is made by adjusting the grid bias on two 6AQ5 tubes with a 50,000 ohm rheostat (R_1). Fine adjustments of the cell current are made by means of a 50 ohm rheostat (R_3).

Approximate current measurements are made with a 0 to 1 ma milliammeter. A four position selector

FIGURE 10.1 Simplified Circuit Diagram of Automatic Coulometric Titrator

switch is used with suitable shunts so that currents of 0 to 10, 0 to 25, 0 to 50, and 0 to 100 ma may be measured. Accurate current measurements are made by measuring the voltage drop across a resistor. A Leeds and Northrup Model 7655 potentiometer is used to measure the voltage drop across the 10 ohm precision resistor (R₂), and the current is calculated using Ohm's Law.

One pole of the double-pole, double-throw relay directs the current either to the cell or to a dummy variable resistor (R₄) of 1000 ohms. The dummy resistor is adjusted so that the current demand will be the same whether the cell is in the circuit or not. The other pole of the relay, switches on the electric timer when the cell is in the circuit.

The titration is controlled and the end point is detected by means of a Beckman Model K Automatic Titrator. It is modified so that the signal which normally controls the addition of titrant is fed to the solenoid of the double-pole, double-throw relay.

Supporting Electrolyte

The solubility of silver chloride in water is such that at low concentrations of chloride ion the rate of change in potential at the equivalence point is too small to permit precise titrations. Organic solvents are frequently used to reduce the solubility of inorganic precipitates. Lingane⁴ used 0.4M sodium nitrate plus 0.05M perchloric acid in 80% ethanol for the supporting electrolyte. Laux and Brown² recommend 95% methanol and 5% nitric acid.

A supporting electrolyte of 95% methanol and 5% nitric acid was chosen because it is easy to prepare and because methanol is cheap and is readily available in the laboratory.

Titration Cell

A diagram of the titration cell is given in Figure 10.2. The electrodes are held in place by a rubber stopper 2½-inches in diameter. The electrode assembly is clamped into place on the delivery unit of the automatic titrator.

The generator anode is made from a piece of 16-gage pure silver wire about eight inches long.

FIGURE 10.2 Coulometric Titration Cell

A flat spiral is formed and positioned horizontally near the bottom of the titration cell. An anode can be used for several successive determinations of chloride ion before the silver chloride coating becomes thick enough to interfere with the diffusion of chloride ions to the silver surface. The silver chloride is stripped from the anode with a solution of dilute ammonium hydroxide.

The generator cathode is a platinum wire isolated from the test solution by immersion in a glass tube whose bottom is closed by a sintered glass disk. The catholyte in this tube is the same as, and its level is kept above, the electrolyte in the cell proper. The purpose of isolating the generator cathode is to prevent the reduction of the small concentration of free silver ion in equilibrium with the silver chloride, since this would decrease the current efficiency below the required 100%.

The indicator electrode is silver wire about four inches in length sealed into a capillary tube with about $\frac{1}{2}$ -inch left exposed.

A Beckman saturated calomel electrode is used as the reference electrode. To prevent contamination of the test solution by chloride ions, the reference electrode is immersed in a solution of sodium nitrate and electrolytic connection to the test solution is completed by an inverted U-tube salt bridge filled with approximately 0.1M sodium nitrate in a 4% agar gel.

The test solution is grounded with the solution ground wire in the delivery unit of the Beckman automatic titrator. The solution ground is used to prevent erratic behavior of the automatic titrator.

Calibration

Detection of the End Point

Just as in ordinary potentiometric titrations, the first step in developing an automatic coulometric titration is the establishment of the equivalence point potential under the particular experimental conditions of the experiment. This was

done by manually determining the indicator electrode potential versus generation time curve in the vicinity of the equivalence point under the same conditions that were to be used in the proposed procedure. Figure 10.3 shows a typical titration curve for 100 micrograms of chloride ion in 75 ml of 95% methanol 5% nitric acid supporting electrolyte. From the data used in plotting the curve it was concluded that the equivalence potential for the system used was about +230 mv.

FIGURE 10.3 Titration Curve of 100 μ g Chloride Ion in 75 ml Volume of Supporting Electrolyte

Adjustment of the Supporting Electrolyte to the Equivalence Potential

In the coulometric determination of macro amounts of chloride ion, slight deviations of the potential of the supporting electrolyte are probably of no consequence. However, in the determination of microgram concentrations of chloride ion, these deviations become quite significant. It, therefore, is necessary to titrate to the potential of the supporting electrolyte, to adjust the potential of the supporting electrolyte to the equivalence potential, or to determine a blank if the potential of the supporting electrolyte is lower than the equivalence potential.

The disadvantage of titrating to the equivalence potential of the supporting electrolyte is that it may be necessary to titrate to a less sensitive point on the titration curve than the equivalence point.

In this study several different lots of methanol and nitric acid were used to prepare supporting electrolytes. In all cases the potential of the supporting electrolyte was found to be between +190 mv and +210 mv. This would indicate a slight contamination of the supporting electrolyte with chloride ion. A turbidimetric analysis of the residue from 100 ml of supporting electrolyte was performed, and it was found to contain six micrograms of chloride ion. The potential of the supporting electrolyte made from redistilled methanol was found to be +260 mv.

Since the potential of the supporting electrolyte was always found to be less than +230 mv, it was decided to titrate the supporting electrolyte to the equivalence potential before adding the sample. This can be accomplished in about 15 seconds. If at some time in the future chloride-free methanol is obtained, 50 micrograms of chloride ion should be added to each liter of supporting electrolyte.

The determination of a blank would serve equally well. This method was not used because it would require subtracting the blank from each calculation and it seemed easier to let the instrument do this automatically.

Interferences

The report of Laux and Brown² gives an excellent survey of the interferences encountered in the analysis of various uranium concentrates and similar materials. They concluded that bromide and iodide ions interfere, but are very rarely encountered. In addition, they found that the only interfering ions which were normally present were Fe^{+3} and NO_2^- . These latter interferences were eliminated by reduction with ascorbic acid or the addition

of ammonium hydroxide until a pH of 4 to 5 is obtained.

In the present study, Fe^{+3} and NO_2^- interference was also observed. To eliminate this, treatment with ammonium hydroxide was first tried. However, the method was abandoned because the control of the apparent pH was too critical, and it was impossible to keep it constant due to the leakage of the acidic catholyte into the test solution.

A 1% solution of ascorbic acid was tried next. This treatment seemed to work, but results on known standards were always low. Increasing the ascorbic acid concentration to 5% and adding 2 ml in excess of the amount needed to reduce the potential of the silver indicating electrode to its lowest point was found to give satisfactory results.

Cleaning and Care of Electrodes

The potentiometric method developed by Laux and Brown was never used here routinely because difficulties were experienced in establishing the apparent equivalence potential of the supporting electrolyte. Shifts in the potential of the same supporting electrolyte were observed. This difficulty was, therefore, anticipated in the coulometric method since, except for the generation of silver ions electrolytically, the methods are almost identical.

After such difficulties were experienced, it was concluded that the trouble was due to the evaporation of methanol from the electrolyte left on the electrodes when they were exposed to air for more than a few minutes. When the methanol evaporates, concentrated nitric acid remains on the electrodes and attacks the silver. The silver nitrate formed dissolves slowly in the supporting electrolyte causing changes of the apparent potential.

After about 10 milligrams of chloride ion have been titrated it is necessary to strip the silver chloride formed from the generating anode. It was found that by adhering closely to the following

procedure the generating anode could be cleaned, and difficulties with the silver indicating electrode could be eliminated.

1. Immerse the electrodes in 10% NH_4OH until all of the silver chloride has been stripped from the generating anode.

2. Immerse the electrodes in 10% HNO_3 for one minute.

3. Rinse the electrodes thoroughly with distilled water.

4. Place 75 ml of supporting electrolyte in a 150-ml beaker, position it on the titrator and add 50 $\mu\text{g/ml}$ chloride standard to the supporting electrolyte until the potential of the silver indicating electrode drops below the equivalence potential. Add 1 ml in excess.

5. Turn on the titrator and titrate to the equivalence potential.

6. Keep the cells immersed in 1% HNO_3 when not in use. They should never be permitted to dry in the air.

Reagents

1. Supporting Electrolyte — Add 50 ml of 70% reagent-grade nitric acid to 500 ml of absolute methanol and dilute to 1 liter with absolute methanol. It is important that the methanol be iron free; therefore, it should be purchased in glass containers.

2. Ascorbic Acid, 5% — Dissolve 5 grams of USP ascorbic acid in 100 ml of distilled water. This reagent should be made fresh daily.

3. Standard Cl^- Solution, 1000 $\mu\text{g/ml}$. Weigh 2.102 grams of reagent-grade KCl and dissolve in 100 ml of demineralized, distilled water. Dilute to 1000 ml in a volumetric flask.

4. Standard Cl^- Solution, 50 $\mu\text{g/ml}$. Transfer 10 ml of the 1000 $\mu\text{g/ml}$ standard to a 200-ml volumetric flask and dilute to volume with demineralized distilled water.

Analytical Procedures

Determination of chloride concentrations of under 300 μg per 75 ml of electrolyte:

1. Transfer 75 ml of the supporting electrolyte into a 150-ml beaker and position it on the beaker platform of the automatic titrator.

2. Adjust the potential of the supporting electrolyte to the equivalence potential.

3. Pipet a volume of the sample which will contain about 100 μg of chloride ion into the adjusted supporting electrolyte.

4. Add 5% ascorbic acid in 1 ml increments until no change in the potential of the indicating electrode is observed, then add 2 ml in excess.

NOTE: Although results obtained using ascorbic acid are satisfactory, the end point is not as sharp when it is used. Hence more precise results can be obtained if it is omitted when interfering ions are not present. The presence of interfering ions can be easily detected by adding 1 ml of 5% ascorbic acid to an aliquot of the sample in 75 ml of the supporting electrolyte. If the potential is not reduced, interferences can be assumed to be absent.

5. Turn the titrator on and immediately adjust the current to exactly 2.0 milliamperes.

NOTE: For low concentrations of chloride ion it is more convenient to set the generating current to exactly 2.0 milliamperes on the milliammeter and determine a factor which relates titration time to chloride concentration by titrating 2, 3, and 5 ml aliquots of the 50 $\mu\text{g/ml}$ chloride standard.

6. Continue the titration until the end point is reached, and record the elapsed time.

NOTE: The "anticipator" of the Beckman Automatic Titrator should be set so that the generating current is applied incrementally, as the equivalence potential is approached. The anticipation adjustment should be such that the titration is completed after about ten to thirty increments have been applied.

Determination of chloride concentrations of over 300 μg per 75 ml of electrolyte:

1. Transfer 75 ml of the supporting electrolyte into a 150-ml beaker and position it on the beaker platform of the automatic titrator.

2. Adjust the potential of the supporting electrolyte to the equivalence potential.

3. Transfer a volume of the sample which will contain about 1 mg of chloride ion into the adjusted supporting electrolyte.

4. Turn the titrator on and adjust the current to some value which will assure the completion of the titration in from 1 to 5 minutes.

NOTE: The higher the generating current is set, the higher the "anticipator" of the automatic titrator must be set to avoid over-titration.

5. Measure the voltage drop across the 10.33 ohm precision resistor with a potentiometer while the titration is in progress.

6. Continue the titration until the end point is reached and record the elapsed time.

7. Calculate the current using Ohm's Law.

8. Calculate the chloride concentration using Faraday's Law.

Performance Data

A standard aqueous feed sample was prepared by evaporating a production sample to dryness three times with nitric acid to remove any chloride contamination. The residue was then "spiked" with a known amount of chloride and rediluted to volume. A blank was also prepared in the same manner.

Precision data were obtained by analyzing the standard ten times by the proposed procedure. The data obtained appear in Table 10.1.

TABLE 10.1 Automatic Coulometric Titration of Chloride Ion in Aqueous Feed Standard

Cl ⁻ Taken (μg/ml)	Time (sec)	Cl ⁻ Found (μg/ml)
Blank	0.0	0.0
	2.1	2.0
	1.8	1.7
99.8	109.9	103
	107.5	101
	101.1	94.8
	104.0	97.6
	111.3	104
	105.7	99.1
	108.8	102
	103.5	97.1
	114.5	107
	101.4	95.1

A statistical analysis of the data in Table 10.1 was made. It was found that the average value was 100.1 ± 2.87 μg/ml, and no bias was detected. The precision of an individual result at the 95% confidence level was found to be ± 9.07 μg/ml.

To compare results on production-type materials, ten samples which had previously been analyzed by the turbidimetric method were analyzed by the proposed method and also by the polarized gold electrode method. The results obtained appear in Table 10.2. For those samples that could be analyzed by the three methods, the agreement was considered to be good.

TABLE 10.2 Comparison of Coulometric Method with Two Other Methods for Determining Chloride Ion Concentration (μg/ml)

Sample Number	Sample Type	Analytical Method		
		Turbidimetric	Coulometric	Polarized Gold Electrode
1	AF	52	49	63
2		225	181	*
3		265	251	*
4		315	328	*
5	HNO ₃	50	42	43
6		56	37	44
7		52	61	62
8		26	26	31
9		37	27	29
10		54	50	51

* Because of interferences it was impossible to analyze these samples by the present procedure using the polarized gold electrode potentiometric method.

Since it was impossible to get reliable results on three of the aqueous feed samples by the direct polarized gold electrode potentiometric method, it was decided to distill the samples so that there would be a comparison between the coulometric and polarized gold electrode method on the three samples. An attempt was also made to run the

99.8 $\mu\text{g/ml}$ aqueous feed standard directly. The curves obtained on the recording titrator for the distilled samples were still not completely satisfactory. The results obtained appear in Table 10.3.

TABLE 10.3 Comparison of Coulometric and Polarized Gold Electrode Methods for Determining Chloride Ion Concentration ($\mu\text{g/ml}$) in Distilled Aqueous Feed Samples

Sample Number	Sample Type	Analytical Method		
		Polarized Gold Electrode	Coulometric	Difference
4	AF	282	328	46
3		268	251	17
2		195	181	14
Std. 99.8 $\mu\text{g/ml}$		123	100	23
Blank		1.1	1.2	0.1

The applicability of the coulometric procedure to the determination of higher concentrations of chloride was proven by analyzing, by the proposed procedure, five samples that were analyzed previously by the Mohr method. The results appear in Table 10.4.

TABLE 10.4 Comparison of the Coulometric and Mohr Methods for Determining Chloride Concentration (%NaCl)

Sample Number	Analytical Method	
	Mohr Method	Coulometric
1	1.05	1.03
2	1.03	1.04
3	1.04	1.04
4	1.04	1.06
5	1.05	1.05

Conclusions

The coulometric determination of chloride ions may be applied to all types of samples received in the Analytical Department. The method is accurate, rapid, and adequately precise. Samples containing interfering ions may be analyzed without prior separation of the chloride ion, thus saving a substantial amount of time. The analytical results are free from biases that plague the turbidimetric method due to variation in operator technique. The instrumentation and methods described are now in routine use for the analysis of production samples.

Acknowledgment

The assistance of J. Kramer, who designed the power supply, is gratefully acknowledged.

References

- ¹C. J. Rodden. Analytical Chemistry of the Manhattan Project, pp. 295-6. New York: McGraw-Hill. 1950.
- ²P. G. Laux and E. A. Brown. Determination of Chloride in Uranium Bearing Materials by a Potentiometric Titration Method, USAEC Report NLCO-751. November 3, 1958.
- ³C. N. Reilly, W. D. Cooke and N. H. Furman. "Derivative Polarographic Titrations", Anal. Chem., 23: 1223. 1951.
- ⁴J. J. Lingane. "Automatic Coulometric Titration with Electrolytically Generated Silver Ion; Determination of Chloride, Bromide, and Iodide Ions", Anal. Chem., 26: 622. 1954.