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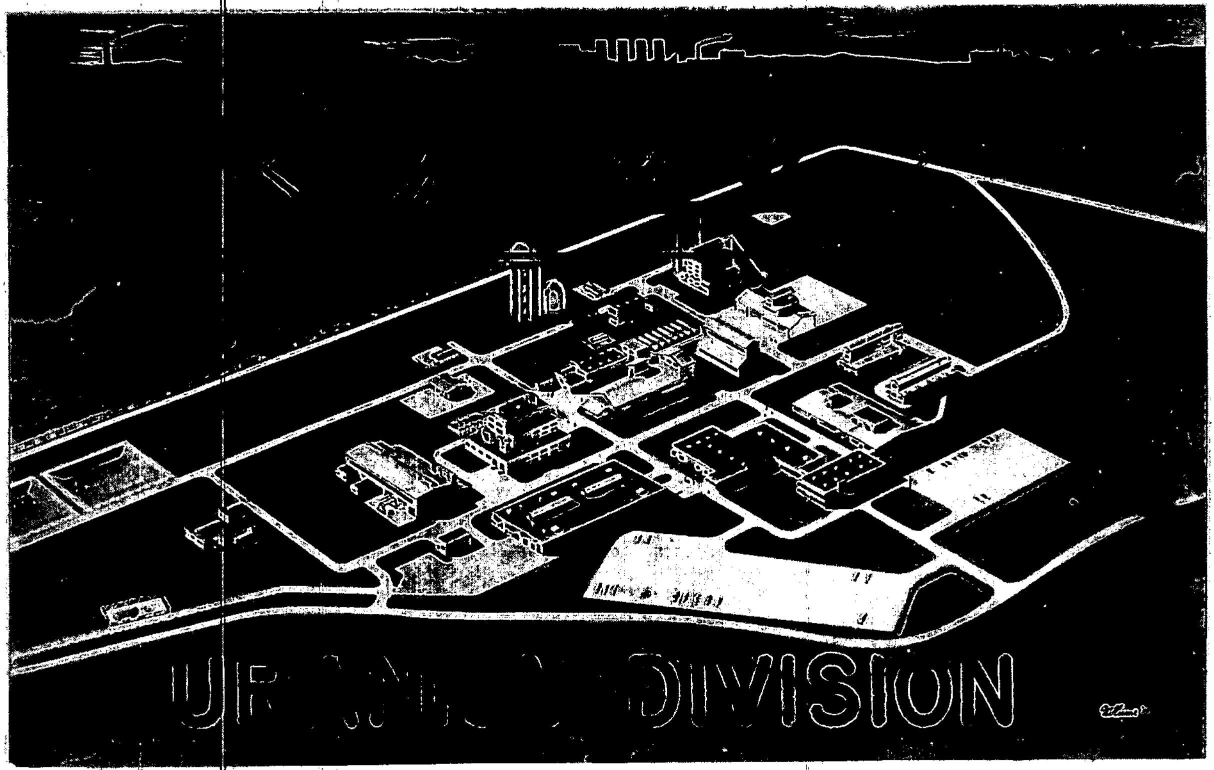

A.E.C. RESEARCH & DEVELOPMENT REPORT

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Date Issue: May 1, 1957

Report Number: MCW-1402
Subject Category: Technology - Feed Materials

PROCESS DEVELOPMENT QUARTERLY REPORT
PART II - PILOT PLANT WORK

edited by Nona Kuhlman

The work reported herein was done under the general supervision of the following

N. E. Berry
Technical Director

A. E. Ruehle
Assistant Technical Director

R. M. Edwards
Manager, Process Development

J. A. Fellows
Manager, Metallurgical Development

C. W. Kuhlman, Jr.
Manager, Laboratory Development

J. U. Shepardson
Manager, Analytical Laboratory

J. H. Yeager
Supertintendent, Production Department

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Mallinckrodt Chemical Works
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Report Number: MCW-1402
Date of Issue: May 1, 1957

Subject Category: Technology - Feed Materials
Title: PROCESS DEVELOPMENT QUARTERLY REPORT, PART II - PILOT PLANT WORK

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GENERAL SUMMARY

During the first quarter of 1957 work has continued in the MCW Process Development pilot plant on the operation of the TBP-hexane extraction cycle for the Weldon Spring refinery with particular interest directed toward a study of the variables affecting uranium purity and the testing of a low-acid flowsheet. The Metallurgical pilot plant has continued to work on the problem of hydrogen in uranium metal, forging and extrusion studies and fuel element studies.

Specific studies are summarized as follows (Roman numeral refers to the section on which the summary is based):

II. Eighteen feed material lots were tested to determine the gross solubility of uranium in digest liquors containing 1 *M* excess HNO_3. Seventeen of the lots demonstrated a solubility in excess of 440 g U/liter at 100°F. The other lot had a solubility of 400 g U/liter at 110°F.

III. A series of 13 runs has been made in the TBP-hexane extraction pilot plant in order to study the effect of various operating variables on product purity. In order to eliminate the variability of feed solutions, the feed was made up synthetically from NOK liquor for each run. The most important conclusions from this study are:

1. Wash efficiencies are influenced favorably by increased wash column height and also by the use of "new" rather than "old" solvent.
2. Product purity is higher when the product is removed at the center of a column rather than at a point near an interface.
3. No improvement in product purity resulted from increasing saturation from 91% to 100%.
4. Comparisons were made between NOK washing and water washing, between carbonate and lime solvent treatment, and between various ratios of organic to aqueous flows in the reextraction system. No significant differences in product purity resulted.

IV. Three ore concentrates were tested in the TBP-hexane extraction pilot plant at a 400 g U/liter, 1 *M* HNO_3 feed level. The data obtained indicate that satisfactory product purity and uranium recovery can be obtained in the Weldon Spring refinery using these feed concentrates at this uranium and acid level.

V. Various equipment changes in the pumper-decanter system of the TBP-hexane extraction pilot plant have reduced apparent back-mixing by a calculated amount of 30%.

VI. A tentative process has been developed for the recovery of uranium values from a mixture of residues from the dingot semi-works operation. About 40,000 lbs. of this mixture has been treated in this manner in the pilot plant with the resultant recovery of almost 100% of the uranium. Difficulties not yet overcome involve slightly high halide values in the refinery feed and incomplete washing of the final discard residue.

VII. A revised procedure in the purging of roasted slag lined 3300 pound dingots (namely, introduction of the helium at the bomb top and withdrawal from the bottom instead of the reverse flow used earlier), has provided both a marked improvement in metal yields and a slightly lower hydrogen content. Attempts to minimize slag roasting costs by using standard MgF_2 side liners in combination with roasted slag bottoms and caps have not been successful in achieving hydrogen levels as low as when 100% roasted slag liners have been employed. An increasing number of bomb treatments tend to show a correlation between low hydrogen content and long firing time; a more exact appraisal of the true contributing factors will be possible with the aid of a new electrical triggering procedure, for example that of the intrinsic influence of roasted slag with normal firing time. Initial results from a quantitative study of liner and charge permeabilities have indicated a favorable situation for purging in that the UF_4-Mg blend offers appreciably less resistance to helium flow than any of the types of liner.

VIII. The forging of dingots has provided low-hydrogen metal for test at HAPO in addition to un-modified metal as billets for gamma extrusion at Adrian and as rod for SRP slugs. Sectioning of forged dingots for suitable rolling lengths has been improved with the use of a revised shear-knife.

IX. Billet preheat temperatures of 1800°F and 1900°F at Adrian have solved the problem of partial rod incursions into the beta phase during gamma extrusions. The partial extrusion of graphite follower blocks provided an effective separation of rod from butt without need for sawing or shearing. The use of phosphate-base glass lubricants eliminated the early scoring of dies observed with "Dag" lubricants.

X. Further micronizing tests of UO_3 and UO_2 have indicated that chemical contamination can be held within acceptable limits by suitable coating of component micronizer parts. In cold compactions, the highest sintered density (94.5% of theoretical) has been obtained with UO_2 reduced from micronized UO_3 and lubricated with a small amount of Sterotex. Maximum densities in extruded solid rods have been achieved with micronized UO_2 plasticized with methyl cellulose.

XI. Plant tests have shown the hydrogen level in production derbies to average 3.5 ppm with a range of 1.0-5.3 ppm. The amount of H_2 in the derby in this range had no measurable effect on the H_2 content of the resulting ingots. The average H_2 content of the ingots was 0.76 ppm. Other factors such as type of graphite, mold dressing, and vacuum in the 13-300 micron range did not have a measurable effect on the H_2 content of the ingot.

Laboratory work for this quarter has been reported in a separate volume as *Part I, MCW 1401.*

GROSS SOLUBILITY OF URANIUM IN DIGEST LIQUORS

by

J. T. Krieg
R. H. Fariss

Summary

The gross solubility of uranium in digestions of Mallinckrodt feed materials was determined. The eighteen lots of digest liquors tested, with the exception of Edgemont (lot 7), were soluble to more than 440 g U/liter in 1*M* excess nitric acid at 100°F, and most ores were soluble to more than 500 g U/liter at these conditions. A 400 g U/liter, 1*M* HNO_3 solution of Edgemont (lot 7) had a freezing point of 110°F. Freezing points of digest liquors were not reproducible from lot to lot because of varying amounts of salt nitrates and other foreign ions in the feed material.

Introduction

A modified TBP-extraction flowsheet based on a 400 g U/liter, 1*M* HNO_3 digest liquor is being considered for adoption at Weldon Spring. The process is described in detail elsewhere in this Quarterly[1]. In conjunction with this proposed flowsheet a program was initiated in the pilot plant to determine the gross solubility of uranium in digestions of Mallinckrodt feed materials as a function of temperature and excess acid concentration.

Experimental Procedure

The uranium solubility in digestions of feed materials was measured by the following procedure:

Two pounds of feed material was digested in two or more liters of 30 wt. % HNO_3 for one hour at 200°F, after which the liquor was filtered and the solids discarded. The filtrate was boiled down until its freezing point was 150°F, and the concentrate was sampled and adjusted to 1*M* HNO_3. A freezing point was determined on the concentrate by slowly cooling to a temperature where solids first appeared. The solids were redissolved by heating, and the liquor was diluted with a measured quantity of 1*M* HNO_3. Another freezing point determination was made, and the procedure was continued until the liquor was diluted to a point where its freezing point fell below 65°F. The final solution was analyzed for U, HNO_3 and total NO_3^-. Compositions of intermediate liquors were determined by back calculating. In this manner data was collected relating uranium concentration to freezing points at constant nitric acid concentrations.

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[1] *Cf.* p. 55

Results

Freezing points of digest liquors as a function of temperature and excess acid concentrations are plotted in Figures 1, 2, and 3. Table I lists saturated digest liquors at 100°F in 1*M* excess HNO_3.

Table I

Solubility of Feed Materials

Feed Material	Gross Solubility of Uranium in 1*M* excess HNO_3 at 100°F g U/liter
Rifle Lot R-9	>452
Kerr-McGee Lot 93	618
Fernald Lot 8F52-151	453
Uravan Lot 506	indeterminate[a]
Monticello Lot A-44	640 at 200°F
Durango Lot 470	512
Vitro Lot 337	indeterminate[a]
Fernald Lot 336	666
Rare Metals Lot 6	indeterminate[a]
Anaconda Lot A-639	>654
Anaconda Lot C-640	513
Fernald Lot 8F52-154	500
Monticello Lot C-18	440
Climax Lot 214	744
Edgemont Lot 7	392
National Lead Lot 46	785
Moab Lot 11	642 at 150°F
Naturita Lot 336	643

[a] Indeterminate because of continued solid formation.

Discussion

Solubility data measured on some feed materials varied from lot to lot as demonstrated by data taken from several lots of Fernald feeds presented in Figures 2 and 3. Solubility data from

FIGURE 1

FREEZING POINT OF ORE DIGEST LIQUORS

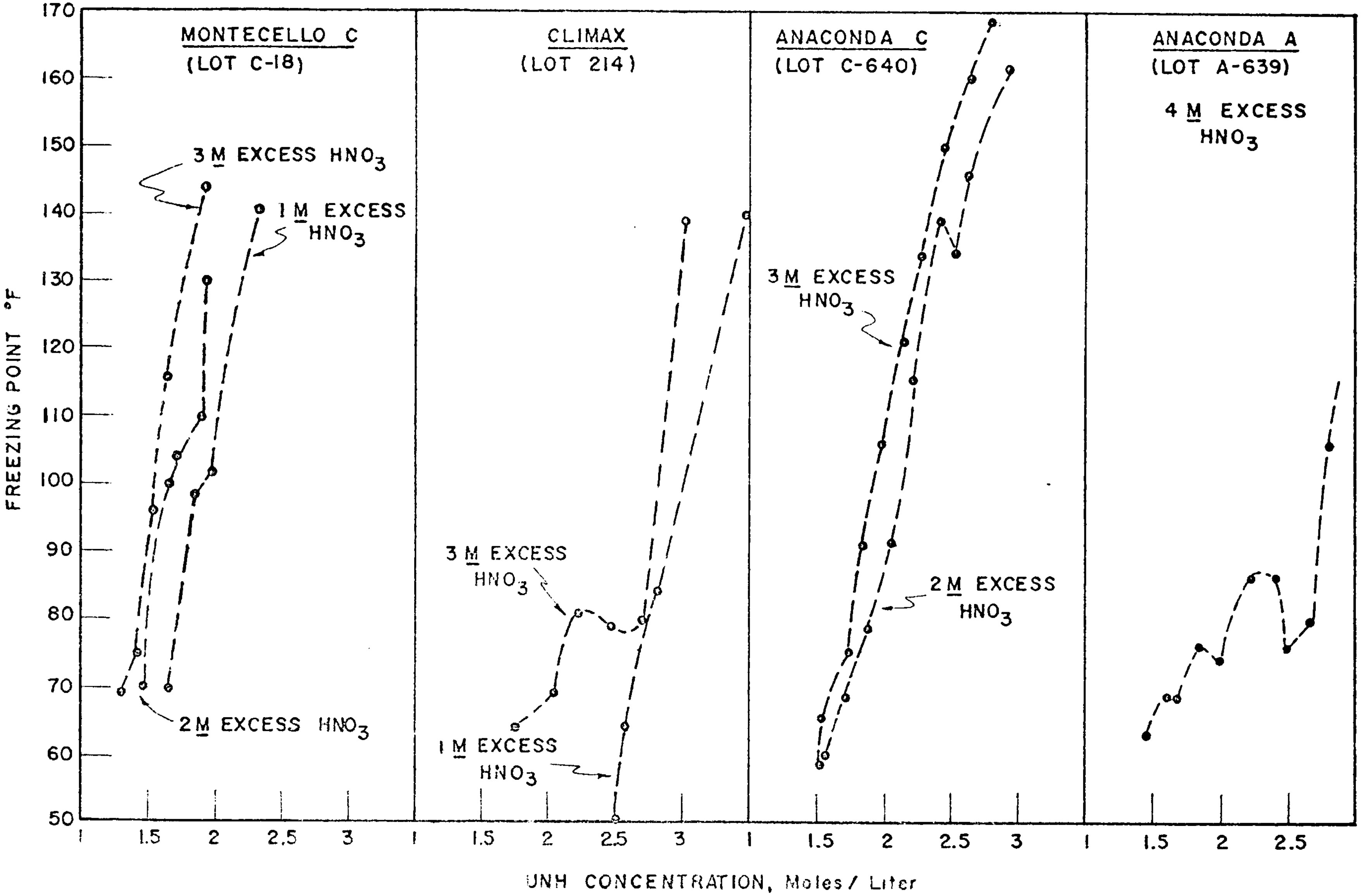


FIGURE 2
FREEZING POINTS OF ORE DIGEST LIQUORS

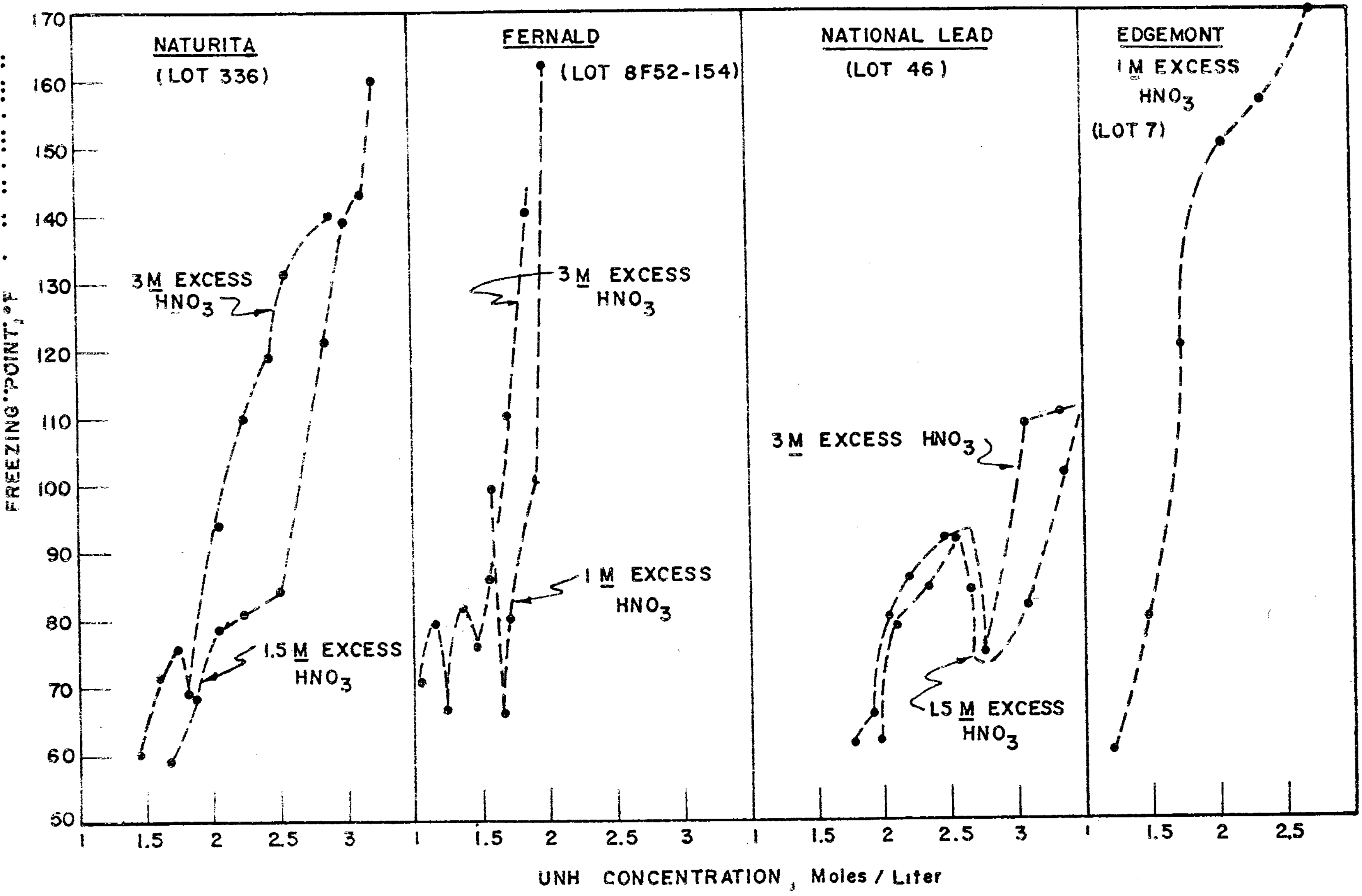
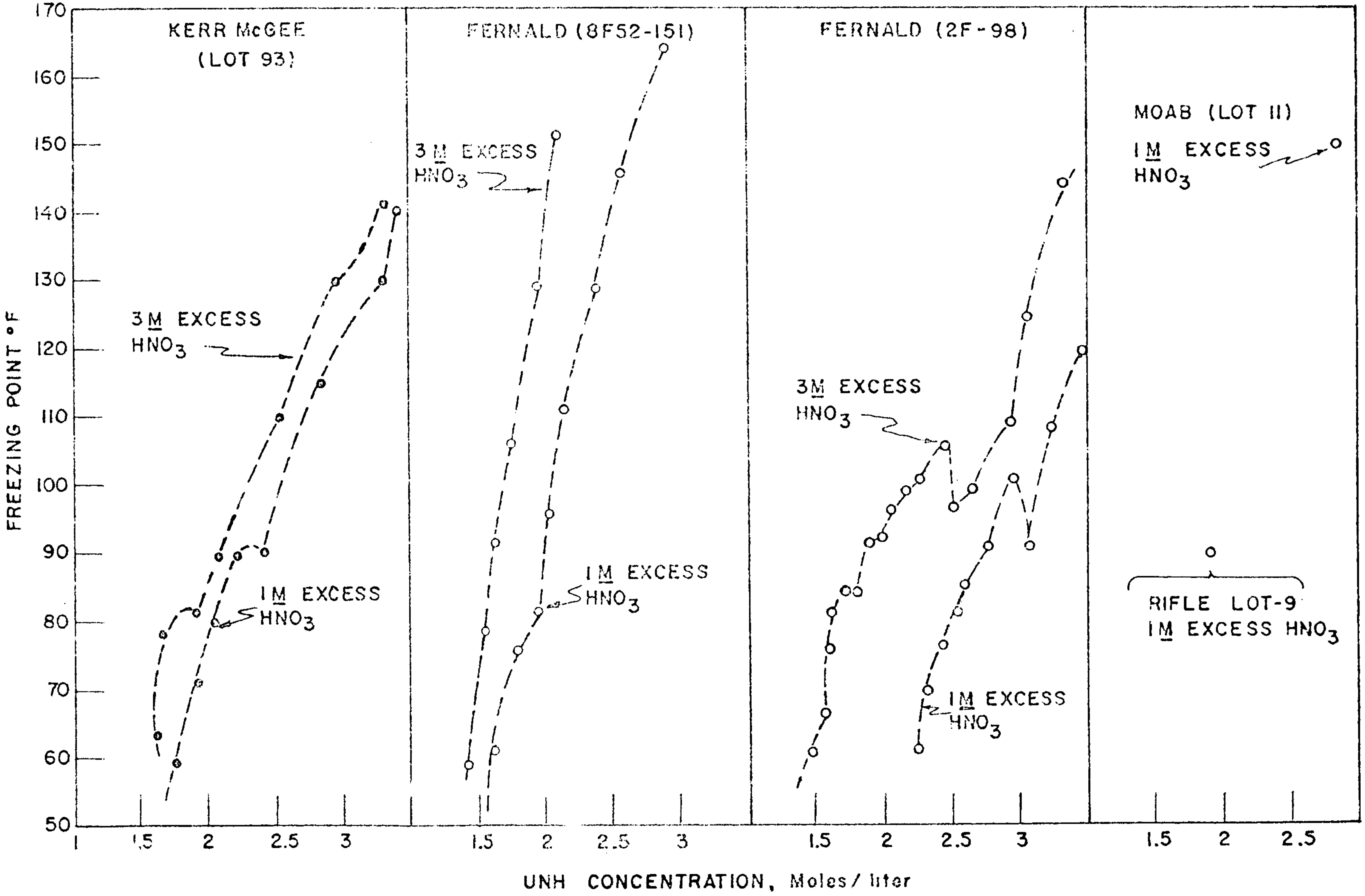


FIGURE 3

FREEZING POINT OF ORE DIGEST LIQUORS



some of the feed materials can be correlated in terms of the product of the concentration of uranyl ion and the square of the *nitrate ion concentration* as shown by Figure 4; however, this correlation was not universal for all the feed materials tested. While concentrating some digest liquors compounds containing uranium, vanadium, molybdenum, silicon, phosphorus, and/or iron precipitated out of solution and would not redissolve upon dilution. Feed materials in this category are tabulated in Table II. These precipitates all occurred at uranium concentrations well above 400 g/liter and so would not be expected to occur in normal 400 g U/liter, 1*M* HNO_3 feeds. Accurate freezing points could not be obtained from Uravan, Vitro or Rare Metals digest liquors because of continued irreversable solid formation during concentration.

Table II

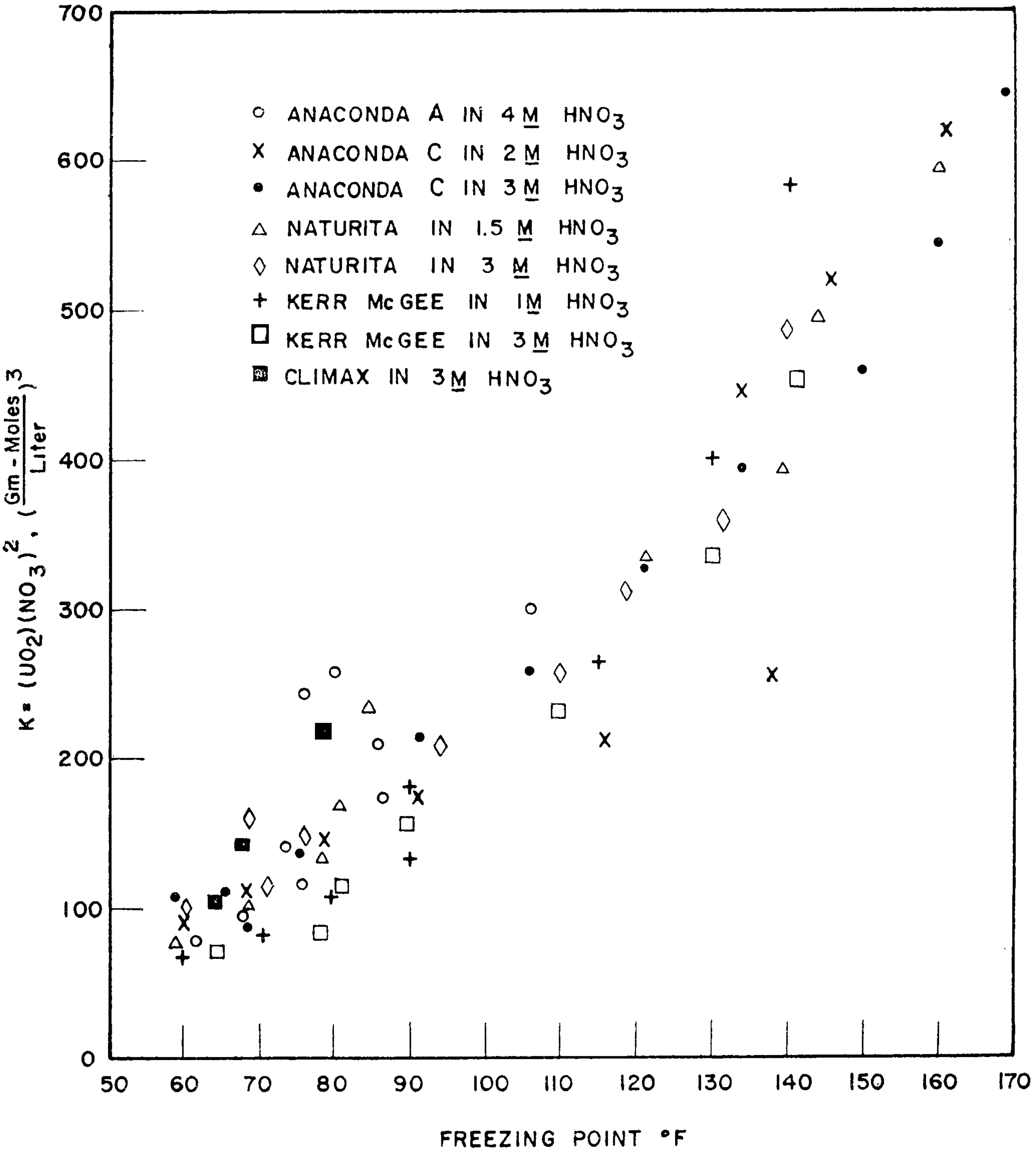
Feed Material Forming Insoluble Precipitates

Feed Material	Principal constituents of[a] insoluble precipitates
Climax Lot 214	U, V, Si
National Lead Lot 46	U, Mo, Si
Monticello Lot A-44	U, Si
Moab Lot 11	U, Si
Uravan Lot 506	U, V, P
Rifle Lot R-9	U, V
Vitro Lot 337	U, V, P
Rare Metals Lot 6	U, Si, P, Mo, Fe

[a] Spectrographic analysis.

FIGURE 4

CORRELATION OF FREEZING POINT DATA FROM SEVERAL DIFFERENT DIGEST LIQUORS



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PILOT PLANT STUDIES OF VARIABLES AFFECTING URANIUM PURITY IN A TBP-HEXANE EXTRACTION CYCLE

by

R. H. Fariss
J. T. Krieg
J. A. Soukup

I. Summary

The most important conclusions reached during the past quarter in the study of variables affecting uranium purity in a TBP-hexane extraction cycle are:

1. Wash column height was found to be a very important variable. The efficiency of impurity removal by washing increased drastically in going from 7 ft. to 14 ft. in column height, and further improvements were obtained at 28 ft.
2. A correlation appeared to exist between solvent quality, "age", as indicated by pulse column flooding characteristics, and wash efficiency. The increase in wash efficiency with column height between 7 ft. and 14 ft. was much less drastic with poor solvent than with good.
3. The most satisfactory results were obtained using 21 ft. as the wash column height, withdrawing product at the middle of the column. The superiority of this procedure to the 28 ft. column method suggests that isolation of product removal from column interfaces, insofar as possible, is very desirable.
4. No improvement could be detected from increasing uranium saturation of the TBP-extract from 91% to 100%. It may be possible therefore to use only one stage for saturation at Weldon Spring, leaving four for extraction.
5. No differences in product purity could be detected between runs with NOK or water washing.
6. No differences in product purity were detected between runs using lime or carbonate for solvent treatment.
7. Variation of product uranium concentration over the range of 46 to 136 g/l (by varying reextraction flow ratio), appeared to have no significant effect on purity.

8. As in previous tests, the excess acidity of the product was easily reduced to a value approaching that for the neutral ether extraction product.

9. Iron, cobalt, and copper removal by washing was very similar throughout the tests. Manganese and lead behaved similarly, but quite differently from the iron-cobalt-copper group. In all the impurity data from this test, only the magnesium wash removal efficiency (98-99.7%) with "new" solvent approximates that which might be theoretically expected from kinetic and equilibrium data. It is apparent that some mechanism other than normal kinetic or equilibrium limitations must govern washing efficiency, at least for iron, cobalt, copper, manganese, lead, and aluminum.

II. Introduction

A. Background

A TBP-hexane extraction process supplemented by an ether extraction cycle will be used at the Mallinckrodt Weldon Spring refinery to extract and purify uranium from ore concentrates. A flowsheet for the TBP-hexane process is presented in Figure 1. The process consists of: (1) an extraction step for removing the uranium from the feed material, (2) a wash step for decontaminating the uranyl nitrate, and (3) a reextraction step for recovering the uranyl nitrate from the solvent. Auxiliary steps include solvent clean up, and solvent removal from the raffinate and product liquors. Pilot plant development of this process has been progressing since early 1955 and has been reported in previous Process Development Quarterly Reports.

B. Objectives

During the past quarter pilot plant work has included an investigation of variables affecting product purity. The purpose of this study was to determine the relative importance of the following process variables on product purity.

a. Number of pumper-decanters used for saturation.

b. Height of wash column.

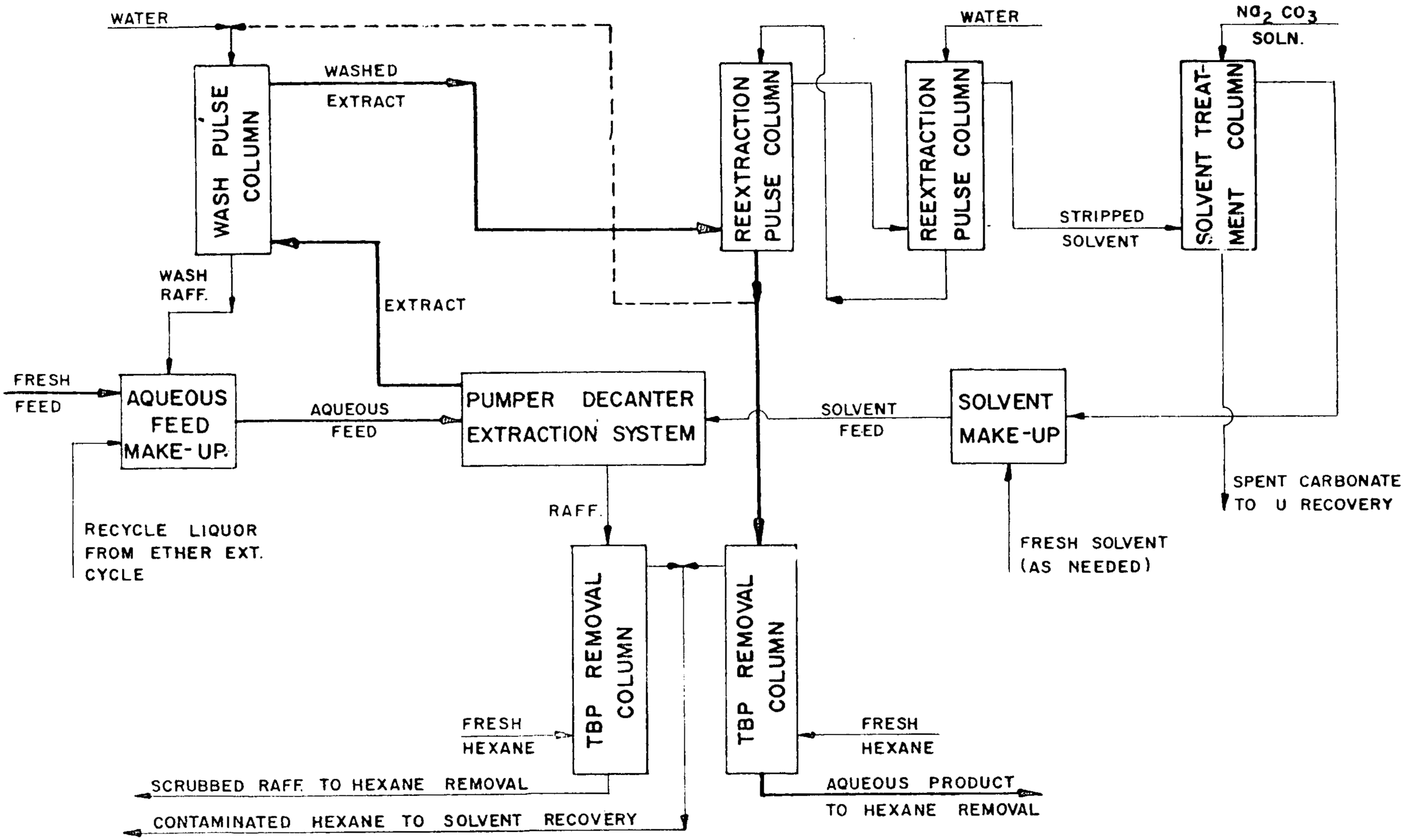
c. Washing agent (water or NOK).

d. Product concentration.

e. Type of solvent treatment.

FIGURE - I

TBP HEXANE EXTRACTION CYCLE



III. Description of Materials and Equipment

A. Solvent

The solvent used in these tests was 25% to 30% v/v TBP in a hexane diluent.

B. Feed

In an attempt to avoid variation in feed properties during these tests feed was made up synthetically to the following specifications:

(1) 200 g U/l (supplied by NOK)

(2) 3 *M* excess HNO_3

(3) 1 *M* $Mg(NO_3)_2$

(4) One part in ten of a stock solution of impurities obtained from the minor elements pilot plant. This solution is a concentrate of impurities found in certain ore concentrates

The latter ingredient was intended to supply a uniform source of impurities capable of extraction by TBP. The magnesium nitrate was included to supply reasonably heavy salting to intensify extraction of impurities. Thorium and rare earth contaminants were not present in the synthetic feed to any appreciable degree.

C. Equipment

(1) Pumper decanters

Four pumper-decanter units were used for the extraction step. The pumper-decanter system is the standard extraction equipment in the pilot plant and is described in detail in a previous report.[1]

(2) Pulse Columns

A schematic representation of the pilot plant pulse columns is shown in Figure 2. All columns contain 14 ft. of plate section and are operated

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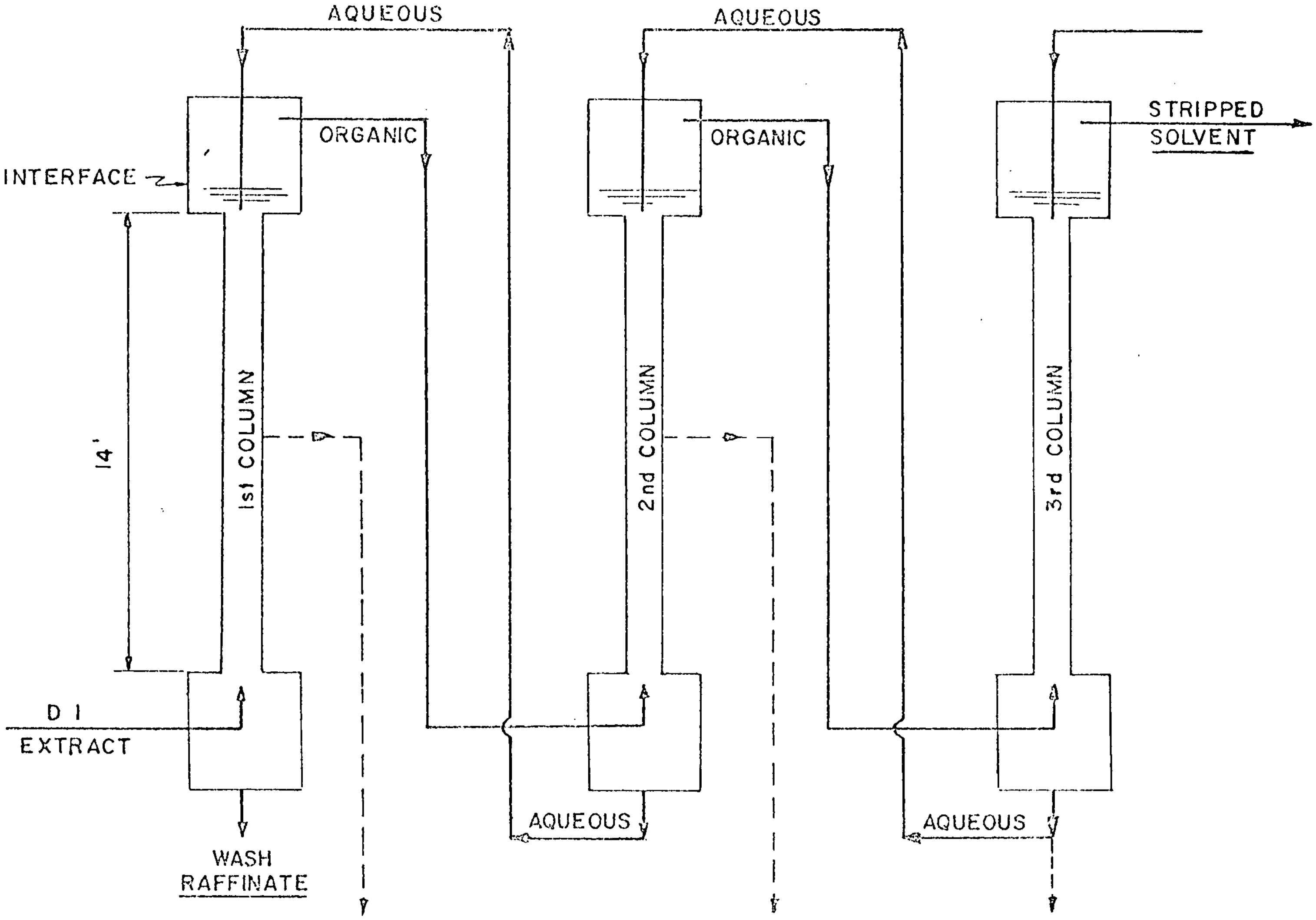
[1] Fariss, R. H., Hemkens, G. C., Krone, L. H., Paul, J. F., Powell, C. S., *Process Development Quarterly Report, Part II*, Mallinckrodt Chemical Works, *MCW-1381* (November 1, 1955), p. 9-102.

FIGURE 2

PILOT PLANT PULSE COLUMN ARRANGEMENT



PRODUCT (NOK) MAY BE REMOVED
FROM ANY OF THE DASHED LINES

with the interface at the top. The first pulse column depicted in Figure 2 is a 4 in. diameter glass column containing $^1/_{16}$ in. thick teflon-coated stainless steel plates with $^3/_8$ in. holes triangular spaced to give 33% free area. The plates are spaced 4 inches apart. The second pulse column is also 4 inch-diameter glass pipe; however, the plates differ from the preceding column in that they are $^1/_8$ in. thick teflon plates, $^1/_4$ in. holes and 23% free area. The third column is identical to the first except it is 5 in. diameter glass pipe. Pulse amplitudes in all columns were set at 2 inches. The columns were so interconnected that $^1/_2$, 1, 1$^1/_2$, or 2 columns could be used for washing, and the balance used for reextraction. The pulse frequency in the wash column (or columns) was 40 to 45 cycles/min.

IV. Experimental Procedure

The conditions employed in the various individual tests are listed in Table I.

Table I

Purity Test Experimental Program

Run No.	Number of units for saturation	Washing Agent[c]	Wash Column Height, ft.	Reextraction Ratio[a]	Solvent Treatment
H52	2	NOK	14	1.25	Carbonate
H53	2	NOK	7	1.25	Carbonate
H54	2	NOK	7	2.0	Carbonate
H55	2	NOK	7	0.8	Carbonate
H57	2	NOK	7	- - -[b]	Carbonate
H58	2	NOK	7	- - -[b]	Lime
H59	1	NOK	7	- - -[b]	Carbonate
H60	2	Water	14	1.25	Carbonate
H61	3	NOK		- - -[b]	Carbonate
H62	2	NOK	14	1.25	Carbonate
H67	2	NOK	28	1.25	Carbonate
H68	2	NOK	21	1.25	Carbonate
H69	2	NOK	14	1.25	Lime

(a) Reextraction ratio is the ratio of NOK flow to TBP extract flow.

(b) Reextraction ratio adjusted by density control of the aqueous effluent.

(c) Wash column flow ratio was A/O = 0.1/1

A. Saturation

The degree of extract uranium saturation was varied by using one, two, or three pumper decanter units ahead of the density control point. The extract saturations actually achieved are listed below:

Number of units for saturation	Extract Saturation, % of Theoretical Maximum
1	91
2	98
3	~100

Most of the tests were run with two units for saturation, which is the system heretofore proposed for Weldon Spring. The Weldon Spring design basis is 96% of theoretical maximum saturation.

B. Wash Column Height

Wash column height was varied from 7 ft. to 28 ft. by varying the number of pilot plant pulse columns used for washing from ½ to 2 (Refer to Figure 2). The number of columns used for washing depended on the exact location of the point of product (NOK) withdrawal from the system. It was possible to withdraw material at the middle of the first two columns as well as at the bottoms. Most runs employed either 7 or 14 ft. of wash column height. Weldon Spring is designed to provide 24 ft., but the system may be altered without major revision to provide 12 or 36 ft. of wash column height.

C. Washing Agent

Most of the runs were made using NOK (UNH) as the wash liquor, as shown in the Figure 2 flowsheet. One run was included, however, in which water was used for washing. In this case water was introduced at the top of the first (wash) column as well as at the top of the last column, and no NOK was carried from the second column to the first.

The Weldon Spring design is for water washing, but the system may be altered to NOK washing without major revision. The proposed advantage in NOK washing is the increase in product uranium concentration of ~15%.

D. Product Concentration

The concentration of uranium in the product (NOK) was varied by the use of different flow ratios of product to TBP extract. Ratio values of 0.5, 0.8, 1.25 and 2/1 were employed, but the 0.5/1 ratio was not successful due to the leakage of a large portion of the uranium through the reextraction process. Runs were also carried out using density control to adjust the reextraction ratio, which yielded an average ratio of 0.75/1. The product uranium concentration was varied from 46 to 136 g U/l as a result of these procedures.

E. Solvent Treatment

During most of the tests the recirculating TBP-hexane solvent was continuously treated with 0.5 lb/gal. Na_2CO_3 - 1.0 lb/gal. K_2CO_3 solution. For runs H58 and H69 the treatment was carried out with a 0.2 lb/gal. lime slurry. Use of lime rather than carbonate has been recommended as a possible means of improving purity.

F. Sampling

Tests were carried out for 48 hours each, with sampling to determine results during the last 36 hours of each test period. The following analyses were performed:

(a) Pumper-decanter extract
  Composite sample - U and HNO_3

(b) Stripped extract
  Composite sample - U

(c) Wash Raffinate
  Composite sample - semiquantitative spectrographic analysis.

  Samples covering three 12 hour periods each - U, HNO_3, Shotgun, semiquantitative spectrographic analysis of shotgun residue, colorimetric iron.

(d) NOK Product
  Start and end samples - U, HNO_3, pH, Spectro - photometric Mg.

(e) NOK Product after TBP removal
  Composite sample - semiquantitative spectrographic analysis.

  Samples covering 12 hour periods (three each) U, HNO_3, pH, colorimetric iron, spectrophotometric Mg, shotgun, semiquantitative spectrographic analysis on shotgun residue.

G. Analysis

For tracing of impurities other than nitric acid, the main source of data is the spectrographic analysis of the shotgun sample residues from the product and wash raffinate samples. Magnesium was found to be a major constituent of the shotgun sample residue in almost all cases, the concentration in this residue being too great for spectrographic measurement. Product (NOK) samples were analyzed for magnesium by the Method Development Section of the Analytical Laboratory using a spectrophotometric procedure. The magnesium concentration in the wash raffinate was too high for practical application of this procedure; these values were obtained from direct spectrographic analysis. The spectrophotometric method produced very consistent magnesium analyses on different samples from the same runs over the range of 30-300 ppm. At concentrations below 30 ppm wide variations were obtained, particularly below 10 ppm; however, five different samples were used for analysis in these cases, and the average result even for the lowest magnesium concentration obtained was probably accurate to within a factor of 2.

Iron determinations were all made by the standard colorimetric procedure which is applicable with fair accuracy over the entire concentration range encountered in this test. Use of shotgun sample residues for iron determination is considered unwise in view of the possibility that corrosion products may have resulted from boiling down the sample. The same is true for nickel and chromium.

The product acid concentrations were determined by pH measurements. This type of analysis is discussed in more detail in the Appendix. For tracing of impurities other than nitric acid, the main source of data is the spectrographic analysis of the shotgun sample residues from the product and wash raffinate samples. In some cases the impurity concentration was high enough to be detected by direct spectrographic analysis on the original sample. As a check on the data, comparisons of direct analysis and shotgun residue analysis have been made for all possible cases and are presented in the Appendix. Direct spectrographic analysis have been used in cases where the residue concentration has exceeded the upper limit of determination, and averages of direct and corrected shotgun residue results have been employed where both are available.

V. Presentation of Data

Impurity concentrations in the product (NOK) and wash raffinates streams for the various tests, determined as outlined above, are listed in Table II and Table III.

Table II

Impurity Concentration in the Product

Analyses-ppm on U basis

Run No.	Al ppm	Co ppm	Cu ppm	Mn ppm	Pb ppm	Fe ppm	Mg ppm
H52	11	0.4	1.6	- -	1.2	3	230
H53	- -	1.9	4	- -	1.2	4	120
H54	- -	1.7	4	- -	0.6	5	180
H55	- -	1.6	3	- -	1.2	- -	160
H56	- -	1.1	4	14	1.7	15	200
H57	- -	1.5	4	- -	2.4	20	140
H58	40	8	4	9	3.3	22	130
H59	9	11	5	9	2.8	7	170
H60	5	0.8	2	3	2.7	6	10
H61	14	24	16	9	2.6	26	140
H62	14	2.2	5	11	1.8	2.7	6
H67	8	2.3	1.9	8	1.3	4	2
H68	1.6	1.6	2	1.1	0.9	3	7
H69	9	3	2.5	20	2.8	7	15

Table III

Impurity Concentrations in Wash-Column Raffinate

Analyses - ppm on U basis

Run No.	Al ppm	Co ppm	Cu ppm	Mn ppm	Pb ppm	Fe ppm	Mg ppm
H52	- -	3	4	20	2.2	7	600
H53	26	2.6	1.8	15	3	6	600
H54	- -	2.7	4	40	2.1	10	900
H55	- -	1.4	3	14	1.2	- -	500
H56	- -	1.5	3	18	1.3	18	600
H57	- -	1.2	2	- -	1.2	11	350
H58	22	18	7	19	4	15	350
H59	40	24	26	30	6	23	600
H60	25	35	35	60	7	40	1100
H61	13	18	18	19	1.5	26	600
H62	50	35	35	35	6	23	1200
H67	35	120	50	30	7	70	2400
H68	50	120	50	20	6	100	3500
H69	70	60	35	22	8	70	2400

Shotgun analysis are listed in Table IV and Table V.

Table IV

Shotgun[a] Analysis on Product

Run	No. 1 %	No. 2 %	No. 3 %	Average
H52	-0.005	0.040	0.035	0.023
H53	0.026	.034	.056	.039
H54	.036	.022	.030	.029
H55	.024	.019	- -	.022
H56	.060	.067	.032	.053
H57	.028	.024	.036	.030
H58	.014	.008	.032	.018
H59	.048	.025	.034	.036
H60	.004	.016	.004	.008
H61	.034	.030	.028	.031
H62	.024	.011	.013	.016
H66	.010	.009	.013	.011
H67	.012	.002	.019	.011
H68	-0.003	.012	.003	.004
H69	0.019	.008	.023 and 0.032	.020

[a] A shotgun is the increase in neutron obsorbtion cross section due to impurities in the uranium sample. The shotgun of pure U_3O_8 is zero by definition.

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Table V

Shotgun[a] Analysis On Wash-Column Raffinate

Run	No. 1 %	No. 2 %	No. 3 %	Average
H52	0.064	0.227	0.057	0.116
H53	.105	.129	.144	.126
H54	- -	.197	.197	.197
H55	.075	- -	.055	.065
H56	.048	.024	.132	.068
H57	.035	- -	.026	.030
H58	.038	.033	.068	.046
H59	.114	.114	.239	.156
H60	.155	.149	.167	.157
H61	.091	.059	.043	.064
H62	.126	.105	.221	.151
H66	.051	.084	.058	.064
H67	.092	.054	.121	.083
H68	.024	- -	.032	.028
H69	.128	.068	.118 and 0.021	.084

[a] A shotgun is the increase in neutron absorbtion cross section due to impurities in the uranium sample. The shotgun of pure U_3O_8 is zero by definition.

Uranium material balances around the pulse columns have been calculated for each run, and results are shown in Table VI. It may be observed that the ratio of product flow rate to extract flow rate calculated from the uranium material balance agrees reasonably well with the value for the run specifications. This indicates that the experiments were run under good flow rate control.

Table VI

Distribution of Extracted Uranium

Run	Percent in Wash Raffinate[a] %	Percent in Stripped Extract %	Percent in Product[b] %	Aqueous/Organic	
				Calculated[c]	Nominal
H52	20.4	1.7	77.9	1.21	1.25
H53	17.5	0.0	82.5	1.30	1.25
H54	16.0	0.0	84.0	2.01	2.00
H55	17.8	0.1	82.1	0.72	0.80
H57	18.0	1.9	80.1	0.76	- - -[d]
H58	17.8	2.2	80.0	0.78	- - -[d]
H59	10.5	2.0	87.5	0.71	- - -[d]
H60	18.7	0.0	81.3	1.41	1.25
H61	18.5	0.0	81.5	0.75	- - -[d]
H62	22.2	0.0	77.8	1.23	1.25
H67	21.3	0.1	78.6	1.19	1.25
H68	20.8	0.1	79.1	1.12	1.25
H69	21.9	0.0	78.1	1.14	1.25

[a] Calculated assuming a wash ratio of $^{1}/_{10}$, Aqueous/Organic

[b] Calculated by difference

[c] Calculated by U material balance

[d] Ratio adjusted to hold aqueous phase from 2nd pulse column at 50 g U/l

Uranium and nitric acid analyses are tabulated below.

Table VII

Uranium and Acid Analyses

			Wash-Column Raffinate		Product		
Run	D-1 Extract U g/l	Stripped Solvent U g/l	U g/l	HNO_3 g/l	U g/l	pH	HNO_3[a] g/l
H52	106	1.8	216	72	68	2.13	0.18
H53	107	0.0	187	56	68	1.90	0.49
H54	110	0.0	176	50	46	2.08	0.36
H55	118	0.1	210	61	134	1.31	1.64
H57	114	2.2	205	23	120	1.57	0.86
H58	117	2.6	208	34	120	1.43	1.29
H59	111	2.2	117	77	136	1.20	2.18
H60	116	0.0	217	35	67	2.21	0.13
H61	108	0.0	200	25	117	1.80	0.37
H62	98	0.0	217	37	62	2.21	0.14
H67	103	0.1	219	37	68	2.08	0.24
H68	105	0.1	218	50	74	2.10	0.19
H69	104	0.0	228	42	71	2.14	0.17

[a] HNO_3 concentrations in the product were calculated from the U concentration and pH values.

VI. Discussion of Results

A. Variables Affecting Uranium Content of Wash-Column Raffinate

The effect of variables on uranium content of the wash column raffinate is summarized below in Table VIII. Changes in product concentration and type of solvent treatment were found to have negligible effect, hence results from runs in which these factors were varied have been averaged with others to obtain the results in Table VIII.

Table VIII

Effect of Variables on Uranium Removal in Wash Column

Effect of column height

(2 units for saturation, NOK wash)

Wash Column Height ft.	Percent U lost to Wash Raffinate %
7	17.4
14	21.5
21	21.1
28	21.1

Effect of saturation

(7 ft. wash column, NOK wash)

No. of Units for saturation	Percent U lost to Wash Raffinate %
1	10.5
2	17.4
3	18.5

NOK *versus* water wash

(14 ft. wash column, 2 units for saturation)

Washing Agent	Percent U lost to Wash Raffinate %
Water	18.7
NOK	21.5

The most significant variable affecting wash-column raffinate uranium content was found to be the degree of saturation of the extract from the pumper decanters. This effect has been noted previously.[2] Increasing the number of saturation units from one to two (actual extract uranium saturation from 91% to 98%) increased uranium removal from 10 to 18%. There was little further removal due to use of three saturation units.

The uranium content of the wash raffinate was found to be very slightly greater with NOK washing than with water washing. With NOK, it increased slightly on going from 7 ft. to 14 ft. in wash column height, but no further increase occured with taller columns. The maximum uranium loss to the wash raffinate for all of the various conditions was about 21%.

B. The Effect of Variables on NOK Acidity

The effect of variables on the acidity of the product (NOK) is summarized in Table IX.

Table IX

Effect of Variables on Acidity of NOK Product

Effect of column height

(2 units for saturation, NOK wash)

Wash Column Height ft.	NOK Acidity g HNO_3/gU
7	0.009
14	.0024
21	.0026
28	.0035

Effect of uranium saturation in decanter extract

(7 ft. wash column, NOK wash)

No. of units for saturation	Saturation % of Theoretical Maximum	NOK Acidity g HNO_3/g U
1	91	0.016
2	98	.009
3	~100	.0032

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[2] *Ibid.* p. 62-65

Table IX (cont)

NOK *versus* water wash

(14 ft. wash column, 2 units for saturation)

Washing Agent	NOK Acidity g HNO_3/g U
Water	0.0024
NOK	.0019

As in the case of uranium removal, changes in product concentration and type of solvent treatment were found to have negligible effect, and results from runs in which these factors were varied have been averaged with others.

The acidity of the product, in g excess HNO_3/g U, could be reduced to 0.002 - 0.003 by using 14 ft. of wash column with an NOK wash and two units for saturation. Use of more wash column height, or water for washing, caused no significant changes. A similar acidity was produced by using three units for saturation with only a 7 ft. wash column, but substantially higher acidities occurred at 7 ft. with less saturation. By way of comparison, the neutral ether system product at Mallinckrodt's Destrehan plant has been found to contain 0.001 - 0.002 g excess HNO_3/g U.

C. Variation of Pumper-Decanter Extract Purity Level

As pointed out previously, the main object in using a synthetically prepared feed for these tests was to insure a uniform feed throughout the test series. This presumably should yield a uniform extract from the pumper-decanters except for those cases in which saturation was varied. Although direct analysis of the D-1 extract for general contamination were not attempted, values for the concentrations of various impurities in this stream have been calculated from the product and wash raffinate analyses by assuming that all impurities in the solvent are removed in the pulse columns. Results of this calculation are listed in Table X.

Table X

Changes in Pumper-Decanter Product Purity During Test

Run No.	Impurity concentration in D-1 extract, (ppm on U basis) Mg ppm	Co ppm	Fe ppm	Cu ppm	Al ppm	Po ppm	Mn ppm	Shotgun %
H52	310	1.0	4	2.1	- -	1.4	- -	0.043
H53	210	2.1	4	4	- -	1.6	- -	.054
H54	310	1.9	6	4	- -	0.9	- -	.058
H55	220	1.6	- -	3	- -	1.4	- -	.029
H57	180	1.5	18	4	- -	2.2	- -	.030
H58	170	10	21	5	40	3	11	.023
H59[a]	220	12	9	7	12	3	11	.048
H60	210	7	12	8	9	4	14	.036
H61[b]	230	23	26	16	14	2.4	11	.037
H62	260	9	7	11	22	2.7	16	.045
H67	510	27	18	12	14	2.5	13	.027
H68	750	27	23	12	12	2.0	5	.009
H69	530	15	21	10	22	4	20	.033

[a] One unit for saturation

[b] Three units for saturation

The data in Table X indicate that a constant D-1 extract composition was not achieved. In particular, the general level of contamination was noticeably higher starting with run H58, the difference being especially apparent for Co, Mn, and Al. The shotgun results do not show any significant trend.

A difference in color was noticed between batches of impurity-concentrate stock solution used for feed preparation. It is suspected that the change in D-1 extract contamination during the test series resulted from variation in the composition of the liquor used as an impurity source.

D. Effect of Saturation on Pumper-Decanter Extract Purity

The effect of saturation on D-1 extract purity is given in Table XI. The values for one and three-unit saturation, runs H59 and H61 respectively, have been compared with the average for two-unit saturation runs, H58, H60, H62.

Table XI

Effect of Saturation on D-1 Extract Purity

Impurity	Impurity Concentration in Extract (ppm on U basis) No. of units for saturation 1 ppm	 2 ppm	 3 ppm
Mg	220	210	230
Co	12	9	23
Fe	9	13	26
Cu	7	8	16
Al	12	24	14
Pb	3	3	2
Mn	11	14	11

The comparison in the above table does not support the generally accepted thesis that increasing saturation improves extract purity. Over the saturation range of 91-100% considered here there is no indication of such a trend; if anything, the purity appears to be slightly poorer at the higher saturations. This is shown by the following average relative impurity levels, obtained by (1) computing the average concentration of each impurity in the pumper-decanter extract for runs H58 - H62, (2) computing the ratio to the average for each impurity in each run, and (3) averaging for each run:

No. of Units for Saturation	Run No.	Average Relative Impurity Level
1	H59	0.83
2	H60	0.87
2	H62	0.98
2	H58	1.07
3	H61	1.25

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E. The Effect of Solvent Condition

One of the most disturbing aspects of these purification studies is the apparent correlation between (1) the quality of the solvent as measured by pulse column flooding characteristics[3], and (2) the efficiency of impurity removal by pulse column washing. Just prior to the start of the purification test series, a flooding test indicated that the pilot plant solvent had the standard "poor" flooding characteristics; *i.e.*, a maximum reextraction rate of 3100 gph/sq.ft. This is the condition referred to as "old". At the conclusion of run H62, following approximately ten tests with synthetic feeds, the solvent was found to have the standard "good" flooding characteristics (maximum rate 3600 gph/sq.ft), *i.e.*, was in "new" condition. The test was repeated at the end of the purification series, after run H69, but no further change was detected.

Table XII shows a comparison of the wash efficiency for run H52, immediately after the solvent was found to be "old", with the efficiency for run H62, just before the solvent was found to be "new". These two runs were identical operations except for timing, and, presumably, solvent quality. Wash efficiency as used here is defined as the fraction of the total impurity recovery from the solvent in the pulse columns which reports in the wash column raffinate.

Table XII

Effect of Solvent "Age" on Wash Efficiency

2 units for saturation, NOK wash, 14 ft. wash column

	Percent Impurities Removed	
Impurity	Old Solvent %	New Solvent %
Mg	42	98
Co	68	83
Fe	39	72
Cu	41	73
Pb	33	46

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[3] Krieg, J. T., Fariss, R. H., Soukup, J. A., *Process Development Quarterly Report, Part II* Mallinckrodt Chemical Works, *MCW-1400* (February 1, 1957), p. 22-27.

It may be observed that the solvent showing good flooding characteristics, *i.e.*, "new", also yielded a much higher wash efficiency.

Unfortunately, no data were obtained which definitely fix the point at which the solvent reverted from "old" to "new" condition. It may be that the reversion occurred gradually due to slow purging of solvent contaminants from the system. In run H58, in which lime was used for solvent treatment, approximately 2 g/l of uranium entered the solvent-treatment column in the solvent. This caused the formation of a gummy precipitate in the treatment column which soaked up solvent. Frequent changes of lime were necessary, and considerable quantities of solvent were discharged in the spent lime-precipitate mass. It is possible that this precipitate may have acted as a trap for solvent contaminants and thus purged the system.

A study of the data for runs H53 through H59, and H61, comprising the 7 ft. wash column tests, shows no time trend for wash efficiency. Since this is the period during which the solvent is believed to have changed quality, it appears the solvent "age" has negligible effect on wash efficiency under these relatively inefficient conditions.

F. The Effect of Wash Column Height

The effect of column height on wash efficiency is shown by the compilation in Table XIII. Run H52 was the only one made during the early part of the test series with other than a 7 ft. wash column. With this exception, then, the data for wash columns of 14 ft. to 28 ft. probably represent the performance of good solvent. In the discussion of wash efficiency which follows, run H52 has been omitted from the compilation except when solvent age is discussed. All data for 7 ft. columns have been included, however, since no effect related to solvent age could be detected for this case.

Table XIII

Effect of Column Height on Wash Efficiency

2 units for saturation, NOK wash

Impurity	Percent Impurity Removed 7 ft. Col. %	 14 ft. Col. %	 21 ft. Col. %	 28 ft. Col. %
With "old" solvent:				
Mg	43	42		
Co	22	68		
Fe	19	39		
Cu	16	41		
Al	10	- -		
Pb	27	33		
Mn	31	- -		
With "new" solvent:				
Mg	43	98	99.3	99.7
Co	22	83	95	93
Fe	19	72	90	82
Cu	16	73	87	88
Al	10	59	89	54
Pb	27	49	64	59
Mn	31	35	83	50

With the solvent in poor condition, there appears to be a general improvement in wash efficiency on going from 7 ft. to 14 ft. of column height. The increase is much more drastic with good solvent. A further but less drastic increase may be noted for good solvent on going from 14 ft. to 28 ft. of column height. The results with 21 ft. are generally superior to those for 28 ft. The reversal of wash efficiency between 21 ft. and 28 ft. of column height is of particular interest. It is difficult to see how such an effect could occur if total wash column were the only variable. This result indicates that the relative position of interfaces and aqueous removal points may be of interest.

It has generally been observed in the TBP system that solid material, usually dark in color, collects at interfaces. This material contains a concentrated collection of impurities. In operation with 14 ft. or 28 ft. of column height, using either a full double or single column, the product is removed at the bottom of one column while an interface is located at the top of the preceding column Thus, material floating around the interface could easily be carried out the top of the wash column and be swept out the bottom of the next column with the product. In operation with 21 ft. of column, however, product is withdrawn at the middle of the second column, a point far removed from all interfaces.

It may be observed that the elements (impurities) under consideration (Table XIII) fall into four behavior groups. Mg stands alone as being more efficiently removed than the other elements in every case. (Mg was also present in the feeds in much greater concentrations). Co, Fe, and Cu are very similar in behavior, with the big difference occurring between 7 ft. and 14 ft. of column height. Fe and Cu removal is almost the same throughout, with Co removal being slightly superior. Al shows a similar trend to Co, Fe, and Cu, but is less effictively removed. Pb and Mn removal, while improving with increased column height, shows no drastic improvement between 7 ft. and 14 ft. as do the other impurities. These elements are removed more effectively at 7 ft. than Co, Fe, and Cu, but less effectively than these elements at other heights.

G. The Effect of Extract Uranium Saturation on Wash Efficienty

The effect of saturation on wash efficiency is shown in Table XIV. There appears to be a slight trend in the direction of poor impurity removal for Co, Fe, Cu, Al, Pb, and Mn as saturation is increased. The opposite effect is noted for Mg, however.

Table XIV

Effect of Saturation on Wash Efficiency

7 ft. wash column, NOK wash

	Percent Impurities Removed		
	No. of units used for saturation		
Impurity	1 %	2 %	3 %
Co	20	22	14
Fe	28	19	18
Cu	38	16	20
Al	34	10	17
Pb	20	27	12
Mn	28	31	32
Average of the above	28	21	19
Mg	29	43	49

H. The Effect of Washing Agent on Washing Efficiency

Table XV shows a comparison of wash efficiencies with water and NOK as the washing agents. No significant difference in trend can be noted.

Table XV

Effect of Washing Agent on Wash Efficiency

Impurity	Percent Impurity Removed Water Wash %	 NOK Wash %
Mg	96	98
Co	91	81
Fe	60	72
Cu	80	73
Al	53	59
Pb	37	46
Mn	82	35

I. Other Variables Having No Effect on Product Purity

Variation of the product uranium concentration by varying column flow ratios has no effect on product purity. The type of solvent treatment (carbonate *vs.* lime) also had no effect on purity.

J. Effect of Variables on Shotgun Analysis

The effect of variables on the shotgun analysis of the NOK product has been summarized in Table XVI. The variance in shotgun results for any given set of conditions is too great to permit making fine distinctions. Fortunately, however, the shotgun results support the conclusions reached from a consideration of individual impurity behaviour.

Table XVI

Effect of Variables on Shotgun Analysis of NOK Product

Effect of solvent age:

(2 units for saturation, NOK wash, 14 ft. wash column)

Solvent Age	NOK Shotgun %
"old"	0.023
"new"	0.017

Effect of wash column height:

(2 units for saturation, NOK wash)

Wash Column Height ft.	NOK Shotgun %
7	0.028
14	0.017
21	0.004
28	0.011

Effect of saturation:

(7 ft. wash column, NOK wash)

No. of units for saturation	NOK Shotgun %
1	0.036
2	0.028
3	0.031

NOK *vs.* water wash:

(14 ft. wash column, 2 units for saturation)

Washing Agent	NOK Shotgun %
Water	0.008
NOK	0.017

VII. Appendix

A. HNO_3 Analyses on Uranium Product Liquor

A considerable descrepancy was found between excess nitric acid concentrations in the NOK product as measured by the normal laboratory titration technique, and as calculated from pH and U concentrations. A comparison of results from these two methods is shown in Table A-1.

Table A-1

Comparison of Product Acid Analyses

Run	Acid Concentration By Acid Measurement g/l	Acid Concentration By pH g/l
H52	13	0.18
H53	6.0	0.49
H54	5.5	0.36
H55	11	1.6
H57	-0.3	0.86
H58	-1.5	1.3
H59	-1.9	2.2
H60	0.1	0.13
H61	0.81	0.37
H62	0.1	0.14
H67	-1.3	0.24
H68	<0.3	0.19
H69	<0.3	0.17

In four cases (H60, H62, H68, and H69) the agreement between acidities as determined by the two methods is excellent. The other nine cases show no agreement whatsoever. Some indication of relative precision may be obtained by comparing the product acidities in runs H52, H62 and H69, which were carried out under essentially identical conditions. The pH measurements gave values of 0.18, 0.14, and 0.17 g HNO_3/1 for these cases. The direct acid measurement yielded 13, 0.1, and <0.3 g/1. On the basis of these results, at least, the pH method appears to offer much superior precision. The pH-U-HNO_3 curves used for the calculation of acidity were prepared from synthetic samples obtained by adding measured amounts of reagent grade acid to a uranyl nitrate solution determined by careful analysis to be approximately of stoichiometric composition. A curve relating pH to UNH and HNO_3 is presented in Figures A-1 and A-2

B. Analysis of Impurities

As a check on the analytical data, comparisons of direct analysis and shotgun residue analysis have been made for all possible cases. Results of this comparison are listed in Table B-1.

Table B-1

Comparison of Direct Spectrographic Analysis With Analysis of Shotgun Residue

Impurity	Average Shotgun Recovery %	Average Deviation Factor[a]
Al	8	3.7
Co	13	3.0
Cr	>100	- - -
Cu	40	3.6
Mn	12	2.7
Ni (NOK)	77	1.7
(Wash raffinate)	>100	- - -
Pb	22	5.0

[a] Geometric mean of the ratios of the individual recoveries to the average recovery.

The data in Table B-1 indicate very low recoveries in the shotgun residue for Al, Mn, Co, Pb, and Cu, ranging from 8% to 40%. Nickel recovery averaged 77% on NOK samples, but exceeded 100% by a considerable amount on the more acid wash raffinate samples. It seems likely that the excess Ni content of the wash raffinate shotgun residues resulted from corrosion during sample boil down or in the shotgun test itself. There is evidently less corrosion from NOK samples, but, due to uncertainty as to the amount, no attempt has been made to employ the Ni data in analysis of purification test results. Chromium recovery exceeded 100% by a considerable amount, and, as with Ni, no attempt has been made to use the Cr data.

FIGURE A-1

THE EFFECT OF NITRIC ACID AND URANYL NITRATE ON pH IN AQUEOUS SOLUTION

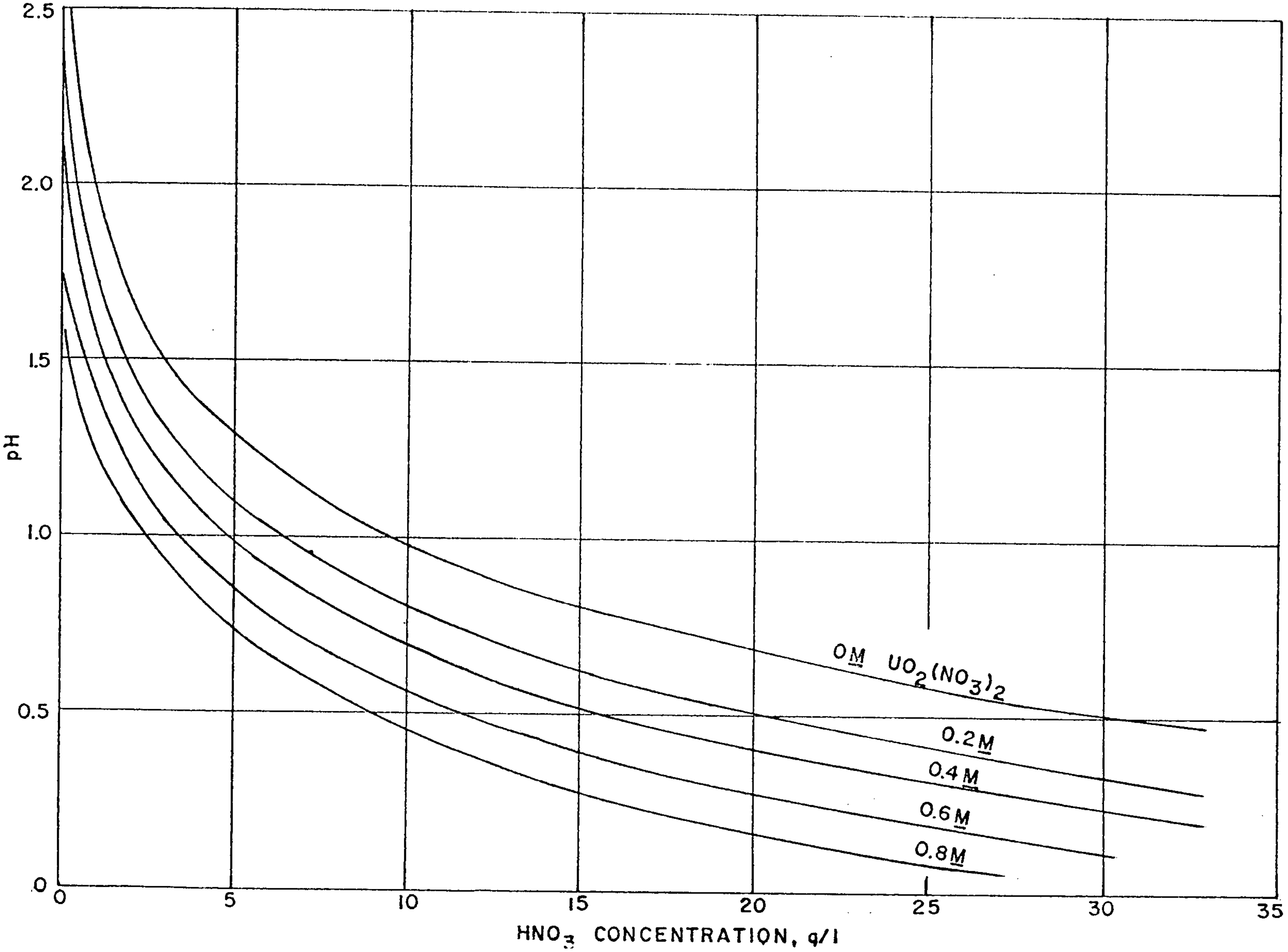
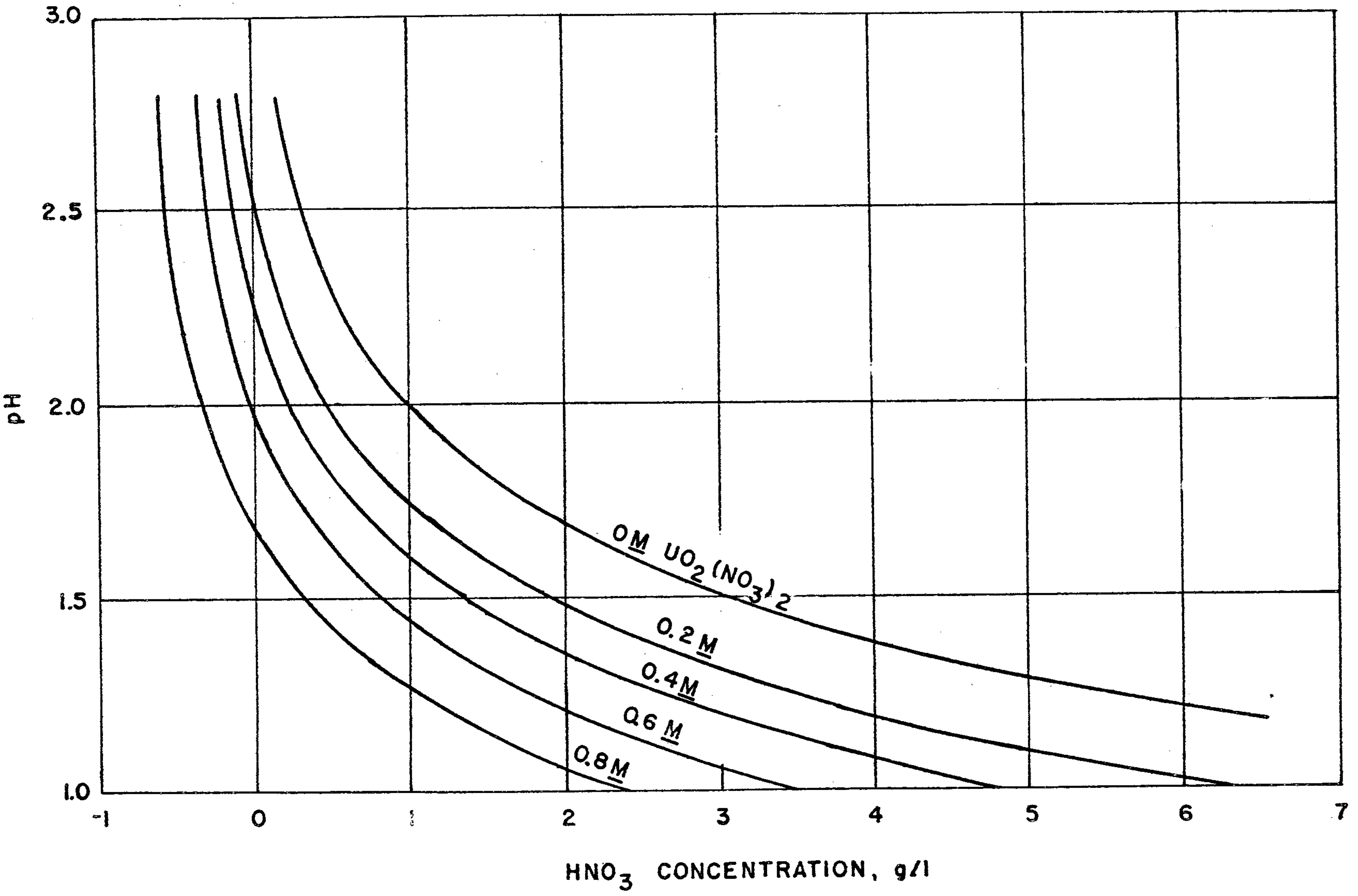


FIGURE A-2

THE EFFECT OF NITRIC ACID AND URANYL NITRATE ON pH IN AQUEOUS SOLUTIONS



The poor precision of the shotgun recovery and/or the spectrographic analysis is shown by the large deviations from average also listed in Table B-1 In spite of the evident low precision, the Al, Co, Cu, Mn, and Pb data have been utilized by applying the average recovery factors of Table B-1 to the shotgun residue analyses.

PILOT PLANT TESTING OF A LOW ACID FLOWSHEET FOR THE TBP-HEXANE EXTRACTION PROCESS

by

J. T. Krieg
R. H. Fariss
J. A. Soukup
D. J. Nerrow

I. Summary

Anaconda A (acid leach), Anaconda C (carbonate leach), and Moab feeds were run through the TBP-extraction pilot plant on a low-acid flowsheet based on a 400 g U/liter, 1 *M* HNO_3 digest liquor. With minor equipment modifications no serious mechanical difficulties were encountered.

Uranium losses to the raffinate were low using Anaconda A and Anaconda C feeds (0.01% and 0.036% respectively[1]); however, uranium losses from Moab feeds were 0.59% in a four-decanter system (one unit for saturation). With the five-decanter system at Weldon Spring, much lower waste losses should be obtainable.

With the exception of sodium contamination product purity was excellent when running Anaconda A and Moab feeds with shotguns[2] averaging 0.016% and 0.01%, respectively. When using Anaconda C feeds, shotguns on the product averaged 0.06%; however, when the wash column height was increased from 14 feet (1 column) to 21 feet (1 ½ columns) product shotguns decreased to 0.004%.

TBP carryover in the raffinate stream was too high (>0.05 g/l) from a safety standpoint if the raffinate were to be boiled down. More work is necessary to improve the efficiency of the raffinate TBP-removal system.

II. Introduction

The design of the TBP-hexane extraction process for Weldon Spring was based on a digest liquor (extraction feed) containing 200 g U/l and 3 *M* HNO_3. This process is described in

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[1] Percent of total uranium in the feed.

[2] A "shotgun" is the increase in neutron capture cross-section due to impurities in the product. The shotgun of 100% pure U_3O_8 is zero.

more detail elsewhere in this quarterly.[3]

A modified flowsheet based on a digest liquor containing 400 g U/liter and 1 *M* HNO_3 has been tested in the pilot plant during the last quarter. The purposes of the low-acid flowsheet are to reduce operating costs by lowering nitric acid requirements and to increase refinery capacity by increasing the amount of uranium processed per unit volume of feed. Comparison of the two flowsheets is made in Figure 1 and Figure 2. The flowsheets differ only in the extraction and wash steps.

Pilot plant tests were made with several feed materials employing the low-acid flowsheet.

III. Description of Equipment and Materials

A. Equipment

The pilot plant equipment which was used in testing the low-acid flowsheet was essentially the same as that used in previous tests on the "standard" flowsheet and is described in detail in previous progress reports; however, some minor equipment changes were made and are described below.

1. Interface Control

At times the aqueous-organic interface-control float in the last decanter could not "see" the interface because of an accumulation of emulsion. The interface-control float system was modified as shown in Figure 3. The static head in the last decanter, being a direct function of interface level, was used for controlling the rate of raffinate removal and hence the interface in the last decanter. This modification resulted in smoother control and reduced the tendency of the interface to emulsify.

2. Air Trap

The air vent in the raffinate recycle line (Figure 3) was installed to degas the raffinate. Formerly air introduced with the recycled raffinate aggravated emulsion formation.

3. Decanter Length

The length of the last decanter was increased from three feet to five feet to allow for

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[3] *Cf.* p. 21

FIGURE I

LOW ACID FLOWSHEET
FOR THE TBP-EXTRACTION CYCLE
(NOK WASH; FLOW RATES ARE RELATIVE)

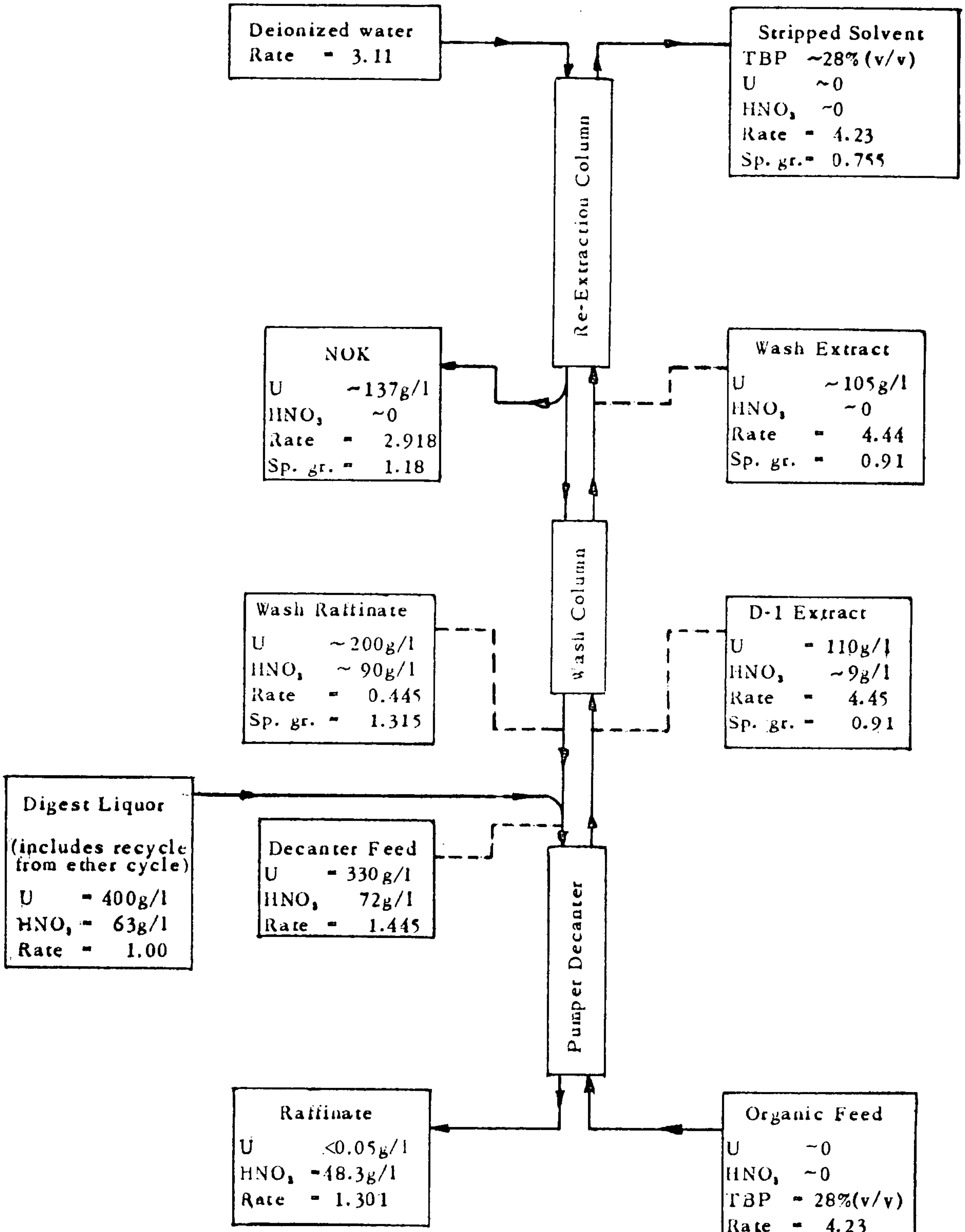


FIGURE 2

NORMAL FLOWSHEET FOR THE TBP EXTRACTION CYCLE (NOK WASH; FLOW RATES RELATIVE)

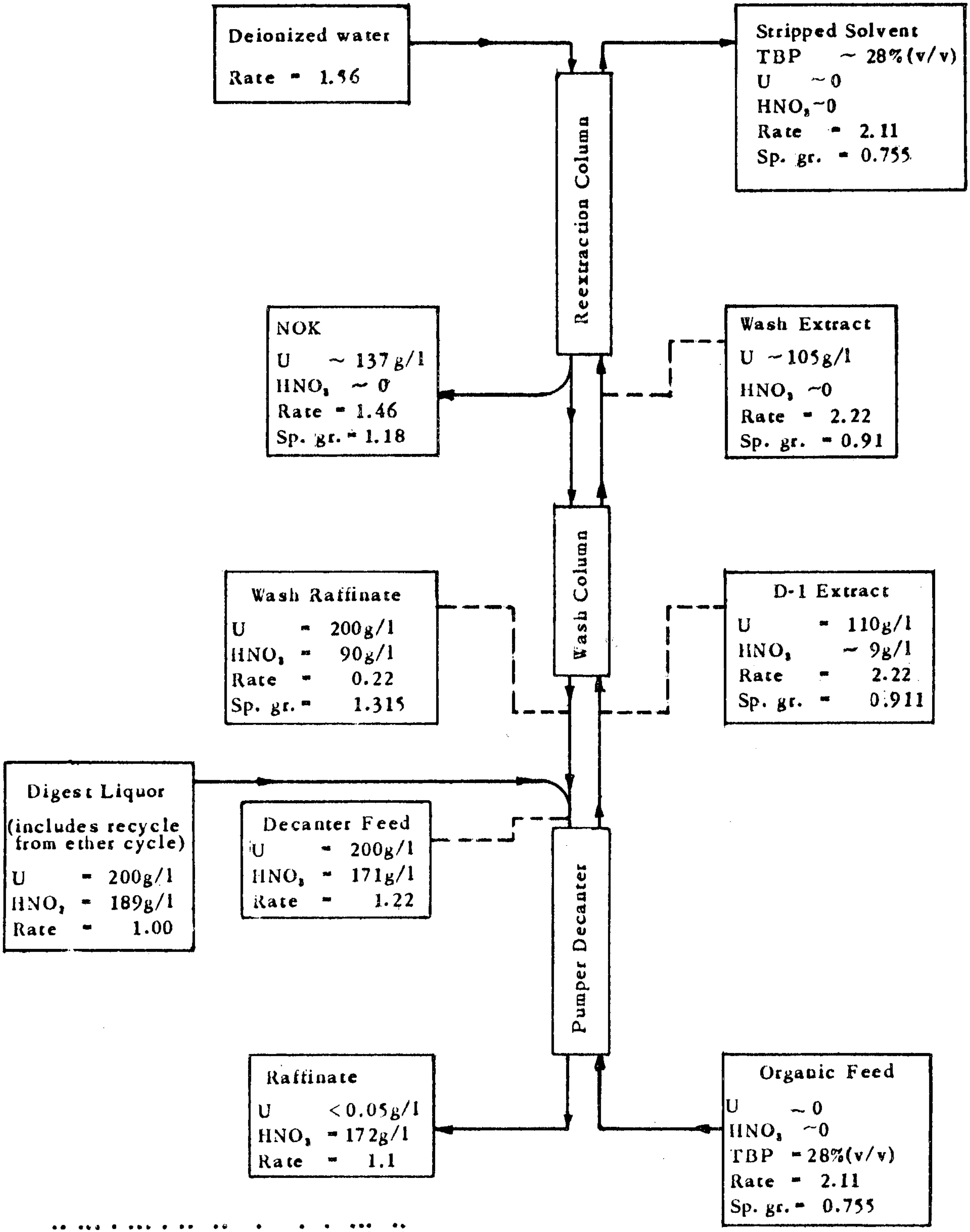
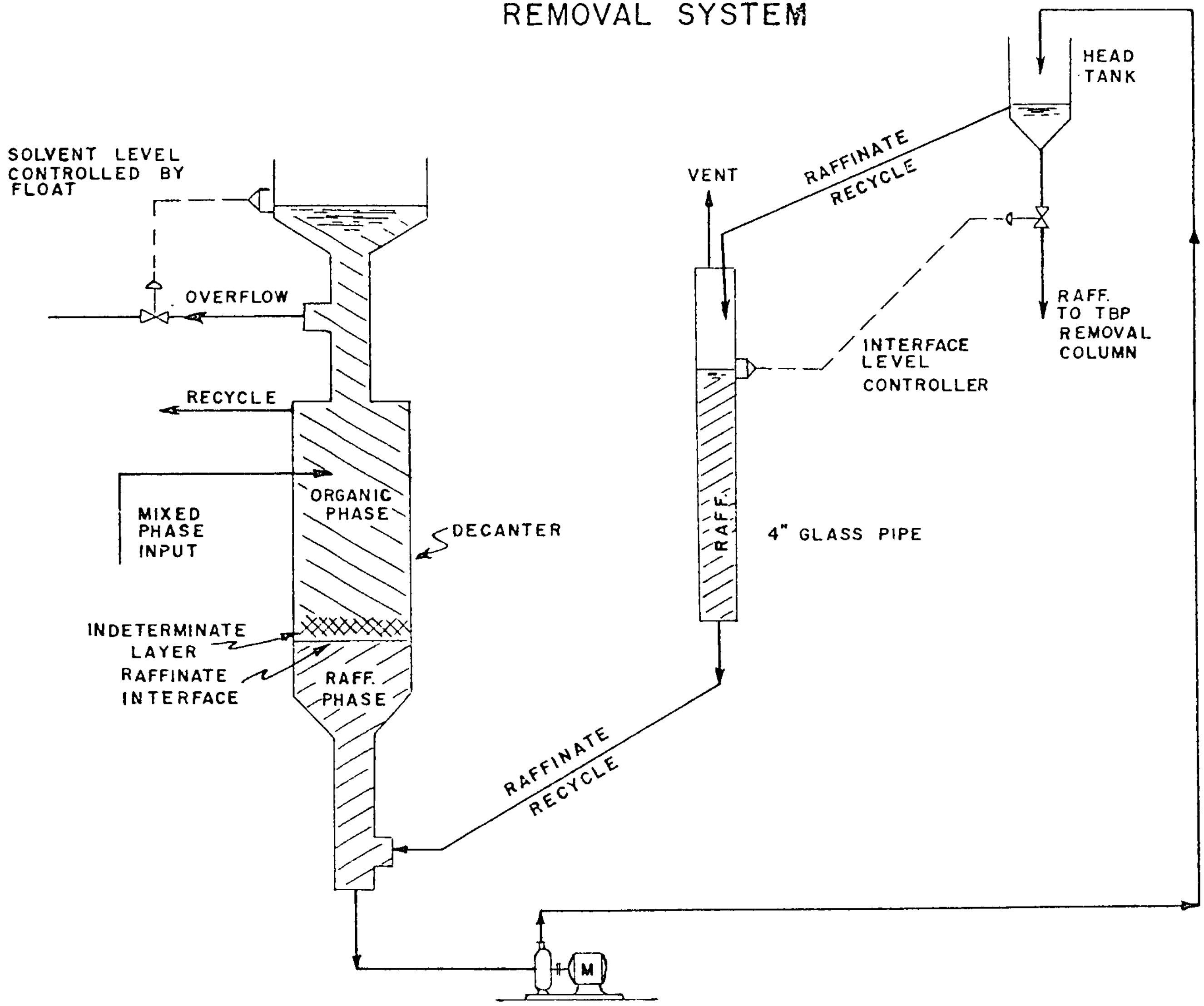


FIGURE 3
REVISED PILOT PLANT PUMPER-DECANTER RAFFINATE REMOVAL SYSTEM



more space for fluctuation of the interface position. Formerly the interface was sometimes operated in the turbulent region where influent streams entered the decanter.

B. Feed Materials

Feed materials tested with the low-acid flowsheet were Anaconda A lot 735 (an acid leach followed by ion exchange), Anaconda C lots 749, 757, 788 (a carbonate leach), and Moab lot 24 (an acid leach followed by ion exchange). Analysis of these feeds are tabulated in Table I below:

Table I

Analysis of Feed Lots Used in Low Acid Flowsheet Studies

	Analysis (Dry Basis)											
Feed	Cu w/o	AS w/o	F w/o	Halogens Less F w/o	SiO_2 w/o	SO_4 w/o	Ca w/o	P_2O_5 w/o	V_2O_5 w/o	Fe w/o	MoO_3 w/o	Uranium (wet basis) w/o
Anaconda A, lot 735	nil	nil	0.01	0.02	1.1	3.1	0.26	0.22	0.02	1.02	0.01	62
Anaconda C, lot 749	nil	nil	0.04	.04	5.5	.18	.57	.11	.38	0.1	Trace	60
Anaconda C, lot 757	nil	nil	Trace	.05	5.7	.24	.65	.16	.52	0.11	0.02	~60
Anaconda C, lot 788	nil	nil	Trace	.04	5.2	.21	.63	.14	.15	0.21	Trace	~60
Moab, lot 24	nil	0.01	0.03	.08	5.5	11.26	.097	1.34	.18	1.2	0.39	40

C. Solvent

The solvent used in these tests was 25 to 30% (v/v) TBP in a hexane diluent.

IV. Procedures

A. Digestion

Feed materials were digested in 30 to 45 wt. % nitric acid for one to three hours at 200°F, after which they were sampled and adjusted to 1*M* excess nitric acid and 400 g U/liter. Digest liquors were held for 1 to 24 hours before use in the pilot plant. Chemical requirements for digestions are tabulated below in Table II.

Table II

Chemical Requirements of Pilot Plant Ore Digestions

400 gU/liter, 1 *M* excess HNO_3 Flowsheet

Ore	gal. water per lb. wet ore	gal. 60% HNO_3 per lb. wet ore
Anaconda A	0.085	0.911
Anaconda C	0.111	1.115
Moab	0.034	0.649

B. Operation of Extraction Equipment

The extraction equipment was operated at steady state for a period of 24 hours before equilibrium was assumed. Operation was extended for an additional 24 hours during which time both composite and spot samples were taken of the process flow streams to determine waste loss to the raffinate, extraction efficiency, product purity, and TBP losses to the raffinate and product liquors. Equilibrium data was obtained by shakeouts on the decanter mixing-pump effluents.

V. Experimental Results and Discussion

A. Mechanical Operation

Scaling occurred in the decanters during the low-acid flowsheet tests. It consisted of a slimy clay-like deposit which did not seem to accumulate to any significant degree after first forming.

Poor phase dispersion resulting in inefficient extraction was observed in the first mixing stage when a conventional recycle ratio of 10/1 was employed (10 volumes of recycled organic to one volume of feed); however, this situation was alleviated when the recycle ratio was increased to 20/1.

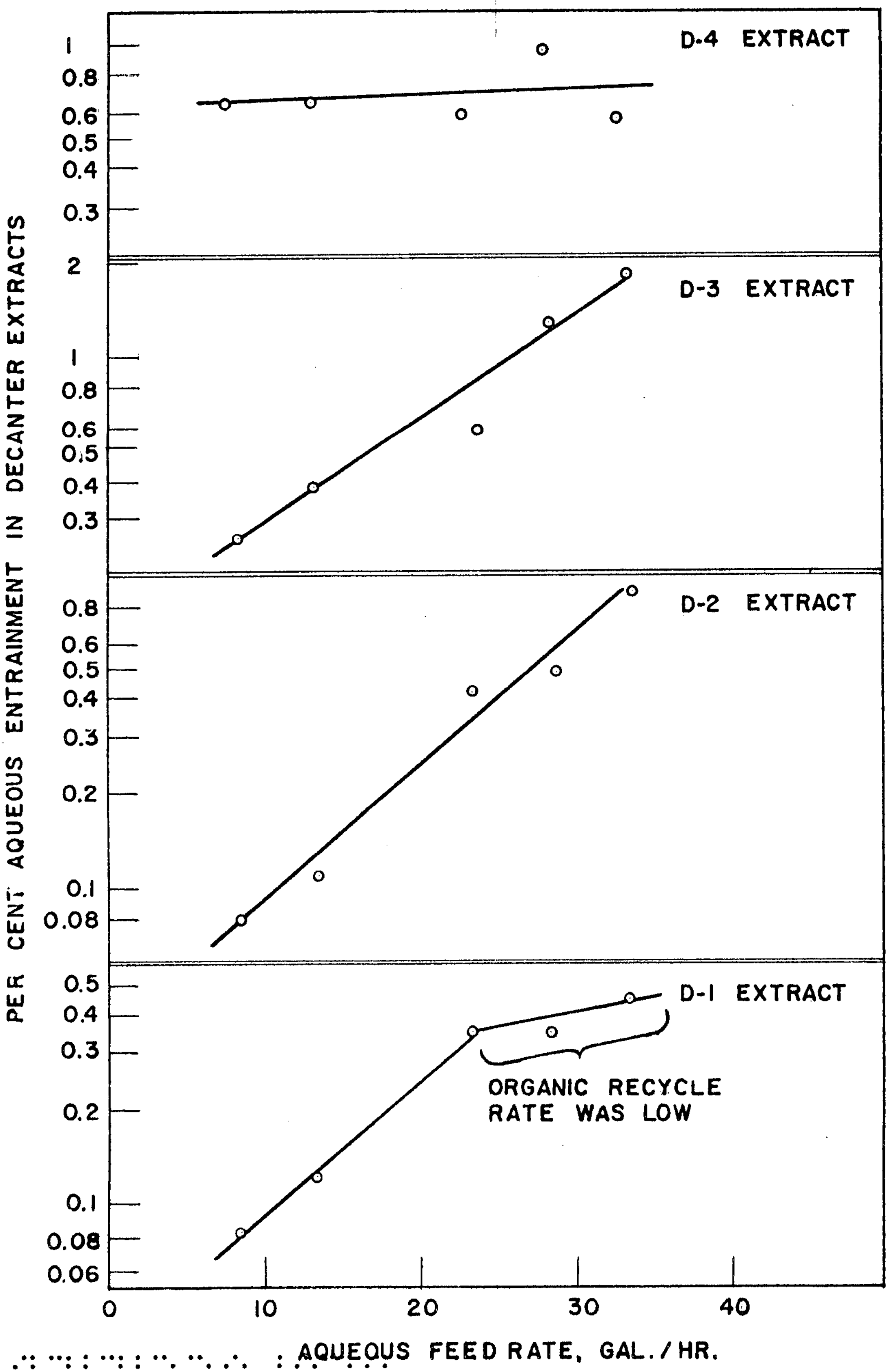
Because of the higher solvent flow rates in the decanters required by the low-acid flowsheet, samples of the decanter extracts were examined for aqueous carryover. Plots of aqueous entrainment in the decanter extracts are plotted in Figure 4 as a function of flow rates. The degree of aqueous carryover was insignificant insofar as extraction efficiency is concerned; however, aqueous entrainment in the first decanter extract was probably instrumental in allowing impurities to leak into the wash column. Further studies on the seriousness of this occurrence are being made by the Research Laboratory.

Emulsion formed on the aqueous-organic interface in the last decanter causing the interface-control float to malfunction. This situation was corrected by modifying the interface control system as described under the section III-A *Equipment.*

The tendency of the raffinate to momentarily plug control valves was evident. Problems with stuck valves have been more serious when testing the low acid flowsheet than generally experienced in past pilot plant work. A possible explanation for this is the increased solids content associated with higher uranium concentrations in the feed. It is not anticipated that this sort of valve sticking will be a problem in plant-scale equipment.

In comparing pilot plant flow rates with Weldon Spring, it should be noted that the design basis for Weldon Spring is a flow of 105 lb. U/hr.-sq. ft. of decanter cross-section. With the higher uranium level in the low acid flowsheet, this process rate is equivalent to 12½ gal. feed/hr. in the 8-inch-diameter pilot plant decanters. Pilot plant feed rates were normally run at 20 to 30 gal./hr., substantially in excess of the Weldon Spring design basis. The highest feed rate successfully processed, 48 gal./hr., is equivalent

FIGURE 4
ENTRAINMENT IN DECANTER EXTRACTS
VS
FLOW RATE



to 3.8 times the Weldon Spring superficial design rate. It appeared that the latter rate was near the upper limit of flow capacity of the decanters.

B. Equilibrium

Equilibrium uranium distribution between aqueous and organic phase in the pumper-decanters are still very favorable for extraction despite the low-acid feed. The most noticeable difference in uranium distribution associated with the low-acid flowsheet occurs at dilute uranium concentrations. Equilibrium data measured at acid concentrations existing in the pumper-decanters at low-acid flowsheet conditions are plotted in Figure 5. The dashed line represents a typical equilibrium curve representative of a "normal" flowsheet. Table III compares the nitric acid distribution in the pumper-decanters for both flowsheets. Internal recycle of nitric acid is evident.

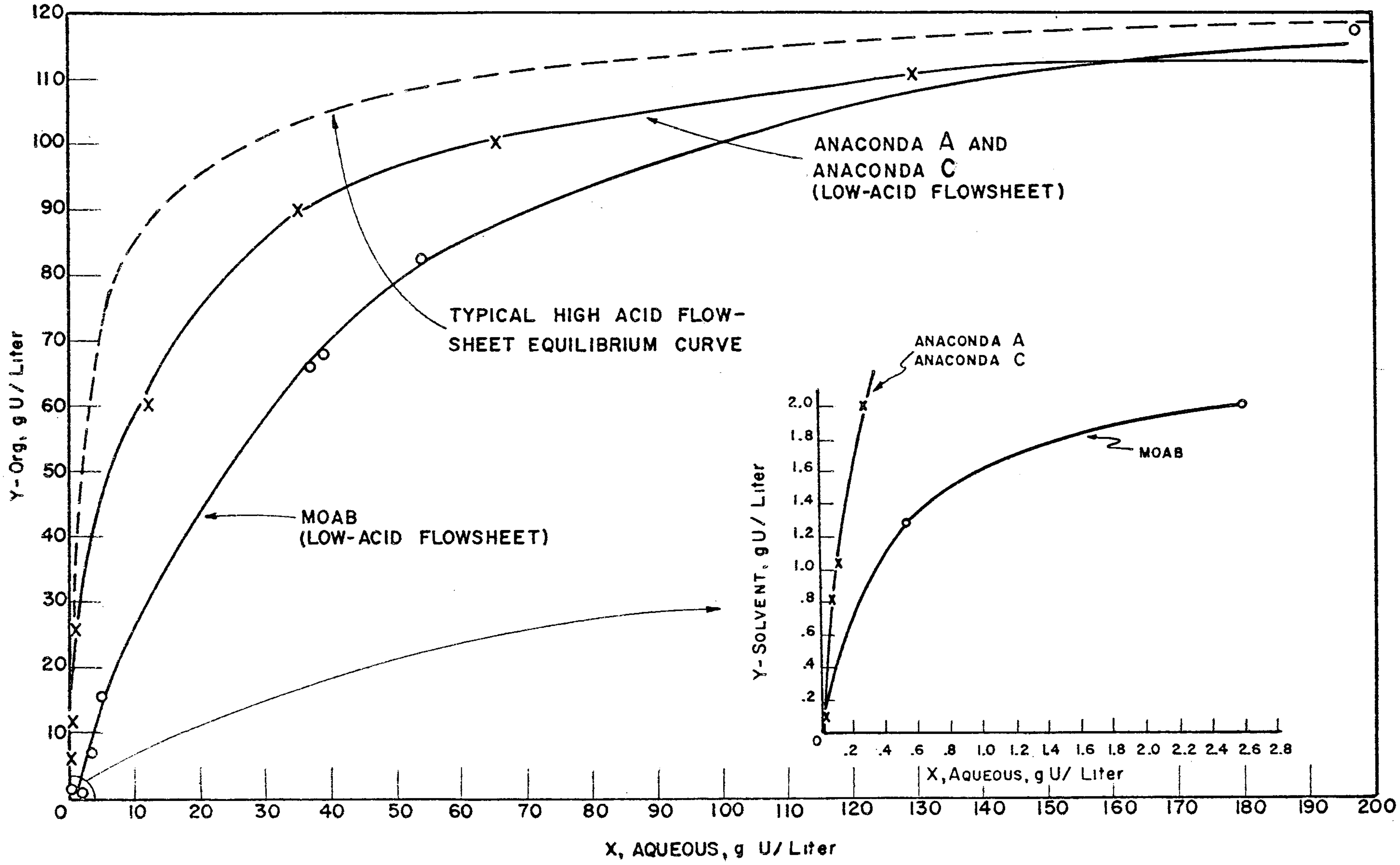
Table III

Typical Nitric Acid Distribution Data Measured in the Pumper Decanters

D-2 Density control at 0.820

	Low-Acid Flowsheet	Normal Flowsheet
	g HNO_3/l	g HNO_3/l
Aqueous feed	72	170
1st stage raffinate	101	246
2nd stage raffinate	145	223
3rd stage raffinate	110	218
4th stage raffinate	62 to 70	153
1st stage extract	2.5	2.5
2nd stage extract	16	20
3rd stage extract	21	36
4th stage extract	10	30
Organic feed	~ 0	~0

FIGURE 5
PUMPER-DECANTER EQUILIBRIUM DATA FOR SEVERAL FEEDS ON A LOW ACID FLOW SHEET BASIS



C. Pumper-decanter Performance

1. Raffinate Losses

The average uranium losses in the raffinate and the conditions at which they occurred are tabulated below in Table IV for the three feeds tested.

Table IV

Summary of Uranium Losses

	Anaconda A	Anaconda C	Moab
Uranium in ore concentrates (wet basis)	62%	60%	40%
Density Control Point	D-2	D-2	D-2
Control Density	0.820	0.820	0.840
D-1 recycle ratio	5/1	10/1	20/1
Extract saturation[a]	97%	99%	96%
Raffinate loss[b]			
1. Soluble Uranium	0.010%	0.023%	0.57%
2. Insoluble Uranium	< .001%	0.013%	≤0.03%
Feed consistency	Thin	Somewhat Thick	Very Thick

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[a] Saturation is calculated by comparing the U/TBP ratio of the D-1 extract with the maximum obtainable from a synthetic 200 g U/l, 3 M HNO_3 feed. The latter has been arbitrarily defined as 100%.

[b] Percent of uranium in the raw materials.

It was anticipated that the greater viscosity of the aqueous phase resulting from the more concentrated feed conditions might reduce stage efficiencies, causing inadequate extract saturation and/or excessive soluble uranium loss in the raffinate. With the two Anaconda feeds no difficulties of this type were encountered. The desired extract saturation ($\geq$ 96%) was achieved with very low raffinate losses, even lower than obtained under similar control conditions with synthetic or regular feeds at the 200 g U/l, 3 *M* HNO_3 feed conditions. A greater raffinate loss was obtained when running the much "thicker" Moab feed having a low uranium assay. While it is difficult to predict the effect of a fifth pumper-decanter stage on the Moab run with the limited data, it is probable that the loss would have been reduced to about 0.05%.

With the Moab ore it was possible to obtain satisfactory extract saturation by resorting to a 20 to 1 ratio of organic recycle to aqueous feed rate in the first mixing stage. This was apparently due more to increased mass transfer rates resulting from better feed dispersion than to greater solvent utilization with the higher recycle rate. The reduction in aqueous flow requirements with higher uranium feed concentration should permit use of about a 20 to 1 recycle ratio at Weldon Spring rather than the design figure of 10 to 1.

Since the "thick" Moab feeds exhibited seemingly lower than usual mass transfer rates it may be advisable to specify a lower limit (such as 50%) on the assay of feeds processed without blending at Weldon Spring. This would, in effect, reduce the solids content of the feed. The only pilot plant experience with standard feed conditions on a comparable feed was with Pronto[4] feeds, which yielded substantially worse results than found with Moab.

The main source of concern relative to the low-acid flowsheet has been the possibility of increased insoluble uranium losses in the raffinate due to the less favorable digestion conditions required. There is no evidence of a serious problem in this regard with these three feeds. Only with Moab feed was appreciable "insoluble" uranium detected, and this may have resulted in part from the difficulty in distinguishing a small amount of insoluble uranium in the presence of a relatively large amount in solution.

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[4] Krieg, J. T., Fariss, R. H., Soukup, J. A., *Pross Development Quarterly Report, Part II,* Mallinckrodt Chemical Works, *MCW-1400* (Feburary 1, 1957), pp. 13-21.

D. Product Purity

Average shotgun results on the uranium product liquor from the low-acid flowsheet runs are summarized below in Table V.

Table V

Average Shotgun Results

Feed	Wash Column Height, ft.	Wash Ratio aq/org.	Average Shotgun[a]	Range
Anaconda A	14, (single column)	0.1	0.016%	0.01-.02%
Anaconda C (lot 749)	14, (single column)	.1	.060%	.01-.14%
Anaconda C (lot 757)	21, (1½ column)	.1	.004%	0-.01%
Moab	14, (single column)	.1	.019%	0-.03%
Anaconda C (lot 788)	21, (1½ column)	.175	.016%	.013-.021%
Anaconda C (lot 788)	21, (1½ column)	.25	.007%	.005-.012%

[a] "Shotgun" is the increase in the neutron absorption cross-section due to impurities in the uranium sample. Pure U_3O_8 has a shotgun value of zero by definition.

On a shotgun basis at least, purity results have been very satifactory except when running Anaconda C feed with a 14-ft. wash column. Since 99% extract saturation was obtained during this run, it is difficult to assign blame in this direction; however, the use of 21 ft. of wash column height (1½ columns), the most effective condition for high purity,[5] produced a remarkable effect. The product shotgun dropped to the 0-0.01% range with an average over four cases of 0.004%. Tests with 21 ft. of wash column at higher wash ratios (A/O = 0.175 and A/O = 0.25) have also been completed, but with a different lot of feed. These tests also yielded excellent shotgun results.

The only spectrographic analyses of uranium product available at this time are for Anaconda C runs, averages for which are tabulated in Table VI.

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[5] *Cf.* p 21

Table VI

Spectrographic Analyses of Product

($1\frac{1}{2}$ columns for washing, two stages for saturation)

U	126 g/l	
HNO_3	0.002 g/g U	
Na	91 ppm	(U_3O_8 basis)
Fe	4 ppm	(U_3O_8 basis)
Si	20 ppm	(U_3O_8 basis)
Mg	12 ppm	(U_3O_8 basis)
V	<10 ppm	(U_3O_8 basis)
Zn	11 ppm	(U_3O_8 basis)
Pb	1 ppm	(U_3O_8 basis)
Cu	1 ppm	(U_3O_8 basis)
Co	2 ppm	(U_3O_8 basis)
B	<0.1 ppm	(U_3O_8 basis)
Cr	<1 ppm	(U_3O_8 basis)
Mo	<1 ppm	(U_3O_8 basis)

E. TBP Carryover

During the low-acid flowsheet tests an effort was made to determine the effectiveness of the TBP-removal column in scrubbing entrained TBP from raffinates. Analyses for TBP made by two different methods were not in agreement; however, it may be concluded from both sets of data that TBP carryover with the raffinate is a serious problem from a safety view-point if the raffinate were to be boiled down. Results are tabulated in Table VII. Figure 6 shows TBP content in scrubbed raffinate as a function of flow rates. TBP analyses based on Method 1 were used because this method gave answers with the best precision.

FIGURE 6

TBP IN SCRUB-COLUMN RAFFINATE AS A FUNCTION OF SCRUB-COLUMN FLOW RATE

AVERAGE TBP CONTENT OF SCRUB COLUMN FEED:

ANACONDA A	2.0 ± 0.2 g/l
ANACONDA C	5.8 ± 0.5 g/l
MOAB	6.6 ± 1 g/l

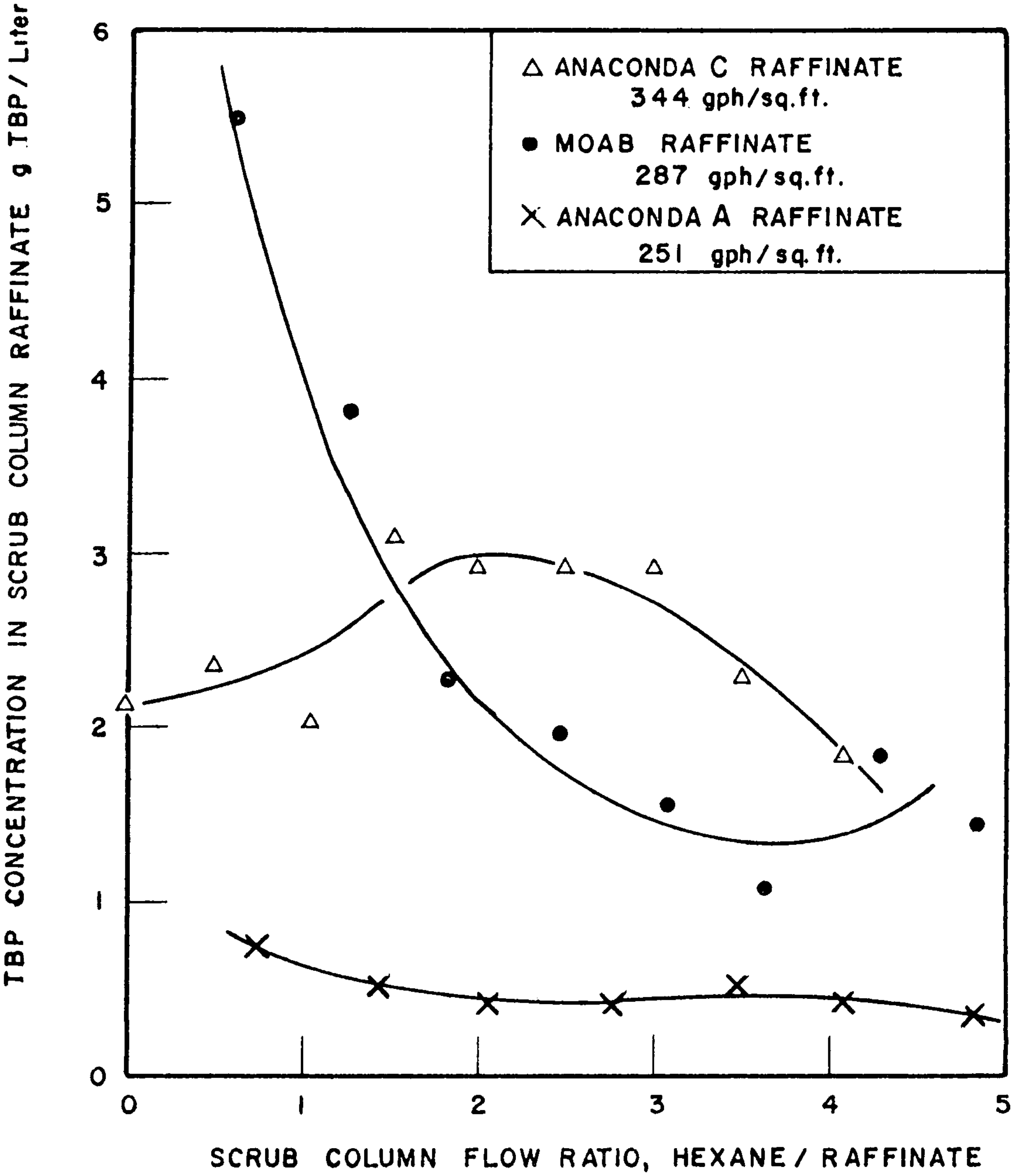

Table VII

TBP in Raffinate (ml/liter)

Hexane Recycle gph	Anaconda A		Anaconda C		Moab	
	Method 1 ml/l	Method 2 ml/l	Method 1 ml/l	Method 2 ml/l	Method 1 ml/l	Method 2 ml/l
0	--	1.0	2.1	3.1	--	0.22
16	0.76	0.72	2.4	4.5	5.5	0.48
31	0.52	0.45	2.0	4.5	3.8	0.50
46	0.4	0.25	3.7	5.0	2.3	0.20
61	0.39	0.35	2.9	5.0	1.9	0.50
76	0.5	0.28	2.9	5.6	1.6	0.25
91	0.43	0.35	2.9	4.8	1.1	<0.03
106	0.37	0.28	2.3	3.9	1.8	0.38
120	0.32	0.22	1.8	3.4	1.4	0.25

It may be observed that the three feeds show very different behavior in TBP carryover.

1. Anaconda A

Raffinates from this feed gave TBP values which were consistently below limits (0.5 ml/l) when > 45 gph hexane recycle rate was employed. The agreement between the two analytical methods was good.

2. Anaconda C

Raffinates from this feed gave TBP values which were far above limits regardless of hexane rate. There appears to be a consistent bias between analytical methods, Method 2 reporting more TBP by a factor of 1.5 or 2.

3. Moab

Raffinates from this feed gave TBP values whcih were consistently above limits by Method 1 and consistently below limits by Method 2.

BACKMIXING STUDIES IN THE PILOT PLANT PUMPER DECANTERS

by

J. A. Soukup
J. T. Krieg
R. H. Fariss

Summary

During the past quarter work has continued on the backmixing problem which exists in the pilot plant pumper-decanter system. Equipment changes have reduced backmixing by approximately 30%.

Introduction

Backmixing of organic solvent in the pilot plant pumper-decanter system has been reported previously.[1] The backmixing was believed to have resulted from the wide fluctuations in overhead organic flow rates. This backmixing had two unfortunate effects: (a) reduction of uranium recovery due to the increased uranium concentration in the solvent in the raffinate-end units, and (b) prevention of accurate stage to stage efficiency calculations by upsetting material balances.

Equipment Description

During the past quarter the decanter system has been revised to minimize backmixing. The pilot plant flow diagram which is in use now is described in Figure 1. Twelve inch decanters were installed above the overhead flow outlet of the eight-inch decanters. The level-control floats were moved from a four-inch diameter glass pipe into the twelve-inch decanters.

The pilot plant has just revised the overflow system on one pumper-decanter unit. A line bypassing the overflow control valve has been installed and is pictured in Figure 1. Flow through this line can be adjusted by a rotameter, thus allowing continous overhead flow.

Experimental Results and Discussion

An attempt was made during the past quarter to minimize fluctuations in the extract flow rate in the pumper-decanter units. By placing the level control floats in the newly installed

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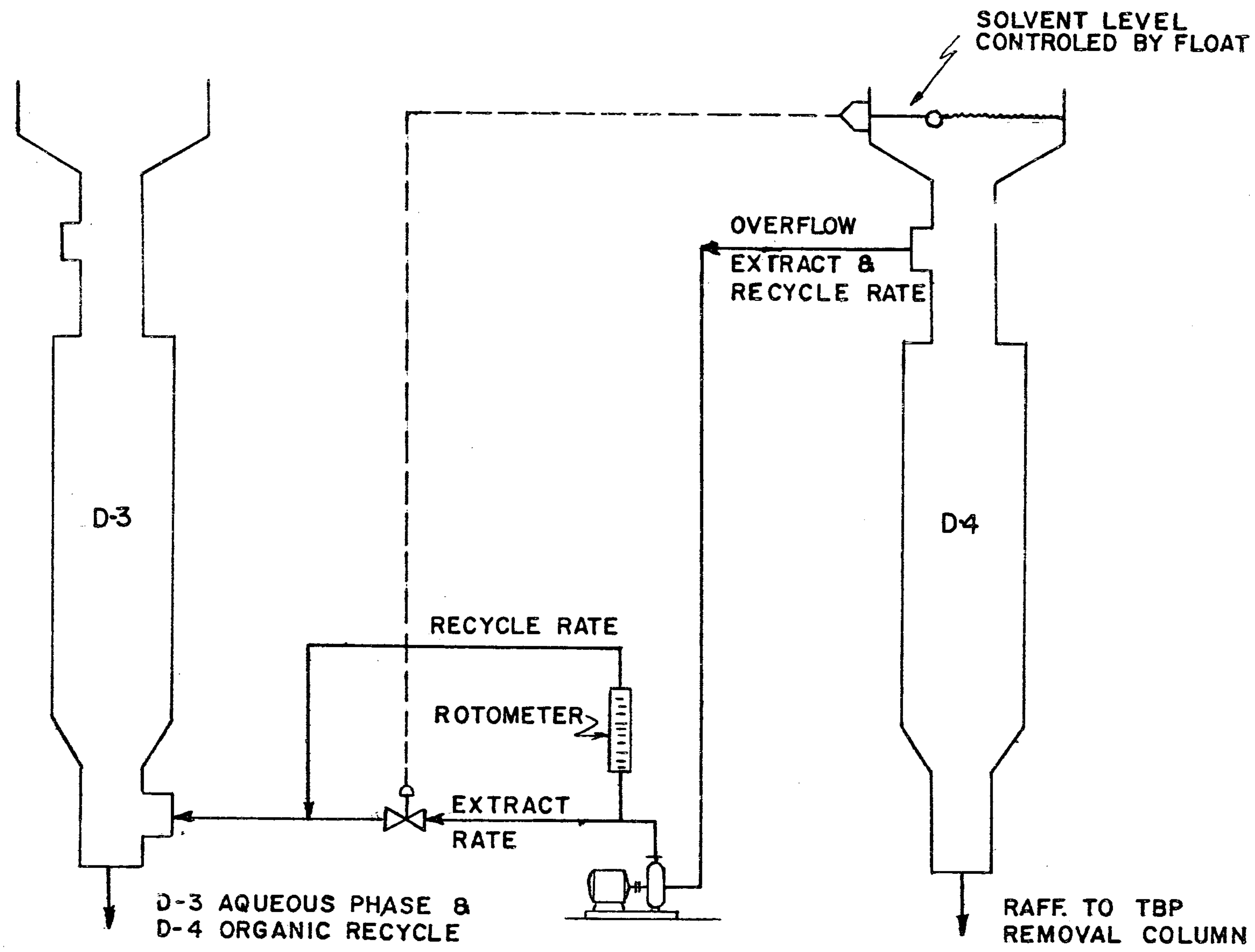
[1] Fariss, R. H., Krieg, J. T., Powell, C. S., Soukup, J. A., *Process Development Quarterly Report, Part II*, Mallinckrodt Chemical Works, *MCW-1398*, (November 1, 1956) p. 27-41.

FIGURE 1

PILOT PLANT FLOWSHEETS TO REDUCE BACKMIXING



twelve-inch decanters, the sensitivity of the floats was reduced by about a factor of nine. With these revisions the operation of the pumper-decanter system has been noticeably smoother. The occasional surging of organic into the vent lines has been eliminated; even though the overhead flow rate can still fluctuate all the way down to zero.

Following the installation of the large decanters the pumper-decanter system was tested in order to determine whether the amount of backmixing had been reduced. By applying the calculations described previously[2], it was found that the rate of backmixing had dropped from 4.3 gph to 3.0 gph. From these calculations it may be concluded that the backmixing had been reduced in magnitude by about 30%.

Future work will involve use of the rotameter which bypasses the extract control valve from D-4 to D-3.

An attempt will be made to allow continuous flow through the rotameter and the overflow control valve. In this manner it is hoped that the backmixing of this pumper-decanter unit will be reduced to a minimum, and more accurate stage efficiencies can be calculated. Better uranium recovery should also be obtained from the raffinate leaving the end pumper-decanter unit because of decreased backmixing.

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[2] *Op. cit.*, *MCW-1398*, p. 27-41.

RECOVERY OF URANIUM FROM RESIDUES FROM THE DINGOT PROCESS

by

D. J. Nerrow
R. H. Fariss

I. Summary

About 40,000 pounds of residues from the dingot process were treated in the pilot plant to recover the uranium values. A simple water-leach treatment was used to dissolve out chlorides and fluorides, leaving 18,000 pounds of product cake containing 47.2 weight per cent uranium. Essentially 100 per cent of the original uranium was recovered in the product cake. Digestion of this cake in nitric acid gave a final residue weighing 3300 pounds and containing 0.82 weight per cent uranium. Roughly 99.7% of the uranium in the product cake was recovered.

The chloride and fluoride content of the product were higher than the specifications for refinery feed materials. The product averaged 0.26 weight per cent chloride and 0.23 weight per cent fluoride on a U_3O_8 basis, as compared with a specification of 0.10 per cent for each of these halides. It is felt that a more vigorous washing procedure would reduce the chloride and fluoride content of the cake to low, acceptable values.

II. Introduction

From the process currently in operation at the dingot semi-works plant, there result several uranium-bearing residues: (1) forge dust; (2) quench tank sludge; and (3) salt bath sludge. All of these residues contain about 20-25 weight per cent uranium, mostly as UO_2. Forge dust consists primarily of scale which flakes off the bars as they are being forged. The second residue is the sludge which accumulates on the bottom of the tank in which the finished bars are quenched in water. Salt bath sludge is composed mostly of graphite with uranium-bearing material adhering to it. These chunks of graphite float on the surface of the molten salt to provide insulation; as the dingots and bars are removed from the bath, a few pieces of graphite stick to the metal and are subsequently knocked off into an empty drum.

During the past quarter the Process Development group has investigated a process for recovering the uranium from these residues. The major problems here are the reduction of the high halide content in these materials in order to produce a satisfactory feed material for the refinery.

III. Discussion

A. Process Description

Since a chloride salt bath is used at the dingot semi-works, the chloride content of the residues prohibits direct digestion in nitric acid in stainless steel equipment; therefore, in order that these materials may be processed in the refinery, a simple method of removing these chlorides is necessary. A schematic flowsheet of the method first investigated by the pilot plant is given in Figure 1. The process was based on the fact that the chlorides in the salt bath (and, therefore, in the residues) are water soluble.

The dry forge dust was unloaded from drums into a volumetric feeder which discharged into a carbon-steel ball mill. Large pieces were placed directly in the mill by hand since otherwise they lodged in the pipe leading from the feeder to the mill. The dust was then wet-milled, merely to reduce particle size and give a larger total surface area to enhance the dissolution of the chlorides. The sludge from the quench tank, being a very thick slurry of fine particles, was not milled but added directly to the milled slurry. This combined slurry was filtered through cotton cloths on an iron plate-and-frame filter press. The filtrate contained less than one pound of uranium per thousand gallons and was discharged to the sewer. The cake was kept in the press and washed with city water to remove chlorides. The wash filtrate was also below the limiting uranium concentration and was sent to the sewer. After the press was blown with compressed air, the product cake was unloaded, sampled, and then digested in nitric acid. A typical analysis of the cake before digestion is given in Tables I and II.

FIGURE I

FLOW DIAGRAM FOR RECOVERY OF URANIUM FROM RESIDUES

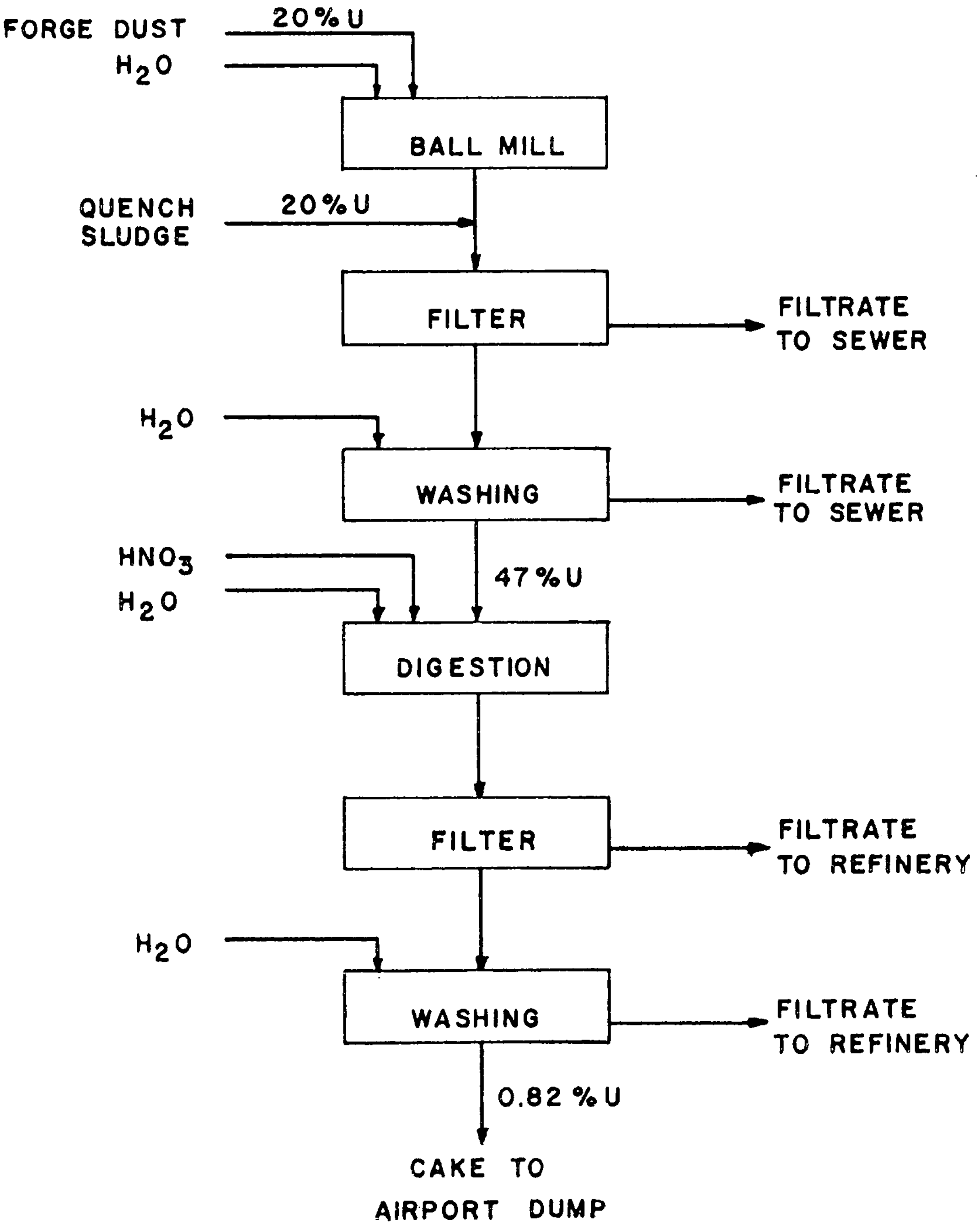

Table I

Analysis of Press Cake[a]

Chloride	0.13%
Fluoride	0.11%
Uranium	54.%
Iron	5.4%
HNO_3 Insoluble	8.8%
Loss on Drying at 110°C.	18%

[a] After dissolution of chlorides but before digestion in HNO_3. Analyses on "as received" basis.

Table II

Spectrographic Analysis[a] of Press Cake

Al	W-M	Fe	S
Ba	M	Mg	M
Ca	W-M	Si	M
Cr	W-M	U	VS

[a] Trace constitutents not analyzed.

W - weak
M - moderate
} minor constitutents, 1 to 0.01%

S - strong
VS - very strong
} major constitutents, > 1%

The resulting liquor was adjusted to about 0.75 pounds of excess nitric acid per gallon and contained 250-300 grams of uranium per liter. No attempt was made to adjust the uranium concentration. Dicalite was added to the slurry and the slurry filtered through precoated Dynel cloths on a stainless steel plate-and-frame press. The filtrate, containing uranium in the form of uranyl nitrate, was then pumped to the refinery feed area. Typical analyses of this filtrate are given in Table III; Table IV gives analyses of the cake. The cake was reslurried in water and refiltered to remove any remaining uranium. This filtrate was pumped to the refinery recovery area and the cake discarded. Analyses of this cake are given in Table V.

Table III

Analysis of Filtrate from Acid Digestion

	Uranium g/l	Fluoride g/l	Chloride g/l
No. 1	228	1.1	0.52
No. 2	300	2.1	0.43

	No. 1	No. 2		No. 1	No. 2
Al	W-M	W-M	Mg	W-M	W-M
As	W	W	Mn	W	W
Ba	W	W	Ni	W	W
Be	T	T	P	LSX	LSX
Ca	W-M	W-M	Pb	W	W
Co	W	W	Si	W	W
Cr	W	VW-W	Sr	W	W
Cu	VW	VW	Ti	VW	VW
Fe	S	S	U	VS	VS
			V	W	W

L - less than

X - identification uncertain due to interference by another element

Ag, B, Bi, Cd, Mo, Sb, Sr, and Zn not detected

Table IV

Cake from Acid Digestion

	H_2O[a] %	Chloride %	Fluoride %	Uranium %
No. 1	21	0.018	0.81	4.8
No. 2	20	0.012	2.2	2.5

[a] Results reported on "as received" basis.

Table V

Washed Digestion Cake

Drum No.	Uranium[a] %	Drum No.	Uranium[a] %
1	0.17	8	0.90
2	2.0	9	0.55
3	1.1	10	1.2
4	0.79	11	1.0
5	0.20	12	0.90
6	0.63	13	0.38
7	1.2	14	0.68

Average = 0.82% U

[a] Reported on "as received" basis.

The salt bath sludge could not be processed in exactly the same manner as the other materials, but it was found that water would separate the insoluble uranium-bearing material adhering to the graphite. After separation from these pieces of graphite, the uranium-laden slurry could be processed in the same manner as the other residues either together or separately. The washed graphite was returned to the dingot plant for reuse.

B. Operational Problems

Except for occasional large pieces of residue and some foreign matter (*e.g.*, paper, wood, pump packing, pieces of metal), the various materials were fairly easily processed. Because of the rapid settling rate of the milled slurry, considerable down time resulted from plugged lines. This difficulty was overcome somewhat by using high-speed pumps. Washing the product cake in the press was not as effective as had been hoped, since the press used was not of the washing type, and considerable channelling occurred. Nevertheless, this washing procedure reduced the chloride content of the cake to about one per cent of its original value; however, the resulting concentration was still above the specification limit for refinery feed materials. Digestion of the cake was somewhat difficult because of considerable foaming, most likely because of the lower oxidation state of the uranium in the cake (UO_2 and possibly some metallic uranium). Precoating the filter and adding filter aid to the digest slurry improved the subsequent filtration only slightly.

After the above mentioned process had been followed for several weeks, some revisions were made. It was found that the best method for treating the salt sludge consisted of filling a wire-mesh basket with the sludge and then suspending it in a tank of hot water until the graphite had been washed free of uranium-bearing material. This procedure was repeated until a fairly thick slurry resulted; this slurry was then filtered and the cake washed. This technique worked so well that eventually all three residue materials were treated in the same manner. To improve the washing efficiency, the cake was reslurried in water and refiltered. At this time, the precoating of the stainless press and the addition of filter aid to the digest slurry were eliminated. A schematic flow diagram of the revised process is given in Figure 2.

C. Conclusions

In all, about 40,000 pounds of material were treated, yielding 18,000 pounds of press cake. Weighted average analyses of the press cake are given in Table VI. It is suspected that a large part of the remainder of the cake consists of iron and graphite. Iron in the cake presents no difficulty, since iron is used as a salting agent in the usual digest liquors in the refinery. The fluoride content of the product liquor from this process appears to be high enough to justify use of aluminum as a complexing agent in the refinery. The water content is about three times the limit for feed materials, but a simple drying procedure could lower this to within limits.

FIGURE 2

REVISED FLOW DIAGRAM

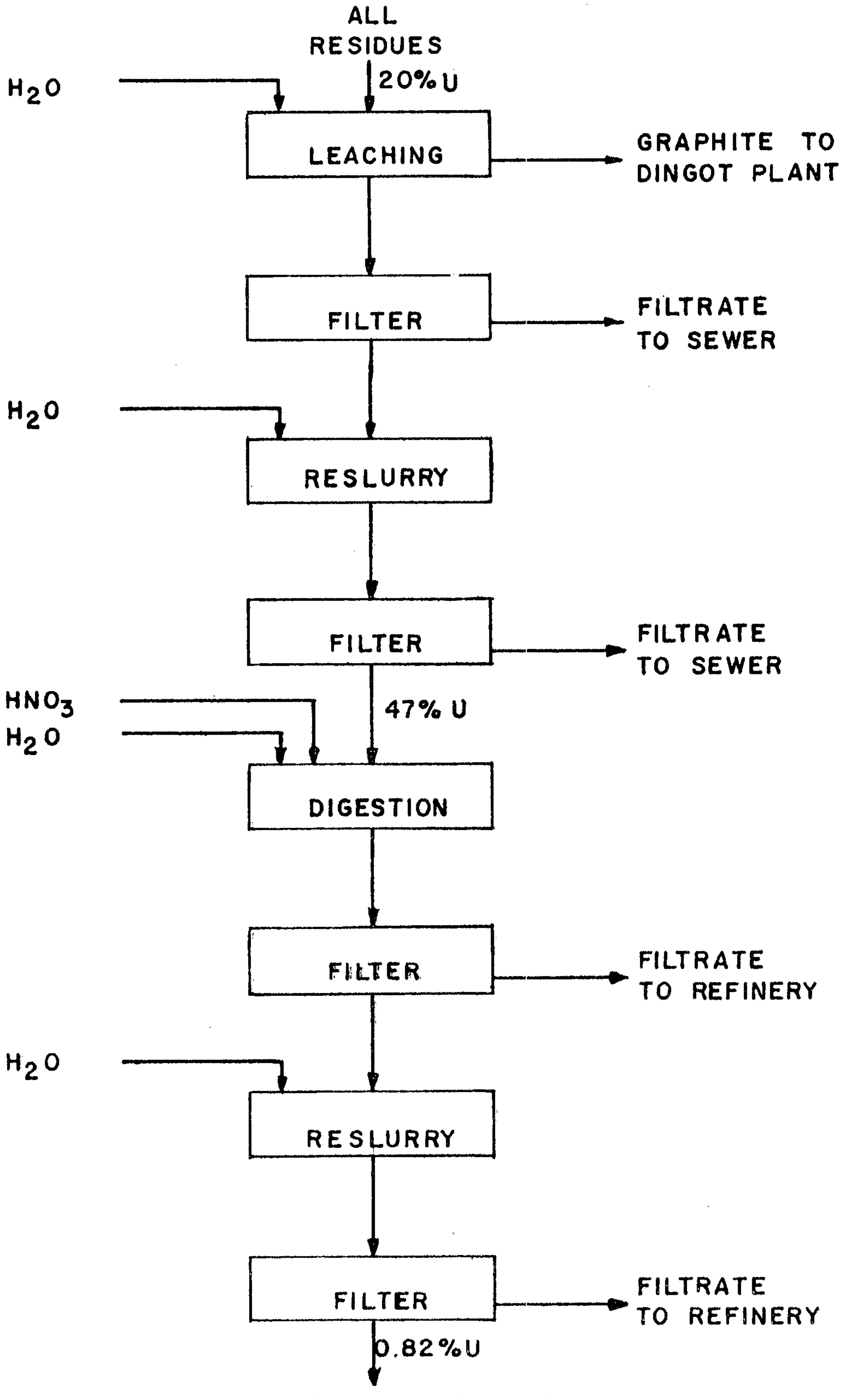

Table VI

Analysis of Press Cake

Uranium, as received	47.2%
Chloride, as received	0.14%
H_2O, as received	18.9%

The major remaining difficulty in connection with this process is the residual uranium content of the washed digestion cake, which averaged 0.82 per cent. Data have not yet been obtained to determine whether this uranium could be removed by more vigorous washing. It might be feasible, alternatively, to recover this uranium by processing the digestion slurry in the refinery without filtration, if the residual uranium is actually in solution.

HYDROGEN IN DINGOT URANIUM METAL

by

R. Becker
L. L. Gidley
G. E. Kerr
W. A. Taylor
W. G. Weber
H. J. Schaffer

I. Summary

1. Top to bottom helium purging of 3300 pound dingot bombs has resulted in higher overall machined dingot yields than did bottom to top purging.

2. Dingots with more consistently low hydrogen contents have been obtained from 3300 pound dingot bombs lined entirely with roasted magnesium fluoride, than from liner combinations of roasted and normal magnesium fluoride.

3. The roasted magnesium fluoride liner has increased the firing time of 3300 pound dingot bombs.

4. Top to bottom helium purging, due to leakage around the shell lid, has been less effective in lowering the firing time of roasted magnesium fluoride lined 3300 pound dingot bombs than was the case with bottom to top purging.

5. A long firing time for the 3300 pound dingot bombs has tended to yield dingot metal with a low hydrogen content.

6. Venting of 3300 pound charges for purposes of easier gas release had no observable effect on the hydrogen content of metal from standard lined bombs.

7. Electric triggering of bomb reactions has been perfected with the use of nichrome resistor units placed within the charge. The physical location of the heater coil appears to be important in determining the quality of the bomb product.

8. Trial of a graphite liner gav e no evidence of benefit in lowering the derby hydrogen level.

9. Inital studies of bomb charge permeabilities have shown marked differences in resistance to helium flow in various liner types compared to the standard UF_4 - Mg charge.

II. Introduction

The dingot process involves the reduction of UF_4 with magnesium to produce uranium metal which can be fabricated into fuel elements directly without an intermediate casting step. This metal is of higher purity than metal which has been vacuum recast, except for hydrogen content. Vacuum cast ingots usually contain from 0.5 to 1.5 ppm hydrogen while dingot metal exhibits hydrogen contents normally ranging from 2 to 8 ppm; recently production of 3300 pound dingots has shown trends approaching an average of 3 ppm. Difficulty in lead-dip canning of dingot metal slugs at HAPO has been attributed to this higher hydrogen content. It has been postulated that the hydrogen interferes with the bonding between the can and the fuel element. This poor bonding is considered undesirable since it may lead to corrosion failures of the aluminum jacket during pile operation.

The material discussed in this report is a continuation of work previously reported concerning the progress in lowering the hydrogen level in dingot metal.[1]

III. Experimental Procedures and Discussion

A. Gas Purging and Roasted Liner Material

The combination of roasted magnesium fluoride liner with helium purging has resulted in consistant, low hydrogen uranium metal in all small bomb sizes. These results have led to a concentration of Metal Pilot Plant efforts toward the testing of helium purging with various combinations of roasted MFL and regular MFL in 3300 pound dingot bombs.

1. Review

Before proceeding further, a review of results derived from past experimental work with roasted MFL and gas purging is in order.

a. Liner Treatment

Treatment[2] of the MFL was initiated during the early stages of the hydrogen program as a process for minimizing the possible hydrogen contribution of this bomb constitutent. Roasting[3] of MFL was selected as a satisfactory treatment. Experiments performed with roasted MFL have resulted in the following observations:

1. The hydrogen contribution of the liner to the uranium regulus formed in the bomb reaction was appreciably decreased.

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[1] Gidley, L. L., *et. al., Process Development Quarterly Report, Part II,* Mallinckrodt Chemical Works, *MCW-1400,* (February 1, 1957), p. 39-91

[2] Hansen, J. W., *et. al., Process Development Quarterly Report, Part II,* Mallinckrodt Chemical Works, *MCW-1393,* (August 1, 1956), p. 57-62.

[3] *Op. cit. MCW-1400,* p. 50-51.

2. A roasting temperature of 1500°F and higher was satisfactory.
3. The firing time of all bomb sizes was approximately doubled.
4. The liner forming characteristics were not so satisfactory as those obtained with normal MFL, but determination of a better particle size distribution presumabley will improve this situation.

b. Gas Purging

The bomb atmosphere[4] has been shown to be nearly 100% hydrogen as the bomb approaches firing. Purging[5] with an inert gas has been used as a method for the removal or dilution of this hydrogen. The following summation of experimental observations is possible:

1. The greater flows possible with helium make it more satisfactory than argon as a purging gas.
2. Helium purging of bombs lined with *normal* MFL has not sufficiently decreased the hydrogen content of the uranium regulus.
3. Helium purging of bombs lined with *roasted* MFL has appreciably decreased the hydrogen content of the uranium regulus.
4. The long firing time of roasted MFL bombs has been decreased to values near those of standard MFL lined bombs as a result of helium purging.
5. Helium purging of bombs up to firing as compared with helium purging until removal of the fired bombs from the furnace has not affected the hydrogen content of the uranium regulus.
6. Top to bottom purging as compared with bottom to top purging of bombs has indicated that higher crude yields may be obtained with the former, while hydrogen contents of the uranium reguli were comparable in both cases.

2. Construction of 3300 Pound Bomb Shells for Gas Purging

The majority of the above observations were based on the experimental results from 8 and 12 inch bombs. Experience in the adaptation of 8 inch and 12 inch shell designs for gas purging was used as a basis for the conversion of 1400 and 3300

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[4] *Op. cit. MCW-1393*, p. 66

[5] *Op. cit. MCW-1400*, p. 51-58

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pound shells. The data from several of these large bomb runs were reported in the last quarterly.[6] Since then the purging techniques for 3300 pound bombs have been modified and the following is presented to described the current gas purging arrangements.

Figure 1 illustrates the shell type and liner dimensions used for non-purged 3300 pound dingot bombs. Figure 2 depicts the shell and liner used for gas purged dingot bombs. The thickness of the bottom liner has been increased to provide space for a gas distribution device. This thickness increase has been achieved by raising the position of the liner-forming mandrel 1½ inches which also increased the thickness of the entire side liner. Figures 3, 4, and 5 present three gas distribution or collecting schemes which have been used. The single pipe (Figure 5) was found to be as effective as either of the other types and has therefore, been selected for general use. Figure 6 illustrates the placement of the single pipe in the bomb cavity, and the makeup of the bottom liner. The grog (- 10, + 25 mesh normal magnesium fluoride) has seemingly provided an even distribution of gases throughout the cross section of the dingot cavity when the purge gas has been introduced at the bottom, and has served as a gas collection chamber when the bomb has been purged from the top. Coarse filter paper has been placed over the grog to prevent liner material from filling in the voids in the grog. The bottom liner has been formed on top of the filter paper using a more permeable (supposedly coarser) grade of roasted MFL. Liner formed from the material was found to be relatively permeable to the flow of a gas, and at the same time substantial enough to retain the molten uranium. This material was prepared at MCW by roasting normal MFL in a small rotary kiln with a forced air draft which resulted in some dusting and consequent removal of fines. Table I compares typical screen analyses for normal MFL, MCW roasted MFL, Vitro[7] roasted MFL, and Vitro roasted air classified fines. Both Vitro-roasted products have had sufficient green strength for forming side liners.

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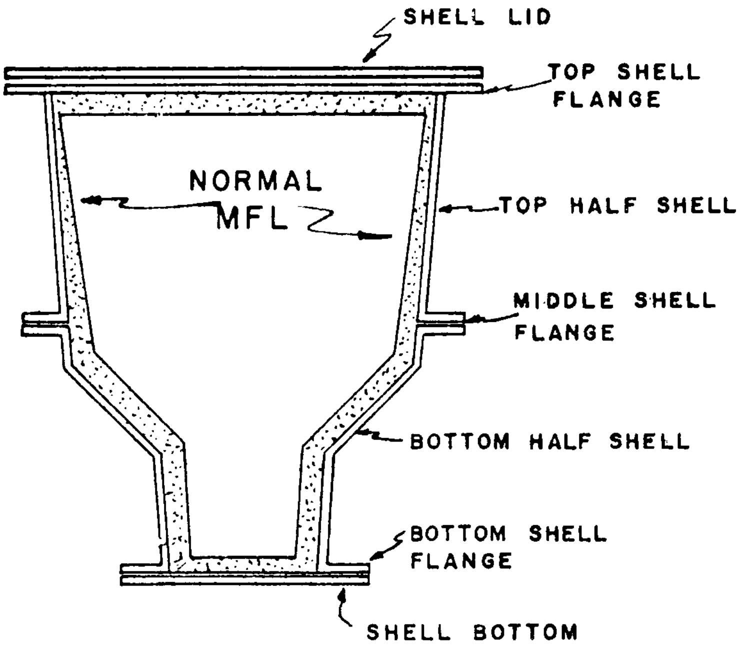
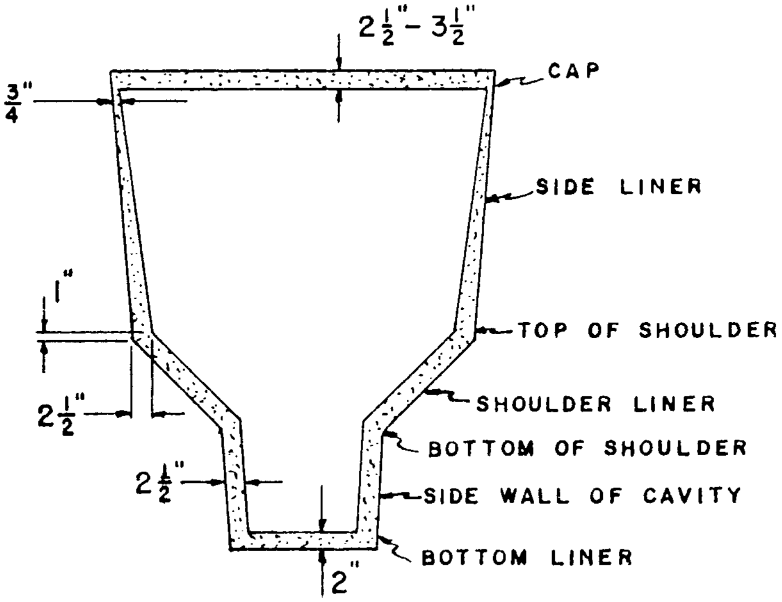
[6] *Ibid.* p. 56-57

[7] *Ibid.* p. 50.

FIGURE I
NON-PURGED DINGOT BOMB

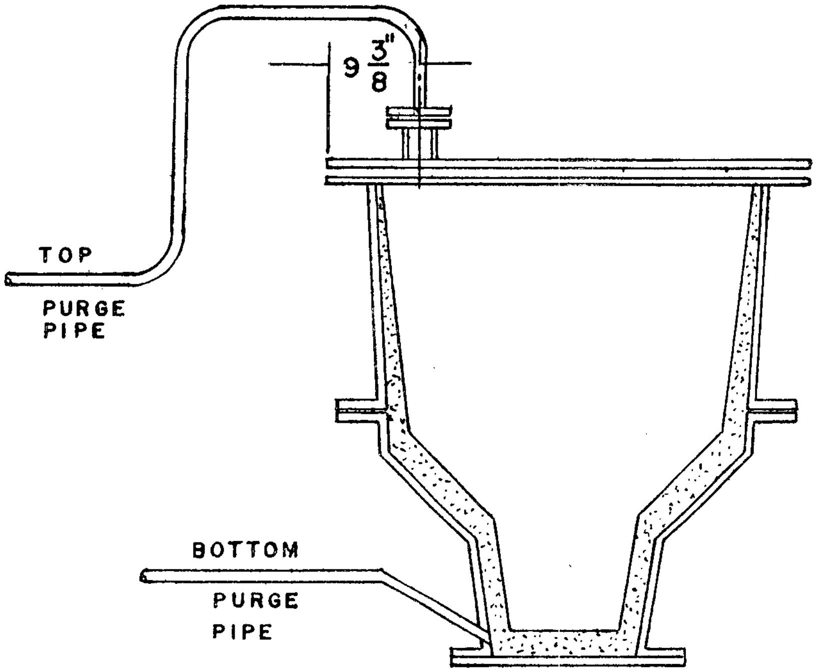


LINED SHELL

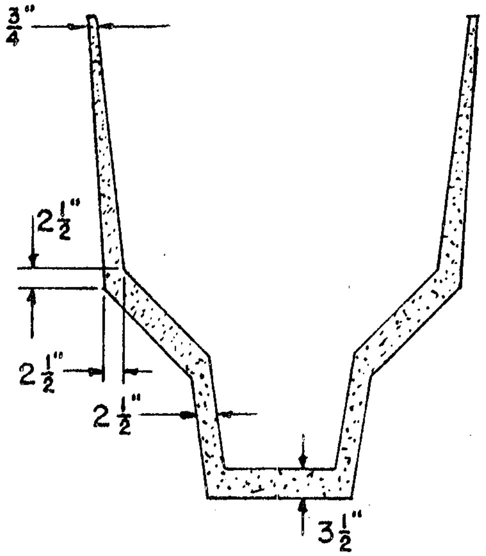


LINER

FIGURE 2
GAS PURGED DINGOT BOMB



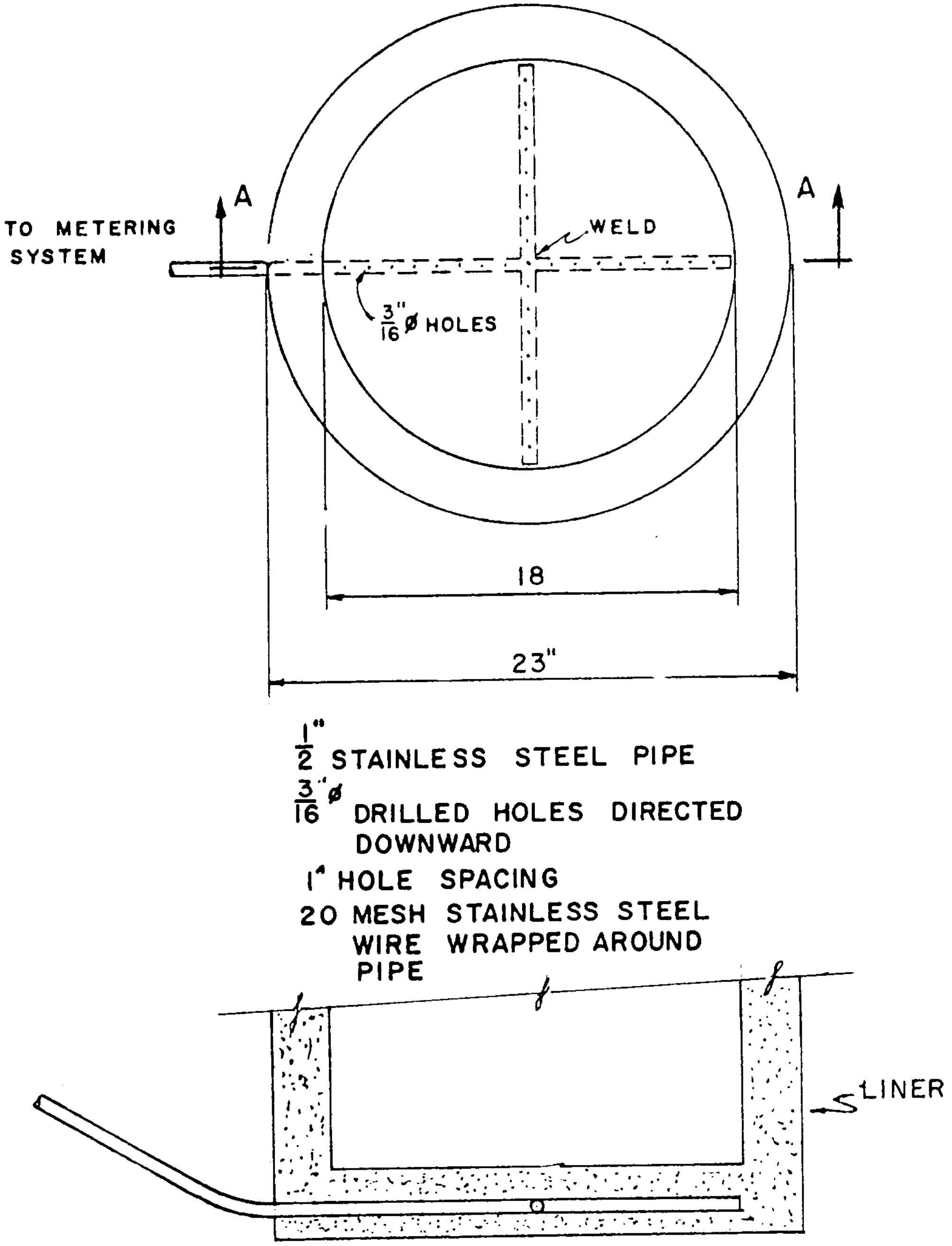
LINED SHELL



LINER

FIGURE 3

CROSS PIPE SYSTEM



1/2" STAINLESS STEEL PIPE

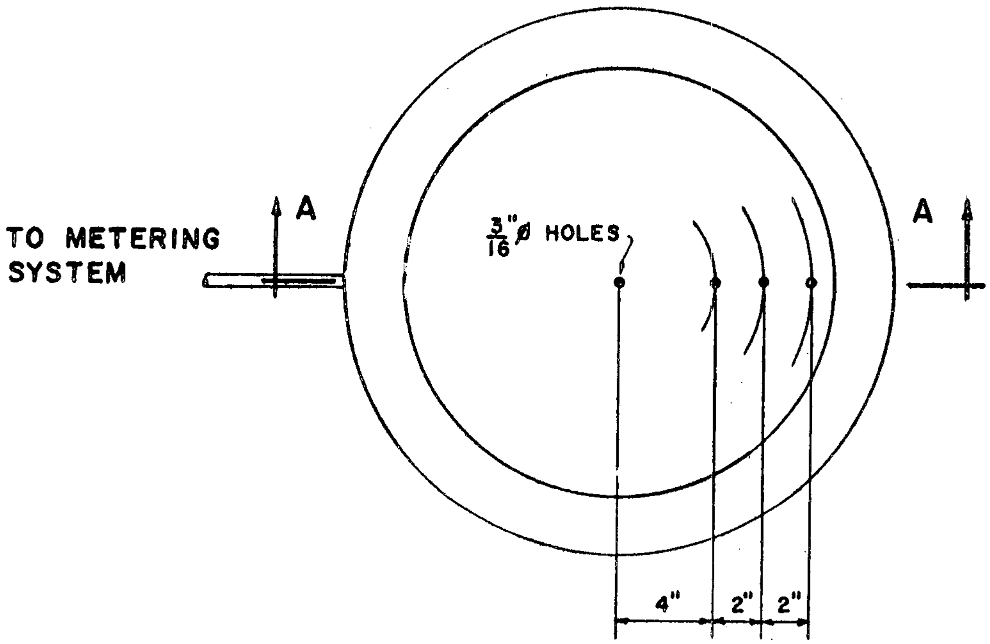
3/16" ø DRILLED HOLES DIRECTED DOWNWARD

1" HOLE SPACING

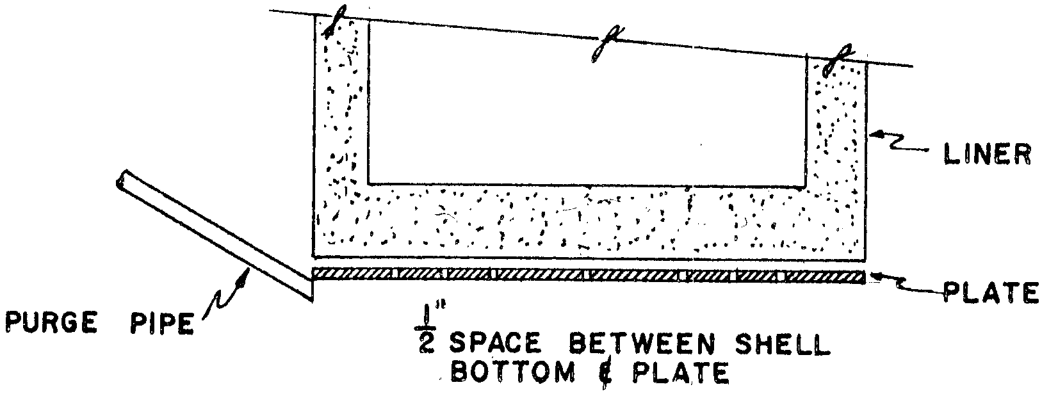
20 MESH STAINLESS STEEL WIRE WRAPPED AROUND PIPE

FIGURE 4

DRILLED PLATE SYSTEM



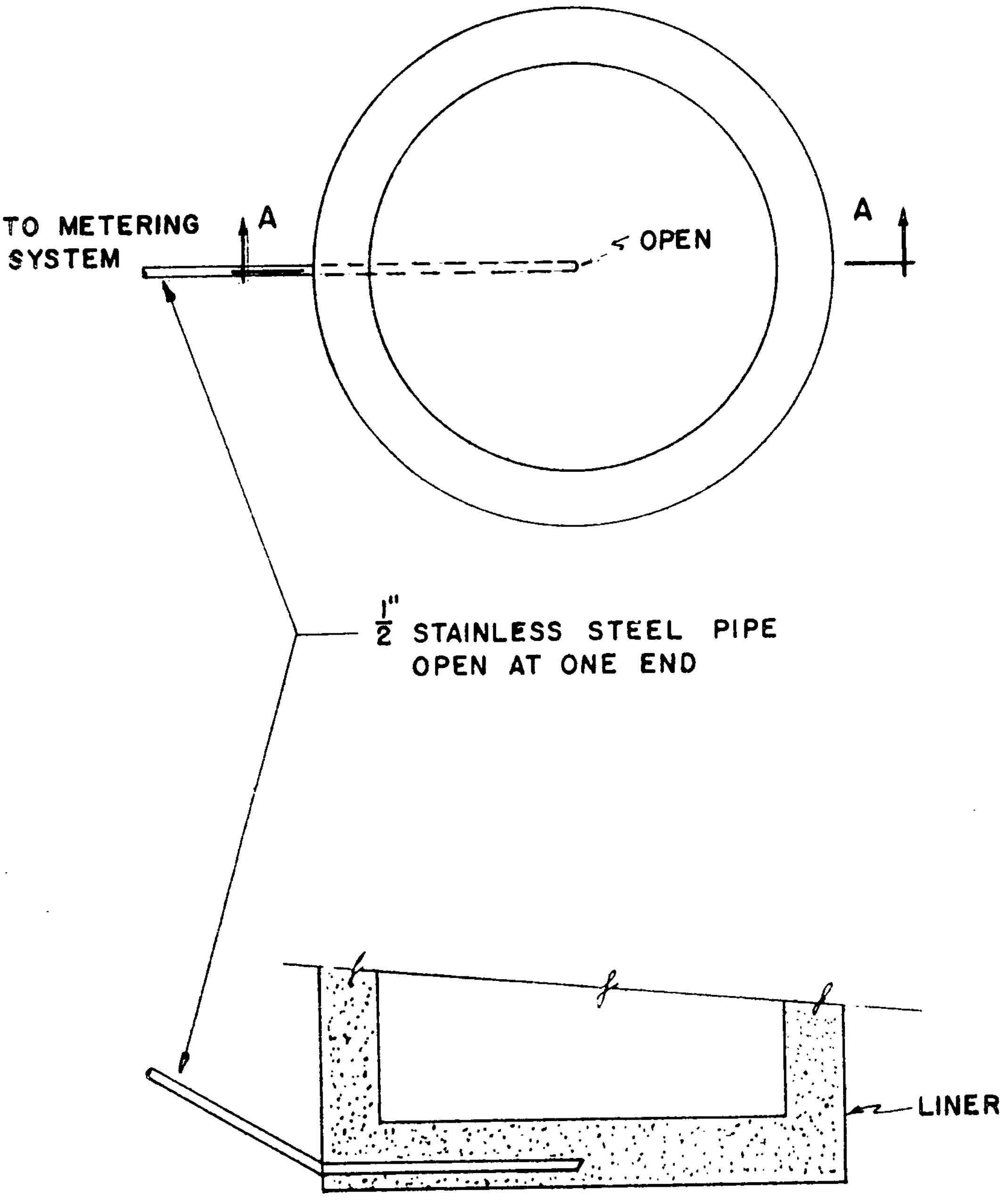
23" dia. STAINLESS STEEL PLATE
$\frac{1}{8}$" THICK.
$\frac{3}{16}$" ø HOLES, 88 SUCH
2" SPACING BETWEEN LINES OF HOLES
$\frac{1}{2}$" SPACE BETWEEN SHELL BOTTOM ¢ PLATE



SECTION A-A

FIGURE 5

SINGLE PIPE SYSTEM



SECTION A-A

FIGURE 6

BOTTOM LINER CONSTRUCTION

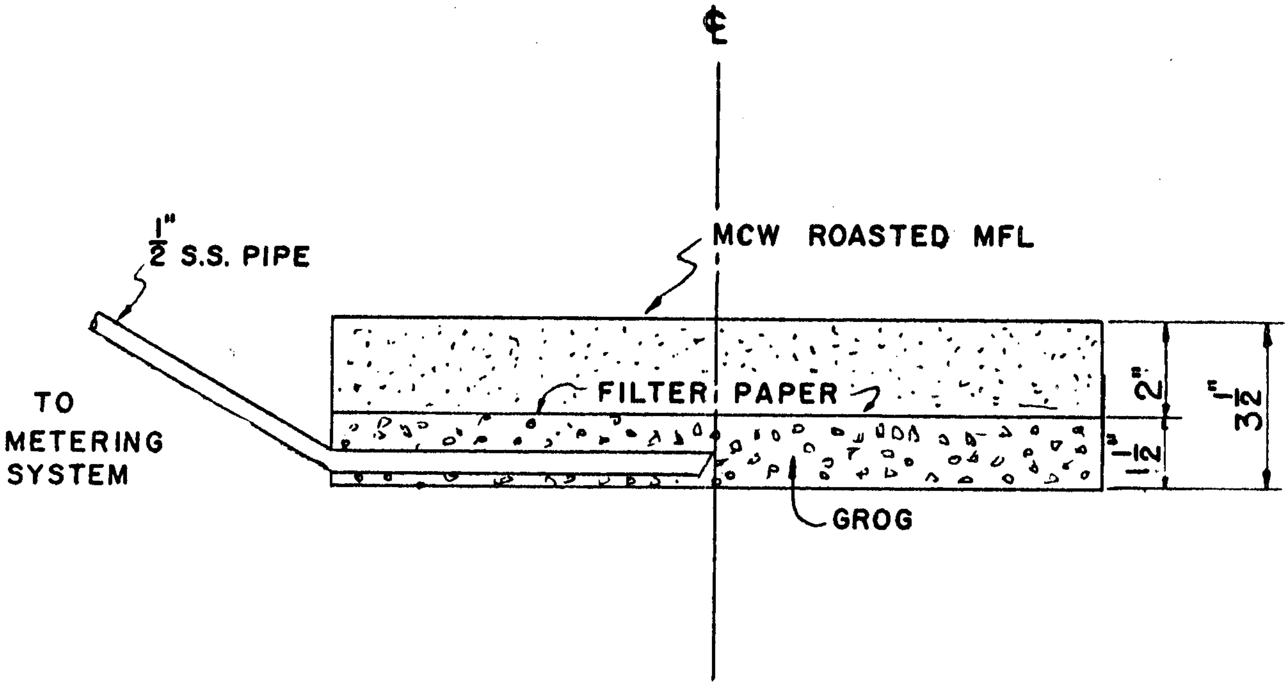


Table I

Comparison of Screen Analyses

Screen Size	Weight Percent on Screen Normal MFL	MCW Roasted MFL	Vitro Roasted MFL	Virto Roasted Air Classified Fines
60	5.1	-	4.1	1.0
80	8.0	8.0	3.8	1.6
100	6.7	7.3	7.6	3.6
200	21.0	19.9	20.2	18.4
325	19.0	17.9	18.5	21.4
-325	40.0	46.6	45.8	54.0

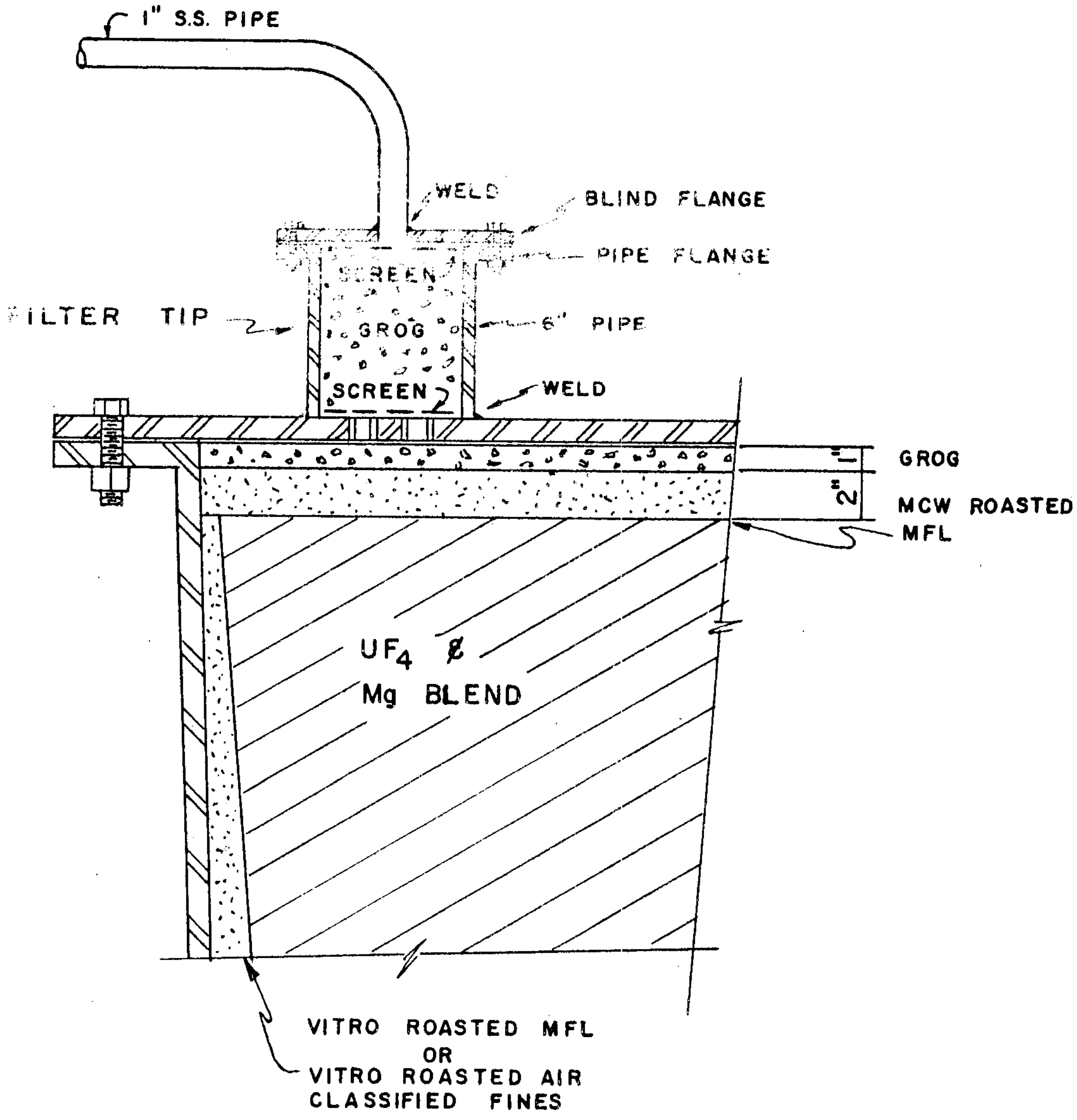
Surprisingly, normal MFL was ranked as the coarsest of the four by this screening procedure. Attempts to form liners and to purge revealed that MCW roasted MFL had the lowest *green strength* and also was the most permeable. It is suggested that the difference was in the −325 mesh material.

Figure 7 illustrates one type of cap which has been used (Gas Dispersion Cap). This cap construction represents the reverse of the liner bottom described above; that is, 1 inch of grog was placed *over* about 2 inches of MCW roasted MFL. The filter tip has served as an arrangement for admitting or removing gases through the lid. The construction of this device is also shown in Figure 7.

The normal assembly procedure first involved the forming of the gas dispersion cap and then the bolting of the filter tip lid to the tip shell flange. Initially no gaskets were used, but excessive purge gas losses resulted in the testing of several types and combinations of gaskets. An asbestos-filled monel gasket in combination with two sheet-asbestos gaskets and rope-asbestos gaskets provided the better seals. Magnesium vapor blowouts however occurred with both types.

FIGURE 7

GAS DISPERSION CAP
AND FILTER TIP



A second type of cap, the vented cap, illustrated in Figure 8, was designed in an an effort to minimize magnesium vapor blowouts and eliminate the need for gaskets. Vitro roasted air-classified fines were used for the entire cap except for a wedge shaped volume located directly under the filter tip. This space was filled with grog to provide a vent between the blend (UF_4 and Mg) and the filter tip, eliminating the need for a porous cap. The fines forming the remainder of the cap were packed firmly to a height of ¾ inches above the top shell flange. As the lid was bolted to the flange, the fines were further packed and had good contact with the lid. This cap construction has not been completely successful due to gas leaks between the vent and the flange. Measurements of the total volume of purging gas input *versus* egress gases were made during top to bottom purging experiments with vented caps and with gas dispersion caps with rope asbestos gaskets. A summary of these data is shown in Table II.

Table II

Total Volumes of Purging Gas and Egress Gases for Two Cap Constructions

Vented Cap Without Gasket		Gas Dispersion Cap With Gasket	
Total Purge Gas In	Total Egress Gases	Total Purge Gas In	Total Egress Gases
889 cu. ft.	0.7 cu. ft.	754 cu. ft.	30 cu. ft.

These data indicate that neither cap arrangement provided a satisfactory gas seal. Furthermore, magnesium vapor losses through the top flange occurred equally with both cap designs. More recently rope asbestos gaskets have been combined with the vented cap design in an attempt to obtain more efficient purging.

A metering system has been developed which has provided both simple control for purging and informative data. Pipes attached to the bottom purge pipe and to the filter tip extended through the back of the Hevi-Duty furnace. Outside the furnace the metering system was connected to these purge pipes as illustrated in Figure 9.

FIGURE 8
VENTED CAP AND FILTER TIP

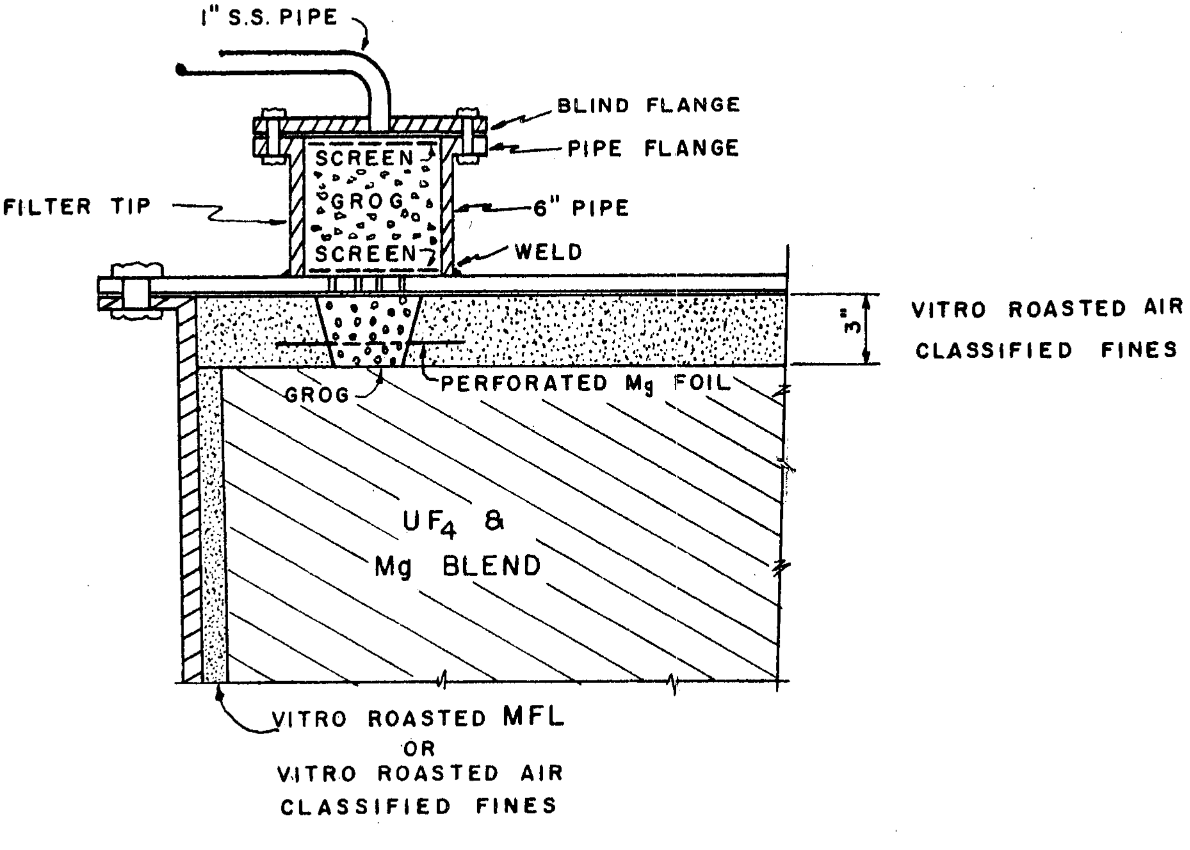
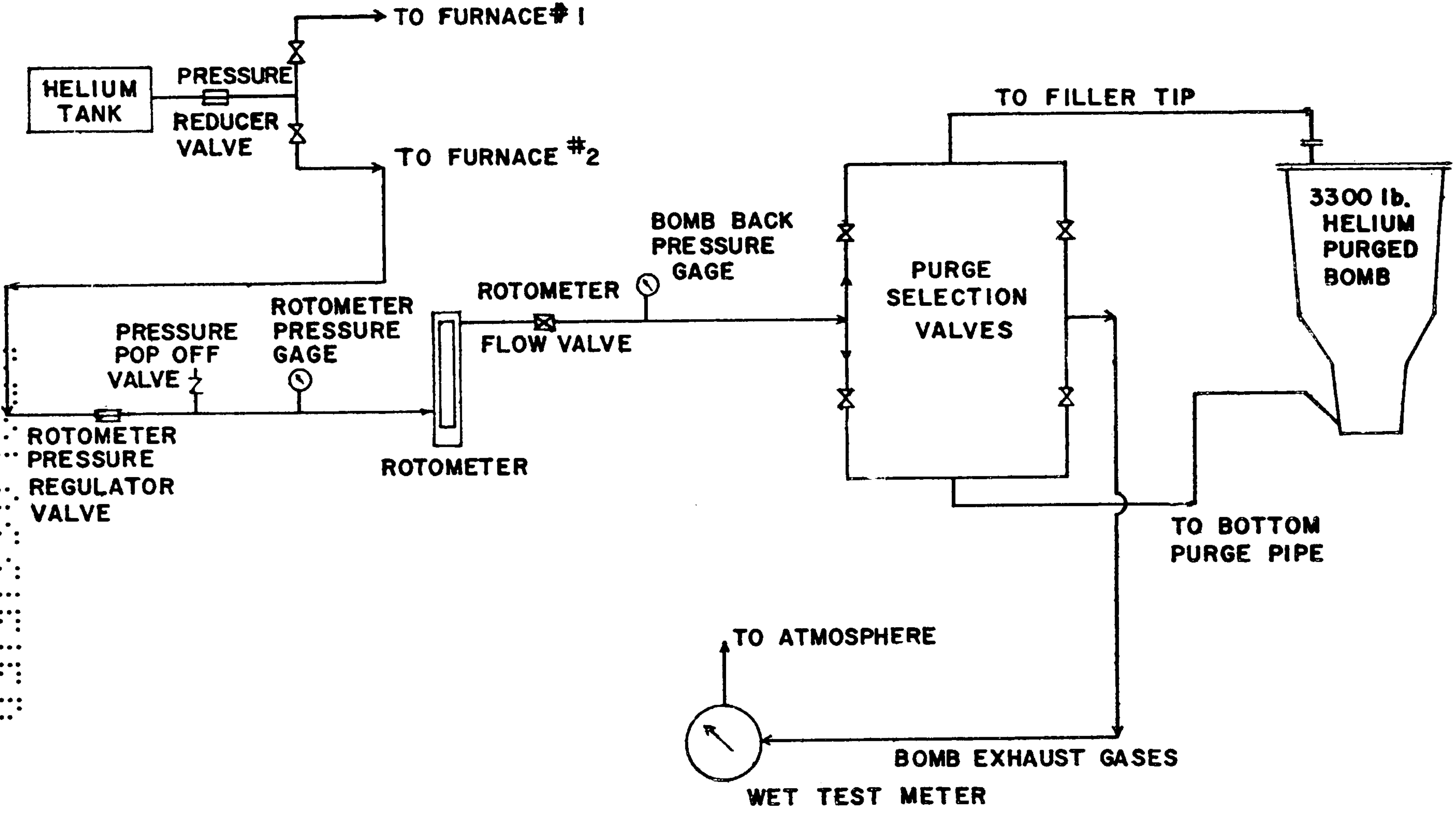


FIGURE 9
HELIUM METERING SYSTEM



A helium tank of large capacity was the source of helium. Helium was piped to either or both of the two available systems where the rotometer pressure regulator valve was adjusted to give the pressure for which the rotometer was calibrated. A pressure pop-off valve prevented operating the rotometer at excessive pressures. The needle valve was slowly opened until the rotometer indicated the desired helium flow. The metered helium then reached a system of purge selection valves where top to bottom or bottom to top purging was selected. Helium passed through the bomb and was exhausted with other gases back to the purge selection valves. Proper adjustment of the valves led the exhaust gases to a wet test meter which measured the cumulative volume of the gases rather than the rate of flow. Finally, the bomb back pressure valve indicated the resistance of the bomb to the flow of helium. The following data were recorded every 15 minutes from the time the purging system was connected to the bomb to the time the bomb fired:

Rotometer pressure
Rotometer flow
Bomb back pressure
Wet test meter reading

3. 3300 Pound Gas Purged Bomb Experiments

Four 3300 pound dingot experiments were reported in the last quarterly[8] in which specification grade uranium tetrafluoride and magnesium were charged into shells lined with roasted magnesium fluoride liner material. These bombs were helium purged from bottom to top until they fired. The average hydrogen content of the dingots was 1.77 ppm, a sufficiently low value to warrant further investigation.

During the past three months of evaluation, the 3300 pound, helium purged, dingot experiments were classified into six types based on the liner composition and the purging direction. These types were:

Type 1 Roasted magnesium fluoride liner throughout, helium purged from bottom to top (25 experiments).

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[8] *Ibid.* p. 56-57

Type 2 Roasted magnesium fluoride liner throughout, helium purged from top to bottom (24 experiments).

Type 3 Normal magnesium fluoride for the side liner, roasted magnesium fluoride liner for the shoulder, dingot cavity, and cap; helium purged from top to bottom (12 experiments).

Type 4 Roasted magnesium fluoride liner for bottom and cap, normal magnesium fluoride liner for the remainder; helium purged from bottom to top (8 experiments).

Type 5 Roasted magnesium fluoride liner for bottom and cap, normal magnesium fluoride liner for the remainder; helium purged from top to bottom (7 experiments).

Type 6 Roasted magnesium fluoride liner for the bottom only, normal magnesium fluoride liner for the remainder; helium purged from top to bottom through a vented cap (10 experiments).

The quantity of roasted magnesium fluoride liner material used per dingot bomb was decreased in this series from an all roasted liner to Type 1 to roasted liner material for the bottom only in Type 6. Since roasting represents an added expense, the interest in this trend has been in any possible reduction of the quantity of roasted liner material required, representing a corresponding decrease in production costs.

The overall machined yields (green salt to machined dingot) for Type 1 averaged 64% which was below that obtained with normal dingot production bombs. Past experiments with small bombs had suggested that top to bottom purging might provide for less disruption of the liner and thus contribute to improved yields when compared with bottom to top purging. Type 2 bombs were scheduled to test this and were identical in construction to Type 1 bombs except the purging was from top to bottom. The resultant overall machined yields averaged 76%, an 11% improvement over yields obtained with bottom to top purging. All subsequent helium purging experiments (the Type 4 experiments had already been performed) were therefore carried out with top to bottom purging. Figures 10 and 11 are bar graphs illustrating the distributions of overall machined yields for the two methods of purging. It is evident that top to bottom purging was definitely beneficial.

FIGURE - 10

DISTRIBUTION OF PERCENT OVERALL MACHINED YIELDS

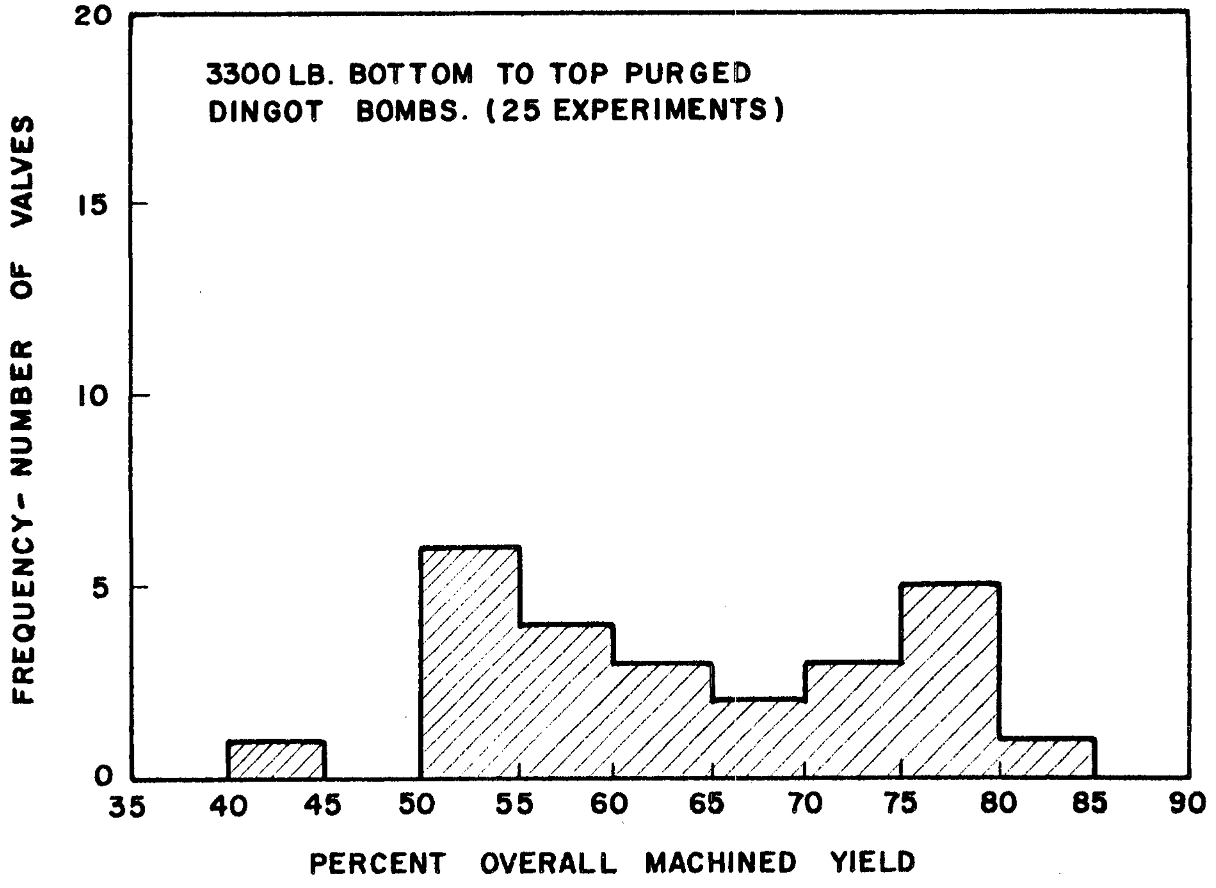

FIGURE - 11

DISTRIBUTION OF PERCENT OVERALL MACHINED YIELDS

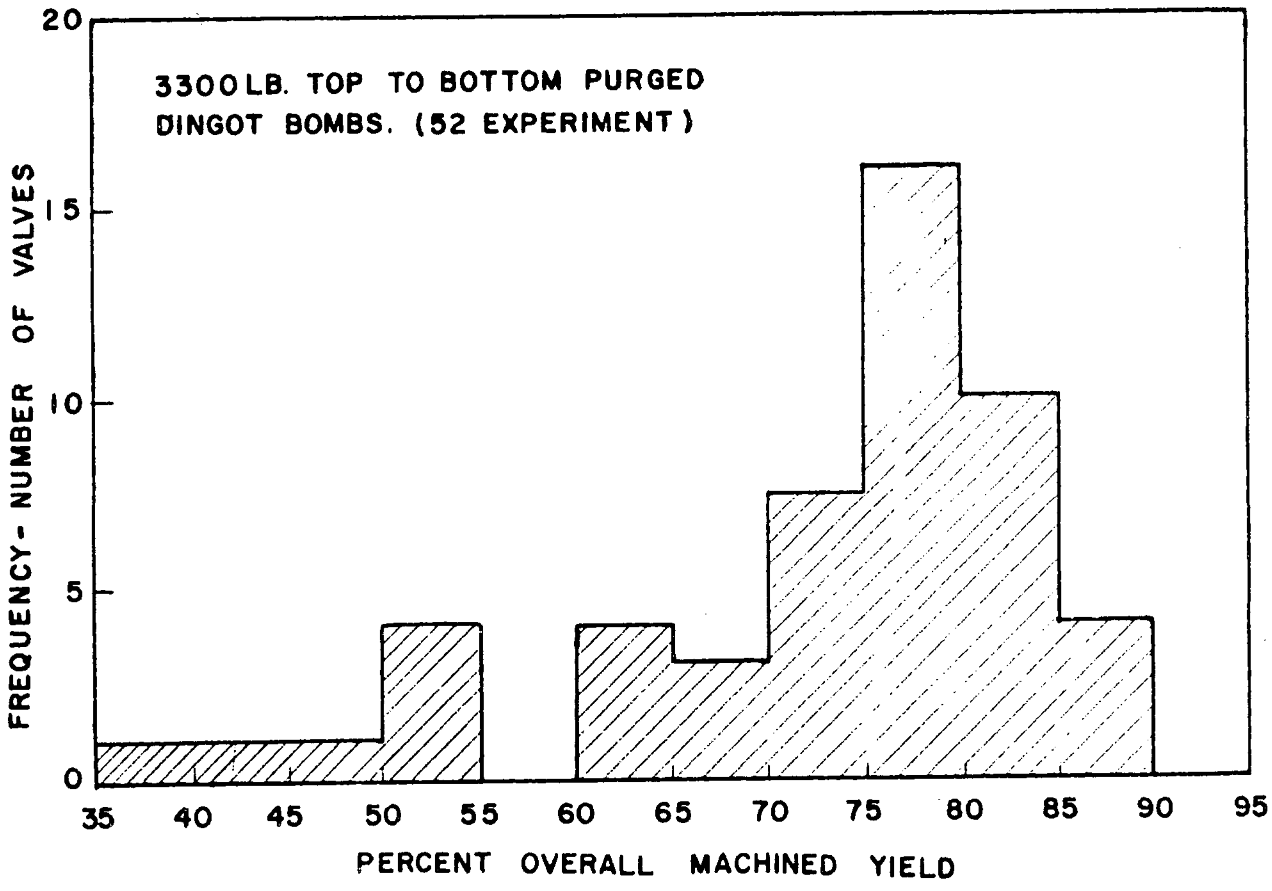

Figure 12 illustrates the distributions of dingot hydrogen contents obtained with the six types of helium purged bombs. The number of values available for Types 1 and 2 was sufficient to provide informative figures. The number of experiments in each of the remaining four types is considered inadequate to be informative.

The values for Types 1 and 2 as one category, and those for Types 3, 4, 5, and 6 as a second have been combined to form the hydrogen distribution bar graphs of Figures 13 and 14. These distributions thus represent 100% roasted magnesium fluoride liner dingot bombs in one instance, and combinations of roasted bottoms and caps with normal magnesium fluoride side-wall liners in the other. Hydrogen values concentrate around 2.0 ppm in both figures, but a greater scatter toward extreme high values is observed in Figure 14. Evidently similar low hydrogen dingot values may on occasion be obtained in either case but the 100% use of roasted slag has given a more consistent and slightly lower average.

The long firing times obtained for small non-purged bombs lined with roasted magnesium fluoride were also occasionally encountered with similarly lined 3300 pound dingot bombs even though gas-purged. Figure 15 is a bar graph illustrating the distribution of firing times for such bombs. Two distinct peaks exist, one slightly below the 500 minute firing time usually experienced with normal dingot production bombs, and a second at twice the normal firing time. The latter peak is equivalent to the firing time expected for roasted magnesium fluoride lined bombs which are not helium purged. Further examination of the experimental data revealed that the majority of the long firing times were obtained with top to bottom purging (Type 2 experiments). Evidently sufficient purging to affect the firing time was not obtained due to helium leaks around the top shell flange. With bottom to top purging (Type 1 experiments) such leaks did not exist. This behavior confirms the premise that adequate helium purging reduces the firing time of roasted magnesium fluoride lined dingot bombs.

FIGURE - 12

DISTRIBUTION OF DINGOT HYDROGEN CONTENTS FOR THE 6 TYPES OF 3300 POUND HELIUM PURGED DINGOT BOMBS

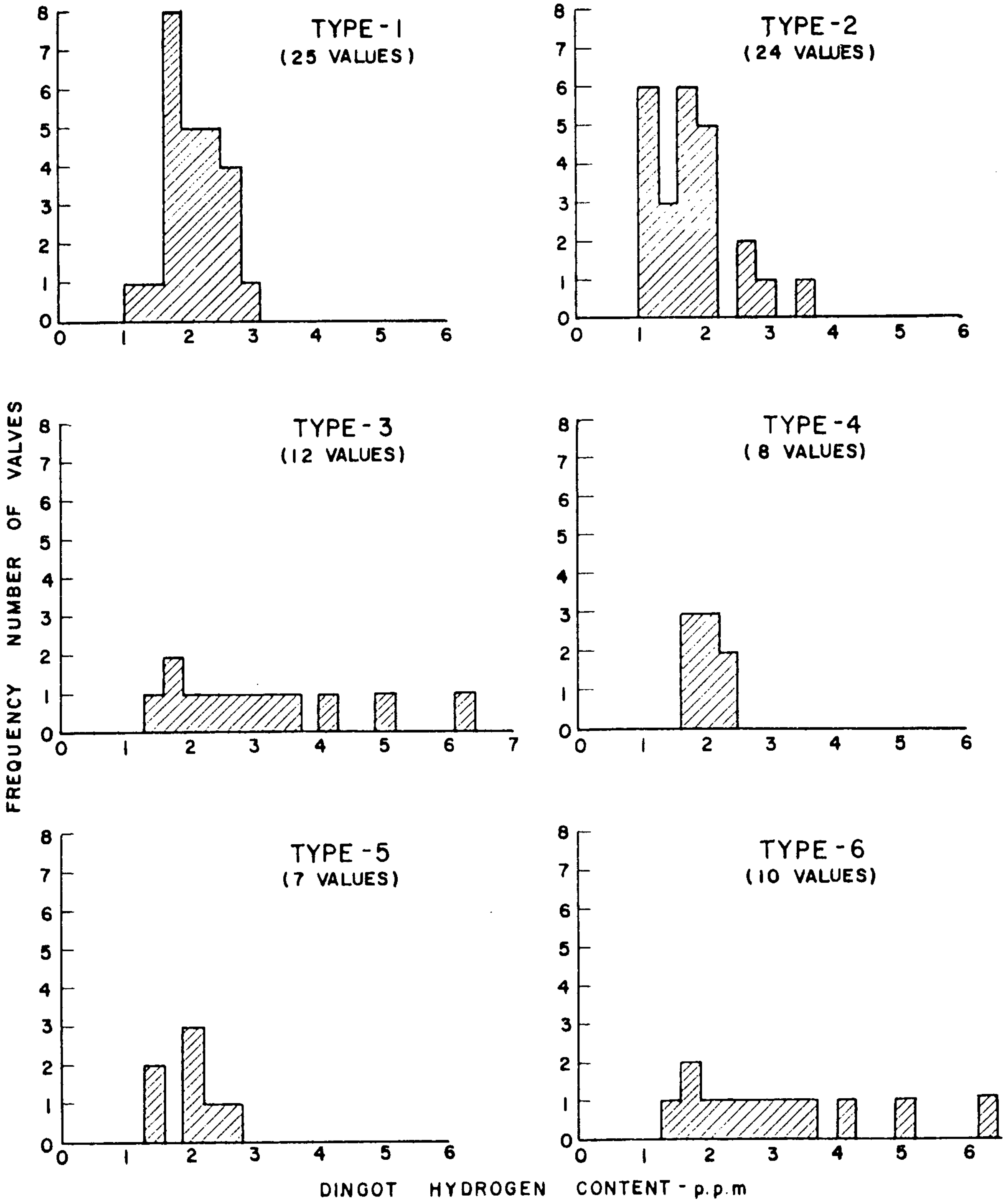

FIGURE - 13

DISTRIBUTION OF DINGOT HYDROGEN CONTENTS

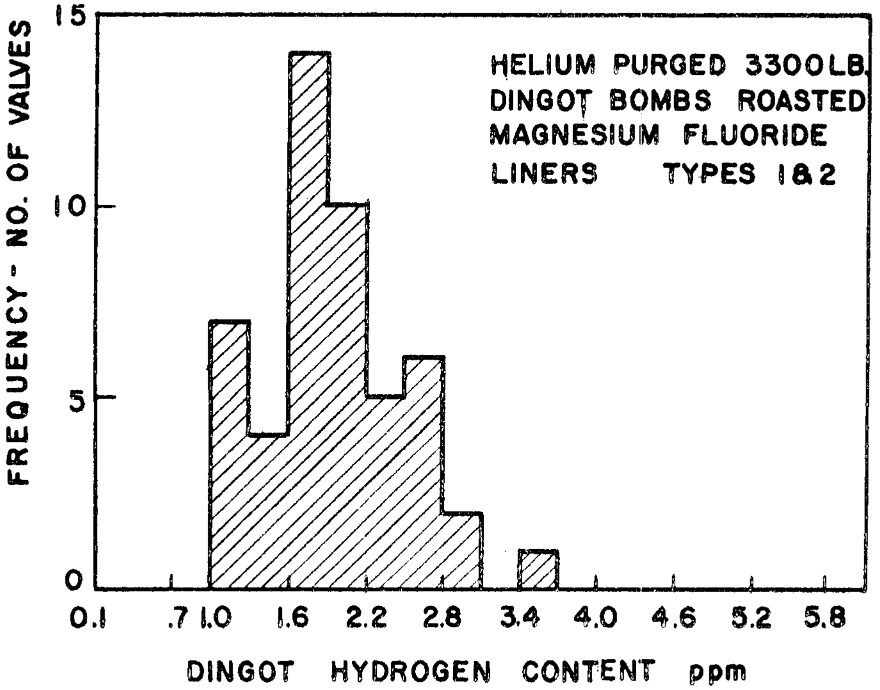

FIGURE - 14

DISTRIBUTION OF DINGOT HYDROGEN CONTENTS

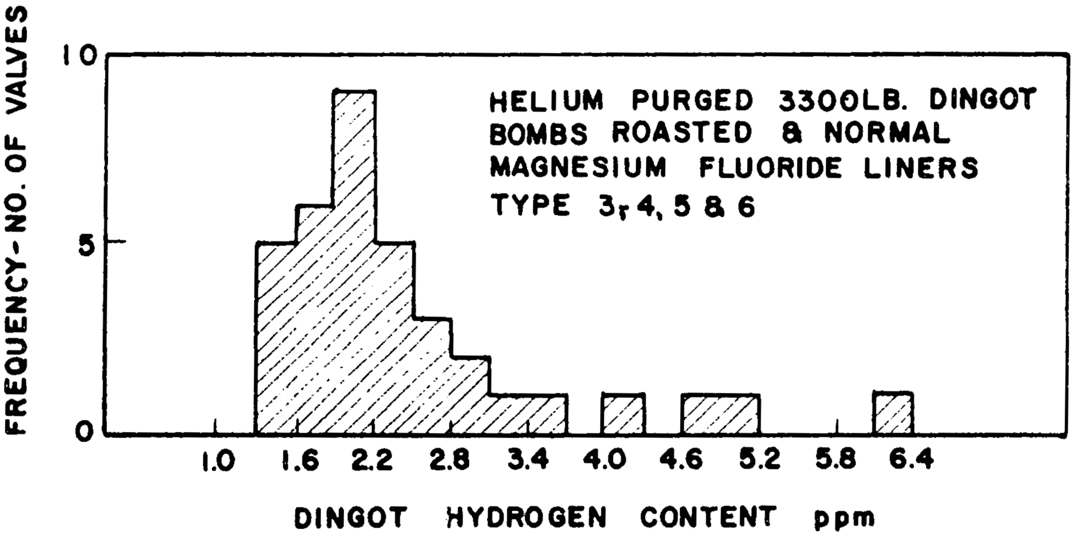

FIGURE - 15

DISTRIBUTION OF FIRING TIME

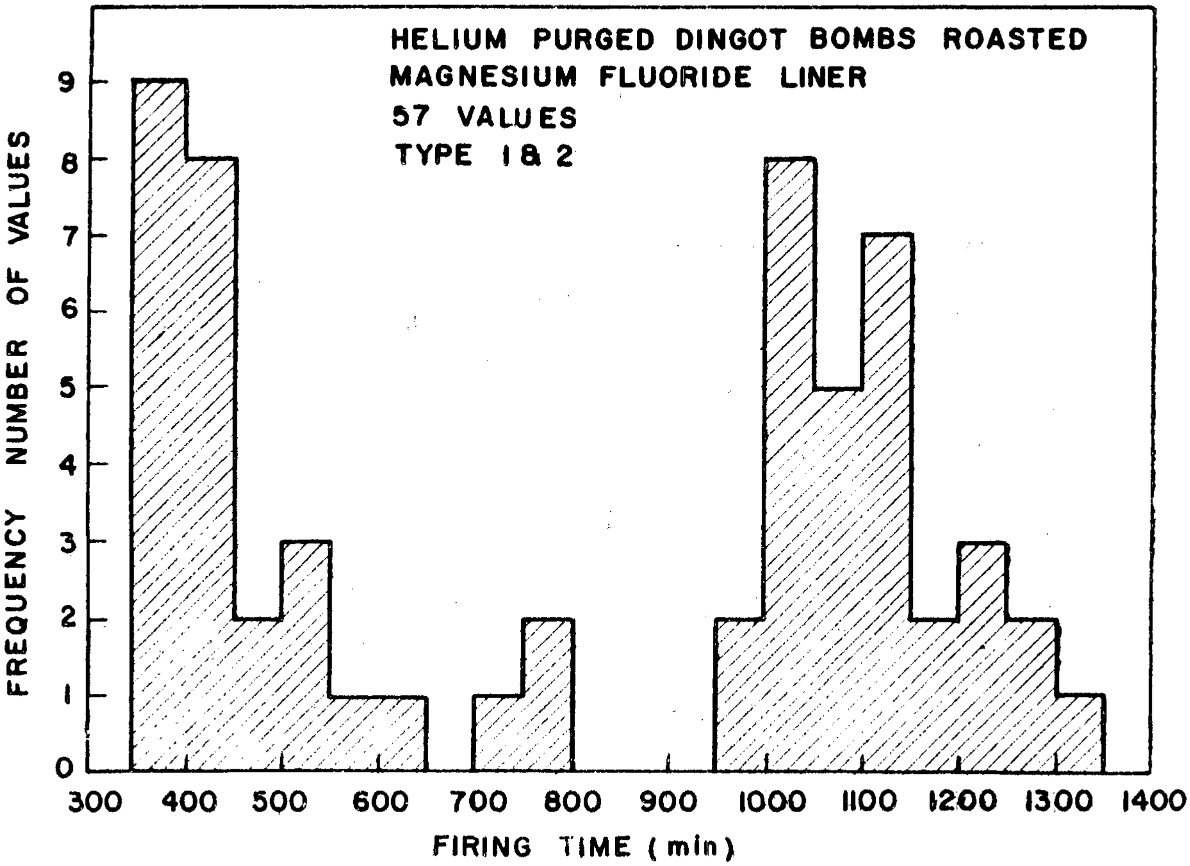

Figure 16 is a bar graph illustrating the distribution of firing times for 3300 pound gas purged dingot bombs lined with combinations of roasted and normal magnesium fluoride. Two connected peaks exist, one on each side of the normal 500 minute firing time. Examination of the data revealed that these peaks represent a distribution around the 500 minute firing time and are not representative of liner construction or purge direction. The extremely long firing times were however obtained with top to bottom purging. But a *majority* of the top to bottom purged dingot bombs did exhibit normal firing times, a trend interpreted as resulting from the influence of the normal magnesium fluoride side-liner in these bombs.

The more consistant low hydrogen values obtained with an all-roasted magnesium fluoride liner, and the increased firing time frequently obtained with such a liner suggested that a correlation might exist between the two. Figure 17 illustrates the relationship of dingot hydrogen contents with firing times for roasted magnesium fluoride lined, helium purged, 3300 pound dingot bombs. A definite trend exists, indicating that a long firing time is associated with a low dingot hydrogen content. The same relationship is illustrated in Figure 18 for combinations of roasted and normal magnesium fluoride lined, helium purged, 3300 pound dingot bombs. Again the trend indicates that a long firing time contributed to a low dingot hydrogen content, even though a large percentage of the liner material was normal magnesium fluoride.

B. Vented Charges

It has been observed that a considerable quantity of gas is evolved from bombs during heating.[9] This has been attributed to an expansion of the original bomb atmosphere and to the liberation of gases from bomb constituents. A more efficient removal of these gases which contain a high percentage of hydrogen, could possibly contribute to the reduction of hydrogen in the reduced uranium.

Six 3300 pound dingot experiments were performed to evaluate a possible method of improving the release of gases from the UF_4 - Mg charge. These bombs were assembled using normal MFL, UF_4 and Mg. Thirteen 1¼ inch diameter vertical vent holes were formed in the charge by driving a steel rod 29 inches into the blend and then carefully

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[9] Neumann, N. F., *et. al, Process Development Quarterly Report Part I*, Mallinckrodt Chemical Works, *MCW-1401*, (April 1, 1957) p. 65-71

FIGURE - 16

DISTRIBUTION OF FIRING TIMES

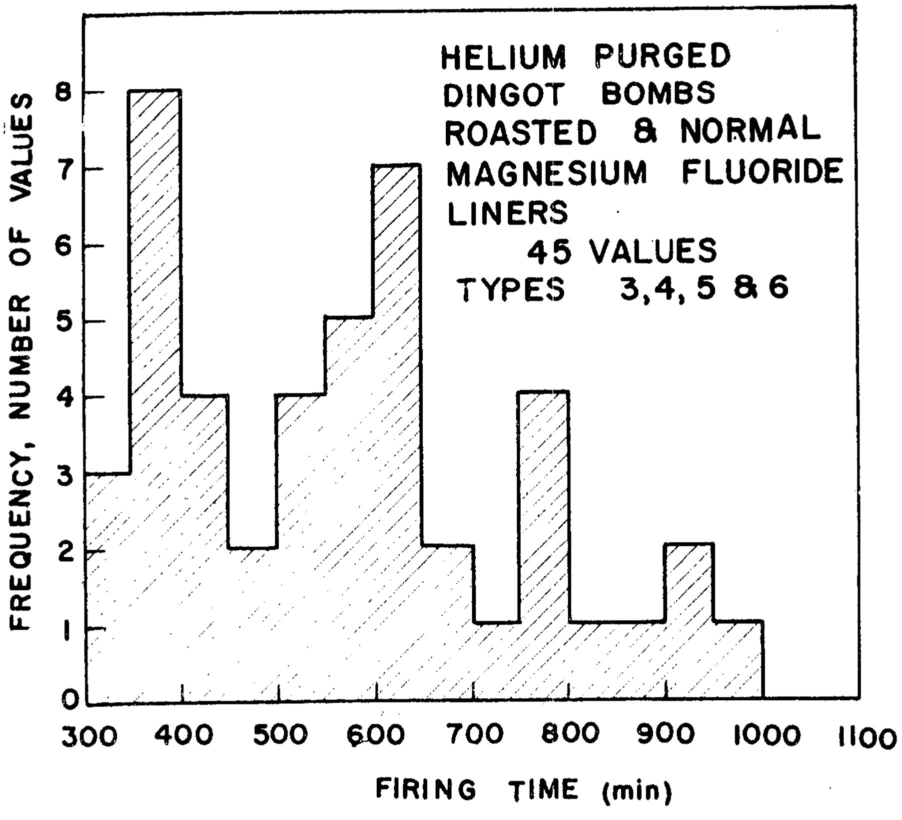


FIGURE - 17

RELATION BETWEEN DINGOT HYDROGEN CONTENT AND FIRING TIME

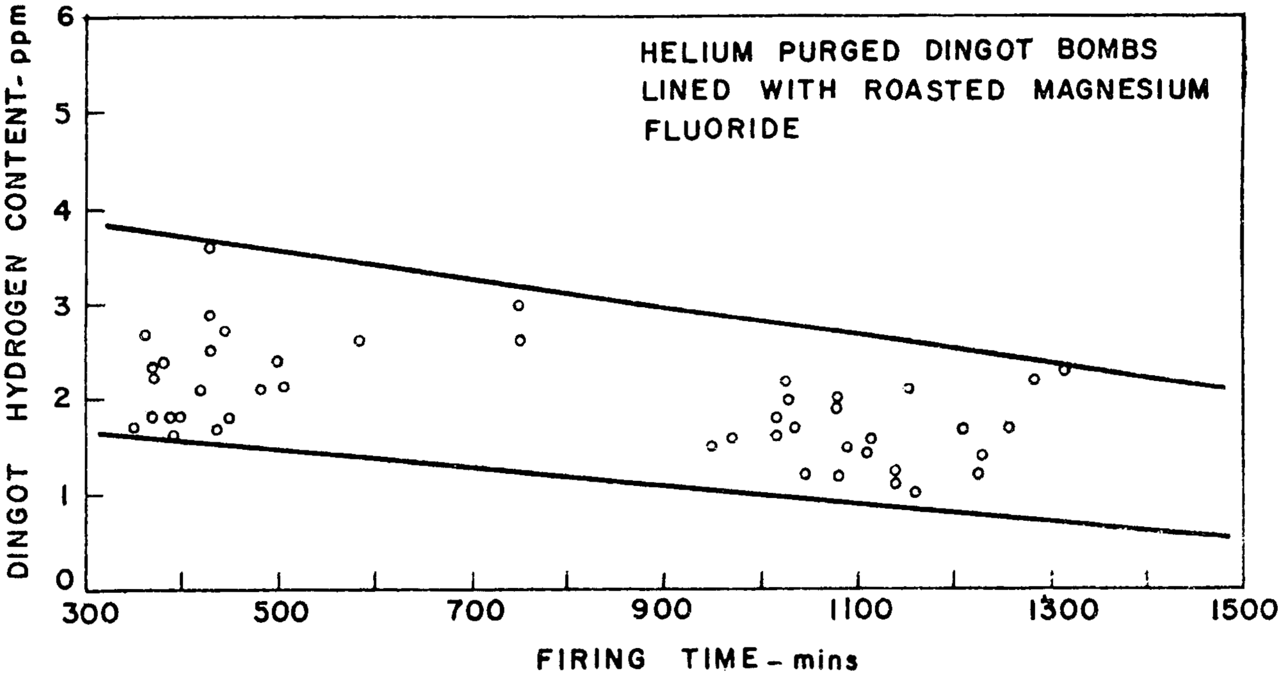
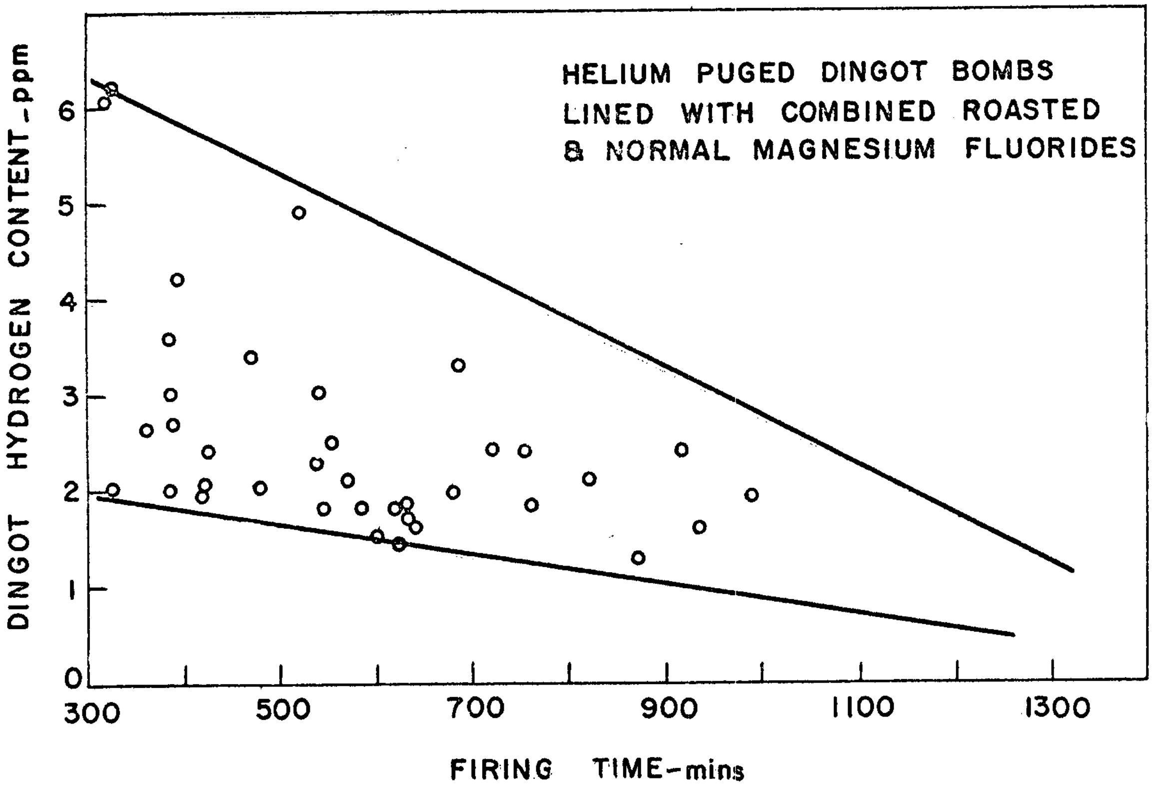


FIGURE - 18

RELATION BETWEEN DINGOT HYDROGEN CONTENT AND FIRING TIME



withdrawing the rod to leave a cavity. These holes symmetrically spaced throughout the charge, were intended to provide a ready path of escape for the bomb gases. Table III contains the results of these experiments.

Table III

Rodded Charge in 3300 Pound Bombs

Run No.	Firing Time min.	Crude Yield %	Overall Machined Yield %	Hydrogen ppm
21763	510	94.87	70.28	2.73
21764	471	96.06	81.27	2.5
21765	410	91.47	60.73	4.2
21766	455	90.73	70.33	3.64
21767	450	95.90	78.91	2.18
21768	445	90.58	68.41	2.62
Average	457	93.27	71.66	2.98

The average hydrogen content conforms closely to standard bomb reduction results. Evidently this method had no appreciable affect on the hydrogent content of the dingots produced.

C. Igniters

The use of roasted liner materials in dingots has contributed to a marked decrease in hydrogen in the metal. However, the firing time for these dingots was lengthened from around eight hours with MFL liners to about 16 hours when roasted liners were used. In order to evaluate separately the effect of long firing time *versus* that of roasted liner material on the hydrogen content of dingot uranium, a method of firing bombs after a predetermined heating period was needed. A resistance type electrical heating element buried in the UF_4 - Mg charge was chosen as a possible means of "triggering" a bomb reaction. Using this scheme, roasted slag lined bombs could be fired after a normal heating time permitting an evaluation of the effects of long firing times *vs.* roasted liners. Another possible advantage of such a system was that the physical location of the point of ignition of the reaction could be controlled and the effect of this variable on bomb yield could be studied.

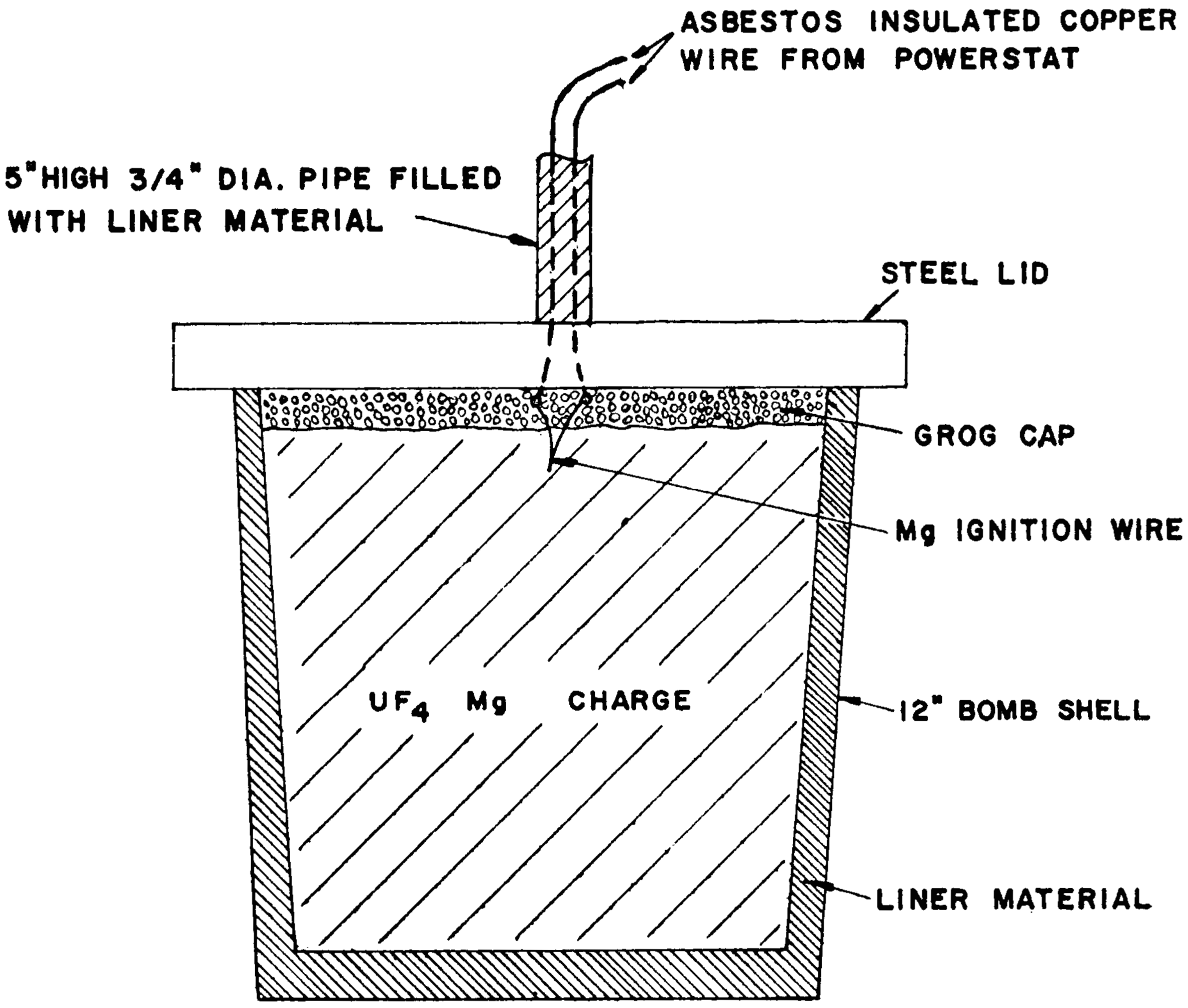
Initial experiments were directed toward the development of a magnesium ribbon ignited using a barium peroxide booster. *The $\frac{1}{8}$ inch by 0.005 inch thick magnesium* ignition wire was looped into the top of the charge so that its center was about 3 inches below the top of the charge. The center section of the loop was reduced to $\frac{1}{32}$inch by 0.005 inch so as to provide a hot spot when an electric current was passed through it. A mixture of 84 grams BaO_2 and 25 grams Mg powders was packed around the "hot spot" of the magnesium ribbon. The ends of the magnesium ribbon were attached to insulated copper wires extending through the lid. These in turn went to a powerstat for controlling the 110 volt power input. A typical assembly is shown in Figure 19.

Several 50 pound, and 12 inch bombs, and one 3300 pound dingot were successfully fired with a magnesium ribbon igniter, but several others assembled in a similar manner failed to fire. A careful dissection of these bombs showed that in some *instances the magnesium igniter ribbon had been almost completely oxidized by the* barium peroxide during the heatup prior to firing. In other instances the magnesium ribbon had melted through at the point of junction with the copper lead wire from the powerstat. The junction was located in the slag cap just above the UF_4 - Mg charge. Since the bombs were heated to 1150 - 1250°F, it was possible that the magnesium had been weakened or had oxidized to such an extent as to form a bad connection with the copper wire.

Later firings were made using an ignition system consisting of copper lead wires from the powerstat joined in the slag cap to a $\frac{1}{16}$ inch diameter manganese-alloy (M1) wire connected in turn to a nichrome resistance coil. It was calculated that the contamination of the uranium metal from the introduction of these ignition wires should amount to only a few parts per million and should not cause concern, since *these impurities are normally very low in dingot uranium*. It was found that successful ignitions could be performed without the use of a barium-peroxide booster, *i.e.*, using the nichrome resistance coil embedded directly into the UF_4 - Mg charge.

By varying the length of the manganese-magnesium alloy wire, it was possible to place the nichrome igniter at any selected position in the bomb, and thereby control the exact location from which the bomb reaction would propagate. Experiments are now being performed to determine the best ignition position. Preliminary work had already indicated that bombs, in which the reaction was initiated at the bottom corner, lost less magnesium through the top flange opening at the time of firing, and had better dingot surface qualities than those which were fired near the top.

FIGURE 19
ELECTRICALLY FIRED BOMB



D. Graphite Liner - 12 Inch Bomb

The effects of slag liner properties on the hydrogen content of uranium metal formed in a bomb reaction have been extensively investigated. Replacement of the MFL by a more satisfactory liner material might completely eliminate the bomb constitutent as a hydrogen contribution.

A 12 inch shell, lined with normal MFL as a safeguard, was provided with a machined graphite crucible to serve as an inner liner. The blend of normal UF_4 and magnesium was charged into the graphite liner and topped with a graphite cap. A normal MFL cap was then packed over the graphite disc. This bomb was fired using normal firing procedures. The results were:

Firing	-	190 min.
Crude Yield	-	93.4%
Hydrogen	-	4.5 ppm
Carbon	-	100. ppm

Considerable effort was required to remove the derby and the graphite liner had to be chipped out of the shell.

The carbon pickup by the derby was no more than moderate. However, the hydrogen content was equivalent to the values obtained with normal 12 inch bombs and the use of the graphite appears to have been without benefit.

E. Liner Permeability

Work has been started on determination of the purge-gas velocity-pressure drop relationships through the charge and through liner materials of dingot bombs.

Materials under investigation are:

1. UF_4 - Mg blend
2. Vitro roasted slag
    a. air classified fines
    b. through 20 mesh
3. Standard magnesium fluoride liner

The test gas purge apparatus is shown in Figure 20. Liner material is jolted in the glass pipe and then purged with helium from the top. The flow rate is recorded from the wet test meter, and the pressure drop is read from the manometer connected to the top and bottom of the glass pipe section. The gas flow is then increased, and new velocity-pressure drop data are obtained. The bed thickness is recorded from the calibrations on the glass pipe. The apparatus is periodically checked for leaks by closing the exit line from the glass pipe and observing the equalization in pressure through the test column.

Essentially the same procedure is used for the UF_4– Mg charge, except that it is packed by rodding the material.

Velocity-pressure drop data, plotted as $\Delta P/L$ *vs.* velocity per unit cross-sectional area, are shown in the following graphs. For the liner material, the number of jolts was held constant. The data for the standard MFL graph (Figure 21) were obtained over a three-day period from the same sample of material. The readings obtained during the first two days gave that section of the curve nearest the coordinates. The second section was derived from the data collected on the third day. The cause of this break in the curve is not as yet understood.

More data are necessary in order to define more clearly the curves obtained for roasted slag liner material (Figure 22).

The experimental data indicate that standard MFL offers at least three times more resistance to gas flow than Vitro roasted slag, and approximately ten times more resistance to gas flow than a UF_4 – Mg blend (Figure 23). Vitro roasted slag appears to offer twice as much resistance as the UF_4 – Mg blend.

At present, the data cannot be applied with assurance to actual dingot liners and charges, since in these first tests, neither the liner material nor the blended charge was packed as hard as in an acutal dingot.

This initial work will be extended so that the criteria for optimum liner materials (*i.e.*, one providing maximum strength and minimum gas flow in the side liner as one grade and a second type with maximum permeability to gas flow for bottom liner) may be established.

FIGURE 20

SKETCH OF GAS PURGE APPARATUS

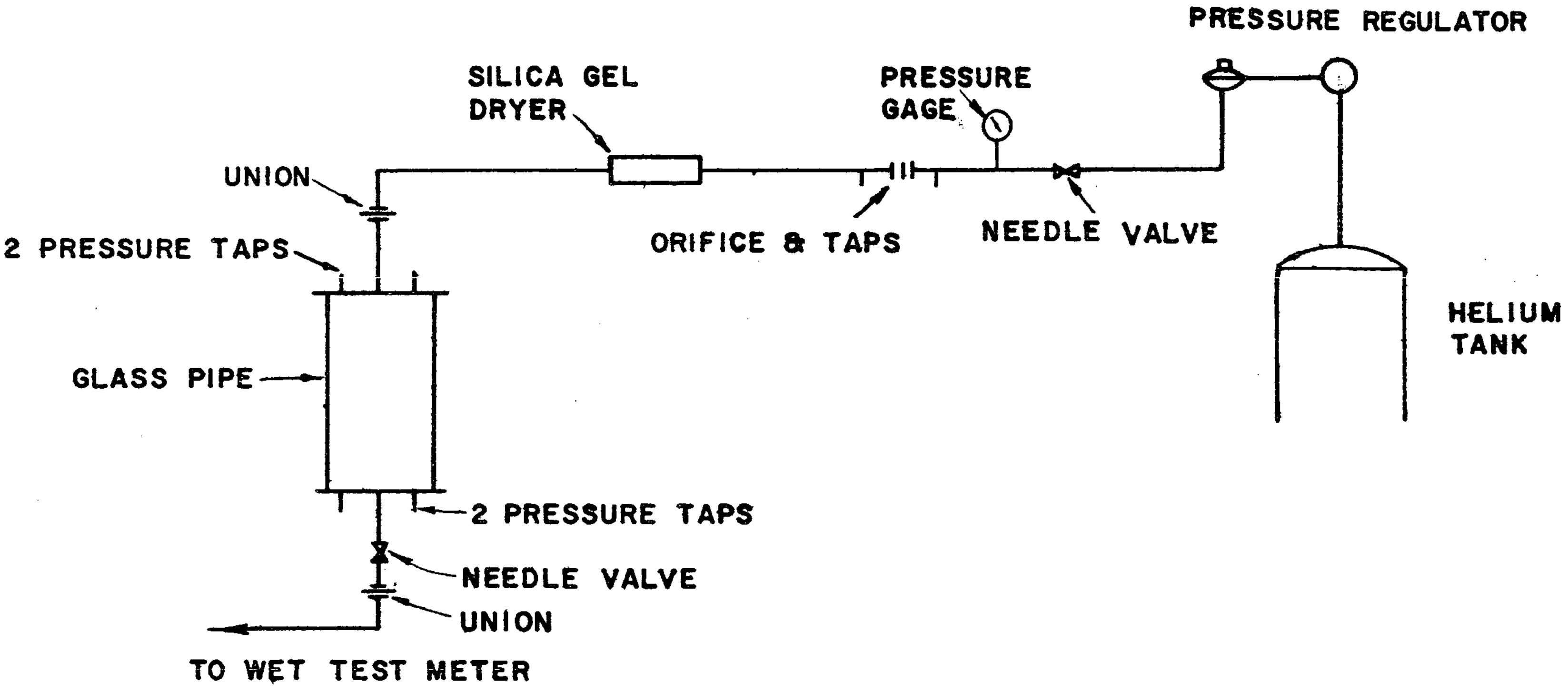


FIGURE 21

ΔP/L VERSUS FLOW

FOR STANDARD MFL

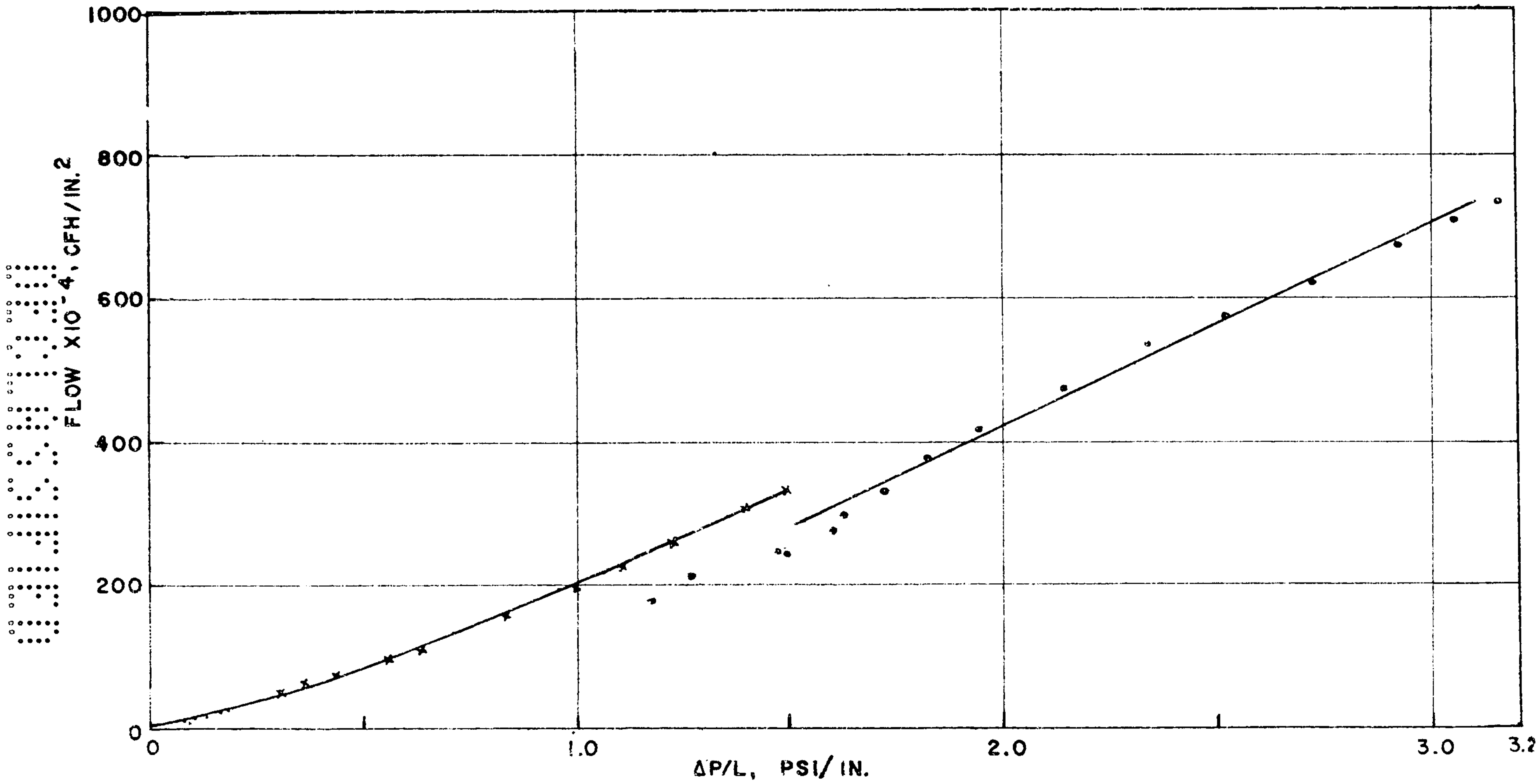


FIGURE 22
Δ P/L VERSUS FLOW
FOR VITRO ROASTED SLAG

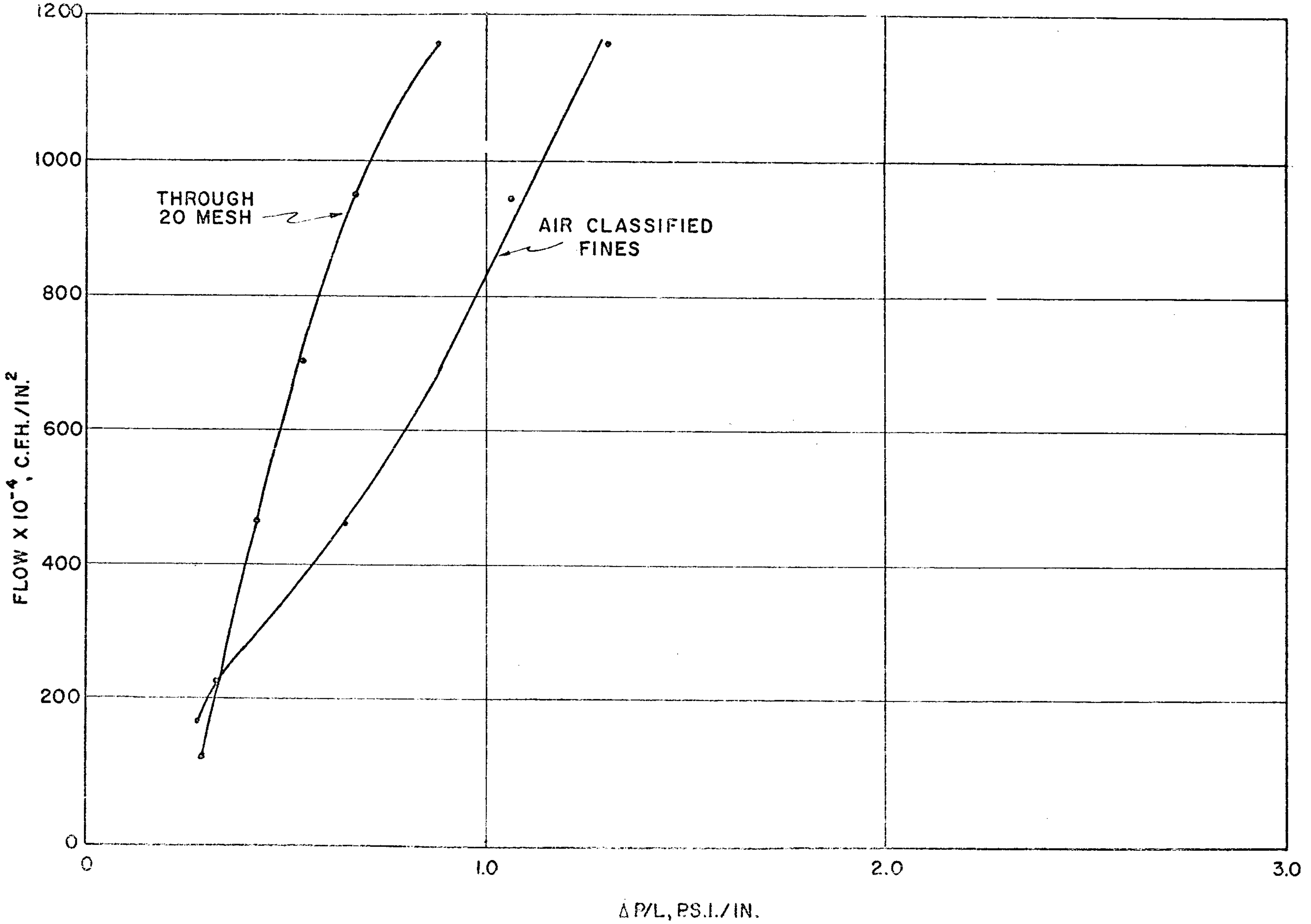
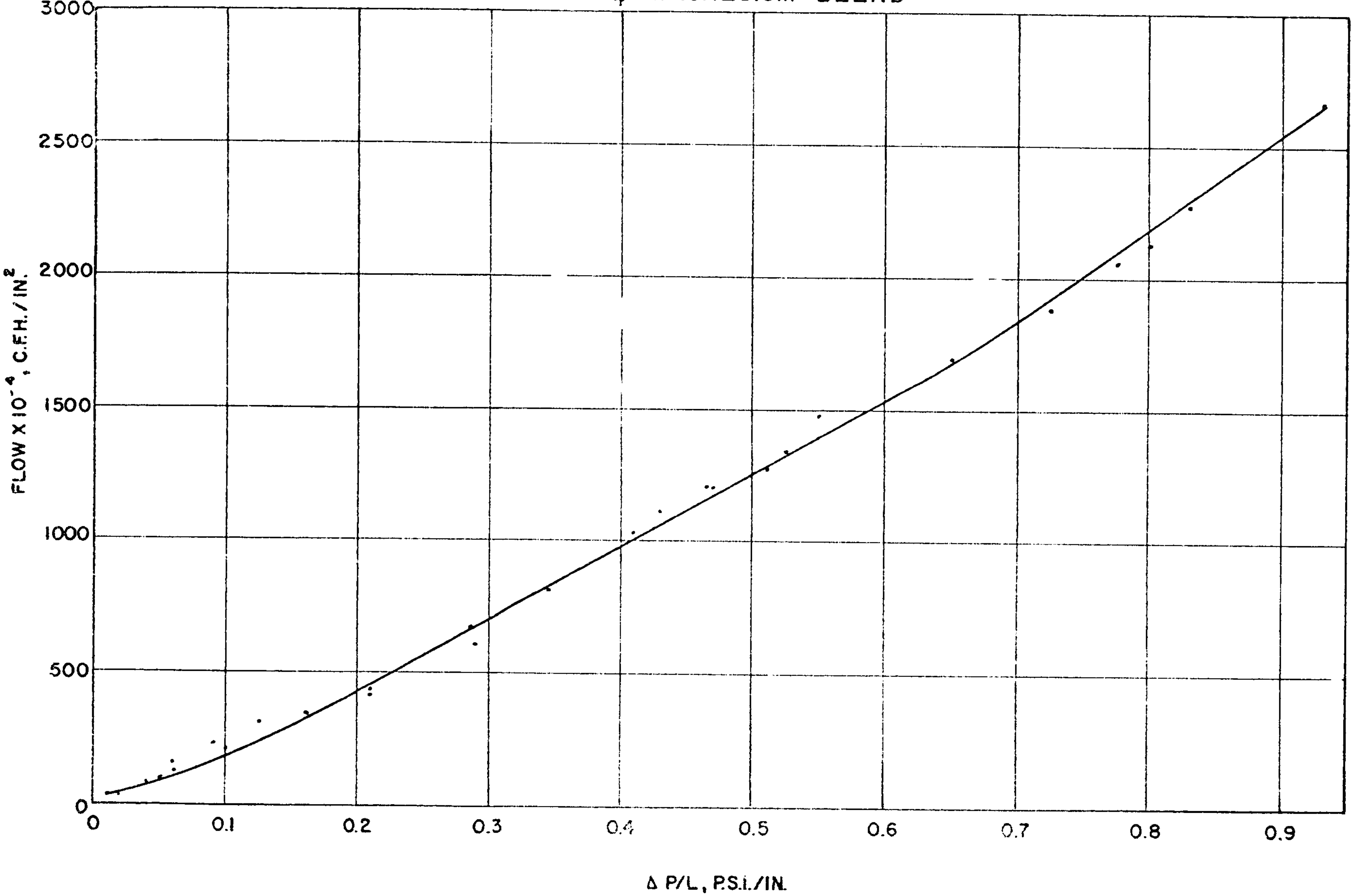


FIGURE 23

Δ P/L VERSUS FLOW

FOR UF_4-MAGNESIUM BLEND



DINGOT FORGING

by

R. W. Becker
H. J. Schaffer
R. F. Hartmann

I. Summary

1. During this quarter, the following quantities of forged dingot bar stock were produced:

Routine metal for SRP slugs -	89 tons.
Low hydrogen metal for HAPO slugs -	24 tons.
Billets for Adrian gamma extrusion -	34 tons.
Total	147 tons

2. Yields for the dingot process have remained at the same level as for the previous quarter.

3. The revised shear-knife used to notch forged dingot bars gives a broader notch and eases removal of samples for analysis.

II Introduction

Acceptance of dingot metal for pile usage has required the piloting of fabrication of fuel elements for irradiation tests. Early in the investigation of the dingot process it became apparent that the most economical shape of dingot required preliminary forming to prepare it for successful rolling at NLO. Initial experiments indicated that press forging a dingot heated in a salt bath would be satisfactory in reducing the cylindrical dingot to a forged bar, which could easily be rolled. Previous work in perfecting this forming technique has been reported in past quarterly reports[1], and current progress is described below.

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[1] Williams, F. H., Schaffer, H. J., *Process Development Quarterly Report, Part II,* Mallinckrodt Chemical Works, *MCW-1398* (November 1, 1956) p. 83-88.

III. Discussion

A. Production

As more experience has been gained in the manipulation and press-forging of machined dingots, it has been possible to maintain production schedules for standard allocations and still fulfill a number of special forging requests.

During this quarter 89 tons of forged dingots were produced for rolling to SRP fuel elements. The metal used for these slugs was from bombs that failed to yield metal with hydrogen contents below 2 ppm. During this same period, 24 tons of dingot bars with hydrogen below 2 ppm were shipped for rolling to HAPO fuel elements for testing at that site. Thirty-four tons of dingots, rough forged to 7.5 inch diameter and machined to 6.865 inch diameter, were produced for use as billets in the gamma extrusion development program.[2]

B. Slug and Dingot Process Yields

Overall slug yields from rolling and slug fabrication have increased slightly during the past quarter. Table I shows the rod and slug yield data for SRP type slugs along with the dingot process yields. The average yield from green salt to good slugs reported in the previous quarterly[3] was 46.21%. This has increased to 50.47% during this past quarter. This overall increase is largely due to an increase from 68.53% to 73.05% in the step from good rods to machined slugs. The yield for the forging of the scalped dingots has remained above 96%.

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[2] *Cf.* p 133

[3] Williams, F. H., Schaffer, H. J., Hartmann, R. F., *Process Development Quarterly Report, Part II,* Mallinckrodt Chemical Works, *MCW-1400,* (February 1, 1957) p. 97-103.

Table I

Individual and Overall Yields for the Dingot Process

Shipment Number	Date of Shipment	Type of Slug	Green Salt to Crude Dingot %	Crude Dingot to Scalped Dingot %	Scalped Dingot to Forged Bar %	Forged Bar to Good Rod %	Good Rod to Total Slug %	Total Slug to Good Slug %	Green Salt to Forged Bar %	Forged Bar to Good Slug %	Green Salt to Good Slug %
58	9/26/56	SRP	96.70	83.02	97.87	93.67	69.66	98.40	78.57	61.13	48.03
59[a]	10/10/56	SRP	96.08	82.31	97.15	91.18	77.82	98.86	76.83	69.60	47.96
60	10/17/56	SRP	96.60	81.99	96.10	93.82	72.34	96.33	76.10	65.23	49.62
61	10/17/56	SRP	96.36	78.38	98.60	93.15	73.69	96.27	74.47	66.23	49.31
62	11/24/56	SRP	96.97	82.51	98.75	b	b	b	79.00	b	b
63	11/24/56	SRP	96.73	81.94	94.61	94.82	b	b	74.99	b	b
64	11/30/56	SRP	96.47	84.99	99.07	95.22	71.90	94.69	81.22	64.83	53.83
[c] 65	11/30/56	SRP	97.20	84.92	96.52	89.59	b	b	79.67	b	b
66	12/14/56	SRP	97.31	81.52	98.11	92.83	75.11	96.54	79.91	67.32	53.79
67	12/26/56	SRP	97.50	84.74	97.13	90.61	70.86	96.10	82.21	61.70	50.72
68	12/26/56	SRP	97.24	80.22	98.68	81.57	b	b	79.47	b	b
69	1/10/57	SRP	97.36	82.64	97.53	b	b	b	78.34	b	b
70	1/16/57	SRP	97.47	75.77	97.80	b	b	b	71.48	b	b
71	1/23/57	HAPO	97.19	76.31	98.06	b	b	b	72.71	b	b
72	2/11/57	SRP	95.21	66.20	92.01	b	b	b	68.49	b	b
73	2/20/57	SRP	94.61	71.56	94.79	b	b	b	63.93	b	b
74	2/19/57	HAPO	94.03	73.88	96.77	b	b	b	67.22	b	b
75	2/28/57	HAPO	92.28	73.91	93.91	b	b	b	64.03	b	b
76	2/28/57	SRP	91.96	72.40	89.96	b	b	b	60.87	b	b
Averages			96.07	78.91	96.50	91.65	73.05	96.74	74.18	65.15	50.47

Table I (cont)

[a] Part of this shipment made into WAPD ovals, the yields for these shipments represent only those forged bars that were made into SRP slugs.

[b] No rolling or slug data are available for these shipments

[c] Data above this line reported previously in *Process Development Quarterly Report Part II,* Mallinckrodt Chemical Works, *MCW-1400,* (February 1, 1957) p. 99

C. Hot Notching of Forged Bars.

The shear-knife used for notching forged bars has been redesigned to give a more desirable nose contour to the forged bar stock. The shear-knife reported in the previous quarterly[4] was successful in forming a nose contour on the bar that could enter the rolls easily at NLO. This ease of entry in the rolls reduced the tendency for "fishtailing" of the bars during rolling. The purpose of this new knife was to give a broader notch to expedite the removal of samples for analysis. Notching with the new shear-knife has not resulted in any operational difficulties, however it appears that the width of the notch should be decreased slightly to eliminate flat sections extending out from the nose of the bar after sampling. Figure 1 is a photograph of the redesigned shear-knife. Figure 2 is a photograph illustrating the contour of a finished, hot-notched, forged bar after the analytical sample has been removed.

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[4] *Ibid,* p. 100

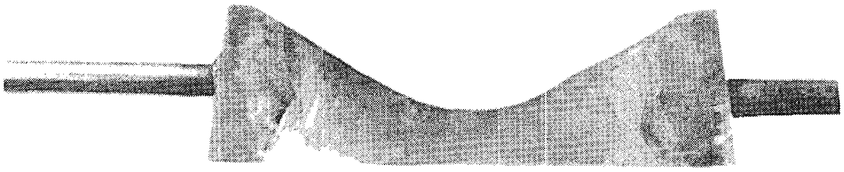

Figure 1

Redesigned shear-knife for Hot Notching Forged Dingot Bars

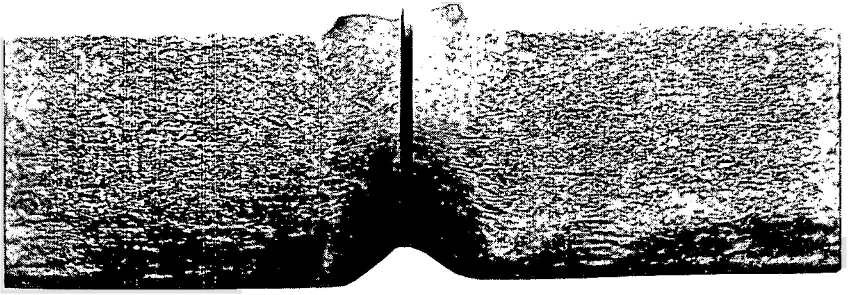

Figure 2

Contour of a finished, hot notched, forged dingot bar after removal of analytical sample.

DINGOT EXTRUSION

by

R. W. Becker
J. W. Hansen
H. J. Schaffer
R. F. Hartmann

Summary

1. Billet temperatures of 1800° or 1900°F permitted complete gamma phase extrusion.
2. The billet was not difficult to handle at 1800° or 1900°F.
3. Quenching the extruded rod in Houghton Liquid Heat No. 980 salt lowered the effect of surface oxidation.
4. There were no particular problems with runout equipment.
5. Partially extruding a graphite follower block eliminated the need for a shear or saw to separate the extruded rod from the butt.
6. Glass lubricants appeared to decrease die wear and yield a lower extrusion constant "K"
7. The use of "Dag" lubricants did not appear to change the behavior of the extrusion.
8. Although the rods reported herewith have some defects, they represent a vast improvement over the badly beta "checked" rods reported in the previous quarterly[1].

Introduction

The present dingot process produces metal in a shape which cannot be rolled successfully at NLO without a primary forming operation. At present this shape is scalped on a vertical lathe to remove surface contamination and then press forged to a section which is suitable for rolling. The scalping plus forging route has certain disadvantages:

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[1] Williams, F. H., Schaffer, H. J., Hartman, R. F., *Process Development Quarterly Report Part II*, Mallinckrodt Chemical Works, *MCW 1400* (February 1, 1957) p 105-119

1. Lathe scalping is a slow process and produces uranium metal chips which are a problem to re-introduce into the production stream.

2. Forging is a multi-step operation which results in low volume production and high labor costs per pound of metal forged.

3. Forging is not versatile, in that the variety of shapes which can be produced is limited, and tooling for possible variations is costly.

On the basis of the inherent disadvantages of forging, an extrusion process was chosen to do the preliminary forming of the dingot in the new production plant at Weldon Spring. Some of the advantages to be derived from this fabricating method are:

1. Extrusion can possibly eliminate scalping by leaving a "skin" in the liner.

2. Extrusion is a single step procedure and is a high volume production operation.

3. Better product uniformity can be expected from an extrusion process than from a forging process.

4. The variety of shapes which can be produced is not limited by the process. Hollow sections are also possible with an extrusion process.

In order to reduce the cost of capital equipment, it was decided that the preliminary extrusion of dingots would be done in the gamma phase, where the force required to deform the dingot would be about one tenth of that which would be necessary to extrude in the alpha phase. A development program, initiated to pilot the gamma extrusion process for the Weldon Spring plant, is reported below.

This work has been conducted by the Bridgeport Brass Company, in Adrian, Michigan as a joint program with the Mallinckrodt Chemical Works. Because of size limitations of the extrusion press used at Adrian, the billets have been limited to 6⅞ inches diameter. These billets are machined from rough forged dingot rounds. Previous work[2] has developed the

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[2] *Ibid*

following conclusions:

1. A billet temperature of 1700°F is too low to permit complete extrusion in the gamma phase using a liner control temperature of 800°F.
2. Follower blocks heated to the 1700°F billet temperature were beneficial in reducing the heat loss from the rear of the billet and thereby led to more complete extrusion in the gamma phase.
3. Use of a 2.910 inch I.D. die, which gave approximately the same reduction ratio as will be used for full size dingot extrusion at Weldon Spring, resulted in an extruded rod which gave no serious handling problems.

Experimental Results

The third (January 17th and 18th, 1957) and fourth (February 28th and March 1, 1957) extrusion programs at Bridgeport Brass Company, were conducted to determine:

1. The effect of 1800° and 1900°F billet temperatures on completeness of extrusion in the gamma phase.
2. The influence of glass lubricants on the life of flow type dies used with cones.
3. The relationship of ram speed to the surface quality of the extruded rod.
4. A comparison of the surface of the butt end of the rod obtained when graphite or steel follower blocks (all heated to the temperature of the billet) were used.
5. The effect of the type of follower block on the amount of butt metal left in the container.
6. The effect of "Dag" lubricants on die life, the extrusion constant "K", and the surface of the extruded rod.

During these two programs a total of 33 dingot metal billets were extruded. These billets were 6.865 inches in diameter and 14 to 18 inches long. They were heated to 1800° or 1900°F in Houghton Liquid Heat No. 1450 salt and extruded at a maximum ram speed of about 250 inches per minute. When follower blocks were used, they were heated with the billets in the salt bath. Oil "Dag" lubricant was sprayed on the inside of the liner and die before some of the billets were extruded. The glass lubricants were applied to the billets by rolling the billets over an inclined plane covered with ground glass, and a glass pad was placed against the cone.

A 7.50 inch I.D. liner and Electrite No. 1 high speed steel, flow type dies with a 2.910 inch orifice were used. The steel for these dies was produced by Latrobe Steel Corporation. The dies han an ½ inch inlet radius and a ⅜ inch length of land. A drawing of these dies is shown in Figure 1. The 33 billets mentioned above were extruded during the third and fourth programs in the following manner:

1. Twelve billets were extruded at 1800°F using maximum ram speed, in some cases without follower blocks and in other instances with graphite or steel follower blocks heated to 1800°F. Flow type dies were used without cones. Oil "Dag'' dispersions were used for lubricating the dies and liner on six of these billets.

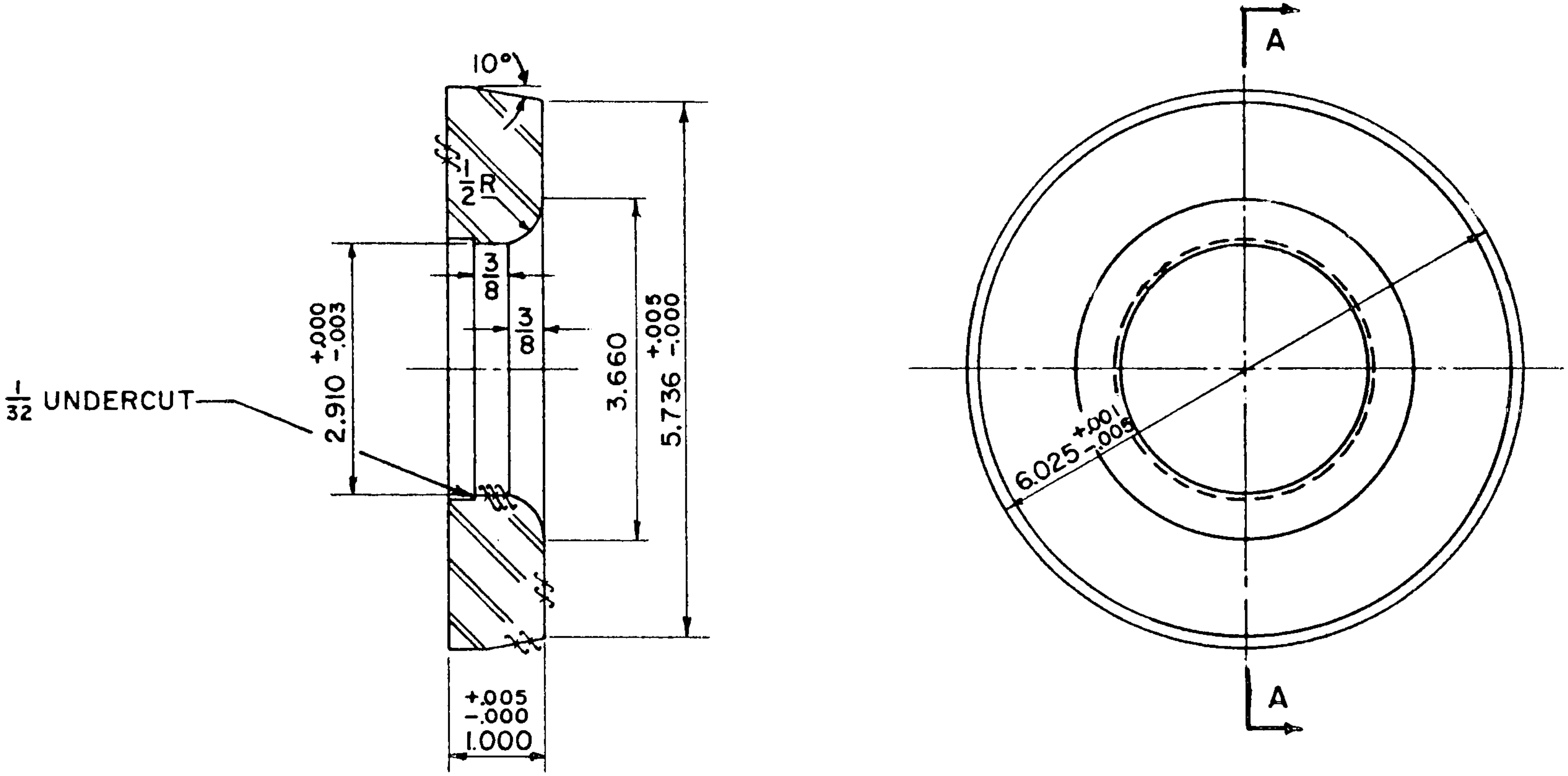
2. Twelve billets were extruded at 1900°F with graphite or steel follower blocks heated to 1900°F, or no follower block at all. Other conditions were the same as for the first twelve billets.

3. Eight billets were extruded at 1800°F using maximum ram speed, graphite or steel follower blocks heated to 1800°F, and three types of glass lubrication.

4. One billet was extruded with a flow die and cone and no glass lubrication or heated follower block as a check on the previous eight.

The data concerning billet temperatures, ram speed, type of follower block, and lubrication for these billets are compiled in Table I.

FIGURE I
DRAWING OF THE EXTRUSION DIE
USED DURNING THE THIRD AND FOURTH PROGRAM



SECTION "A-A"

Table I

Data Sheet for Third and Fourth Gamma Extrusions at Bridgeport Brass Company, Adrian, Michigan, on January 17, February 28, and March 1, 1957

Time of Day	MCW No.	BrBC Billet No.	Die Type	Lubrication: Die and Container	Lubrication: Billet	Transfer Time sec	Extrusion Time sec
January 17, 1957							
12:25pm	21697D	16	flow	oil dag	salt	109	5.0
2:38pm	21653B	17	flow	none	salt	140	4.7
2:50pm	21653D	18	flow	oil dag	salt	97	4.2
3:05pm	21658A	19	flow	none	salt	87	4.2
February 28, 1957							
1:20pm	21587A	20	flow No. 8 with cone	none	salt	104	3.6
1:35pm	21612D	21	flow No. 8	oil dag	salt	116	4.8
1:50pm	21587B	22	flow No. 8	oil dag	salt	73	4.2
2:10pm	21629B	23	flow No. 7	none	salt	92	3.6
2:30pm	21612C	24	flow No. 7	none	salt	85	4.2
2:50pm	21613B	25	flow No. 7	oil dag	salt	108	4.2
3:00pm	21587D	26	flow No. 7	none	salt	76	4.2
3:15pm	21629D	27	flow No. 7	oil dag	salt	85	4.8
3:55pm	21612B	28	flow No. 7	none	salt	70	4.8
4:05pm	21557A	29	flow No. 7	none	salt	111	4.8
4:20pm	21556D	30	flow No. 7	oil dag	salt	93	4.8
4:32pm	21556C	31	flow No. 7	none	salt	100	4.8

[a] Tool oven and liner temperature was 800°F.

[b] Billet and block temperature was 1800°F

[c] Billet temperature was 1800°, block temperature was 830°F.

[d] Billet and block temperature was 1900°F.

Heating Time mins	Billet Length inch	Butt Length in.	Length of Billet Extruded in.	Ram Speed calc. in/min	Follower Block Type	Remarks[a]
75	18	½	17½	210	graphite[b]	
55	18	½	17½	224	steel[b]	
45	18	½	17½	250	steel[c]	
45	18	½	17½	245	graphite[b]	
66	18	⅛	17⅞	300	none[b]	
75	18	⅛	17⅞	225	steel[b]	
73	18	⅛	17⅞	257	none[b]	die striated slightly front to rear
80	18	⅛	17⅞	300	steel[b]	die oil quenched. too large for holder
60	18	½	17½	257	graphite[b]	
70	18	⅛	17⅞	257	steel[b]	graphite stuck to billet side
65	17⅞	⅛	17¾	255	none[b]	
61	17⅞	0	17⅞	223	graphite[b]	pushed graphite out die
75	17¾	0	17¾	222	none [d]	
75	15	0	15	188	steel [d]	graphite stuck to side
75	15	0	15	188	steel [d]	
72	14⅞	0	14⅞	186	graphite [d]	

continued on next page

Table I continued

Data sheet for Third and Fourth Gamma Extrusions

Time of Day	MCW No.	BrBC Billet No.	Die Type	Lubrication		Transfer Time sec	Extrusion Time sec
				Die and Container	Billet		
March 1, 1957							
8:25am	21653C	32	flow No. 7	oil dag	salt	104	4.8
8:35am	21644B	33	flow No. 7	oil dag	salt	82	4.2
8:45am	21658C	34	flow No. 7	oil dag	salt	83	4.8
8:55am	21658B	35	flow No. 7	none	salt	96	4.2
9:18am	21651A	36	flow No. 7	oil dag	salt	66	4.2
9:25am	21644D	37	flow No. 7	none	salt	90	4.2
9:35am	21563D	38	flow No. 7	oil dag	salt	83	3.6
9:55am	21658D	39	flow No. 7	none	salt	85	4.2
10:05am	21644A	40	flow No. 3 with cone	No. 2	salt	100	4.8
10:20am	21670D	41	flow No. 3 with cone	No. 2[e]	Salt+ No. 2[e]	112	4.2
10:35am	21670A	42	flow No. 3 with cone	No. 4[e]	Salt+ No. 3[e]	102	4.2
11:10am	21670C	43	flow No. 3 with cone	No. 3[e]	Salt+ No. 3[e]	110	4.8
11:20am	21671B	44	flow No. 3 with cone	No. 3[e]	Salt+ No. 3[e]	98	6.0
11:35am	21644B	45	flow No. 3 with cone	No. 4[e]	Salt+ No. 4[e]	102	4.8
11:45am	21671D	46	flow No. 3 with cone	No. 4[e]	Salt+ No. 4[e]	108	4.2
12:00noon	21670B	47	flow No. 3 with cone	No. 2[e]	Salt+ No. 2[e]	105	4.8
12:08pm	21671A	48	flow No. 3 with cone	none	salt	60	4.8

The No. 3 die from BBC numbers 40 to 48 was in good condition at the end of this series.

[a] Tool oven and liner temperature was 800°F.

[b] Billet and block temperature was 1800°F

[c] Billet temperature was 1800°, block temperature was 830°F.

[d] Billet and block temperature was 1900°F.

[e] Number indicates type of glass.

Heating Time mins	Billet Length inch	Butt Length in.	Length of Billet Extruded in.	Ram Speed calc. in/min	Follower Block Type	Remarks[a]
73	15⅜	⅛	15⅜	192	none[d]	
50	15½	0	15½	251	graphite[d]	
50	17½	- - -	- - -	219	steel[d]	
50	17¼	- - -	- - -	247	graphite[d]	
48	16⅜	⅛	16¼	234	none[d]	
45	15 7/16	0	15 7/16	221	steel[d]	
45	15¼	- - -	- - -	254	graphite[d]	
50	17⅛	- - -	- - -	245	none[d]	
43	18	- - -	- - -	225	graphite[b]	¼ in. of glass left on cone, billet missed stop
50	18	- - -	- - -	257	steel[b]	¼ inch of glass left on cone
55	18	- - -	- - -	257	graphite[b]	¼ inch of glass left on cone
85	18	- - -	- - -	225	steel[b]	¼ inch of glass left on cone
72	18	- - -	- - -	180	graphite[b]	¼ inch of glass left on cone
72	18	- - -	- - -	225	graphite[b]	¼ inch of glass left on cone
67	18	- - -	- - -	257	steel[b]	¼ in. of glass left on cone; missed stop, glass on top of billet only
46	18	- - -	- - -	225	graphite[b]	¼ in. of glass left on cone; missed stop, glass on top of billet only Die in good condition
41	18	- - -	- - -	225	none[b]	

During the third program, the basket hangers for supporting the billets in the salt bath broke, dropping the billets into the salt bath. The stainless steel support members were made heavier in the hangers used during the fourth program to give them more structural strength at 1800° or 1900°F. The original hangers indented the billets with a groove 1½ inches deep and three inches long at the areas of contact between the billets and the stainless steel hangers. This grooving was eliminated in the fourth program by the use of a machined graphite pad on the bottom of the hanger and woven asbestos cloth spacers on the top edge.

During the third program four billets were extruded before the salt bath sprang a leak. These four rods were extruded into a graphite trough filled with Houghton Liquid Heat No. 980 salt to reduce surface oxidation. In the fourth program the rods were extruded into an empty graphite trough and were then rolled over a bed of Houghton Liquid Heat No. 980 salt. This practice was equally effective in reducing surface oxidation.

The die used for the four extrusions of the third program grooved on the inlet radius, indicating a need for an improved die design. Figure 2 is a photograph of a similar die used for seventeen extrusions during the fourth program, showing grooves of this same type.

The extruded rods when viewed after cleaning, exhibited certain shallow surface defects in some cases covering up to two-thirds the area of the rod. However, these defects were not so severe nor of the same type as those reported in the previous quarterly.[4] Figures 3 - 10 are photographs showing the surface quality of these rods. None of these rods was badly checked on the butt end due to the billets cooling into the beta phase during extrusion.

Figure 3 illustrates the lead end of a rod free from surface defects. In Figure 4 is shown the back end of a rod extruded without a follower block. This rod was separated from the butt metal by running the dummy block against the face of the die. Figure 5 gives a view of the butt end of a rod in which the heated graphite follower block was partially extruded. This automatically separated the rod from the butt. A hole in a rod surface toward the back end of the rod is shown in Figure 6. A section through this defect indicated the hole to be a continuation of the extrusion defect emerging out the side of the rod. "Pipe" or "extrusion defect" is a characteristic flaw encountered in extrusion caused primarily by the rough, oxidized outer surface of the billet flowing into the center of the extrusion. Because of

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[4] *Ibid.*

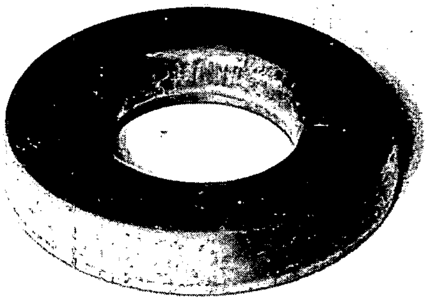

Figure 2

Die used for seventeen extrusions during the fourth program.

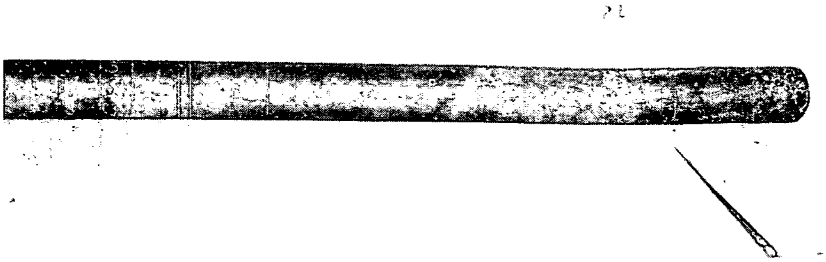

Figure 3

Lead end of Rod 26 showing the surface of a good rod.

Figure 4

Butt end of rod 32, which was extruded without a follower block.

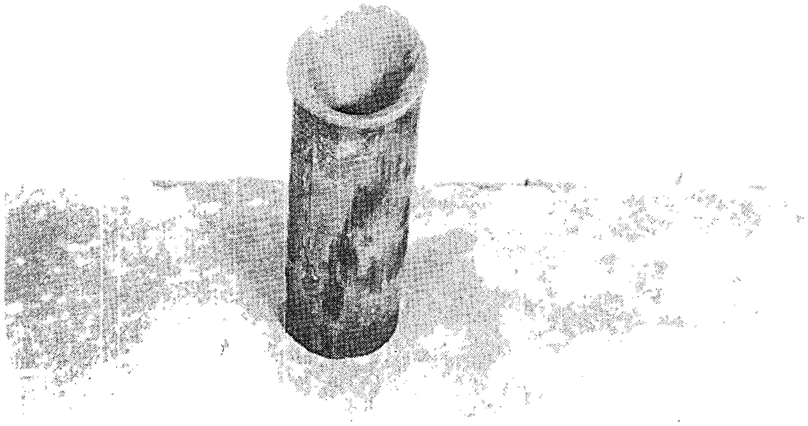

Figure 5

Butt end of rod 27, in which graphite follower block was partially extruded.

Figure 6

Hole near butt end of rod 37 from the "extrusion defect" emerging at the side of the rod.

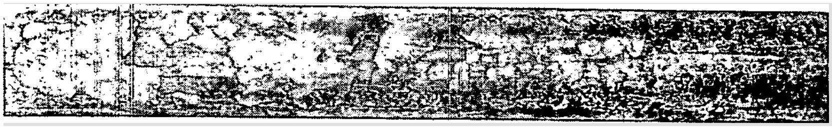

Figure 7

"Scabbing" on rod 33.

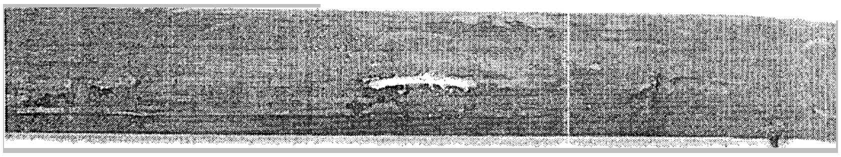

Figure 8

Blisters on rod 36. One blister has been opened and the other one to its right is opened.

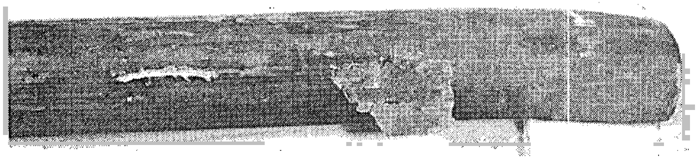

Figure 9

Both Blisters on rod 36 opened.

Figure 10

Gouging on Rod 47, which was extruded with glass lubricants.

interfacial friction with the liner wall, the forward flow of the billet "skin" is retarded, while metal at the center is forced through the die. This causes the skin at the dummy block end of the billet to flow toward the center and then toward the die orifice. The result of this action is that the billet turns inside out. The point at which the skin first emerges as "pipe" in the extruded product is usually expected to be in the last 5 to 10% of the rod to leave the die.

Figure 7 illustrates a "scabbing" defect on the center section of an extruded rod. The cause of this type of defect is a much debated question among authorities on extrusion. One theory is that "scabbing" can be due to the billet oxide skin extruding to form a thin subsurface layer surrounded by a sound central portion and clean outer layer. Any salt, "Dag", or glass lubrication on the billet would follow the skin into the "scab". If these "scabs" do not break, they take the form of "blisters" such as are shown in Figures 8 and 9.

In Figure 10 is shown a "gouged" rod. This defect has been found largely on rods extruded with glass lubricants. From the appearance of these gouges or grooves, it would appear that the glass was not completely fused during the moment of extrusion and the hard glass particles had gouged the rod.

When this information is complete a more thorough evaluation of the variables in this experiment can be made. However, the following observed results are pertinent:

1. There were no particular mechanical handling problems with dingot metal billets heated to 1800°F or 1900°F. The billets did not sag noticeably in the billet hangers. The use of normal extrusion plant practice resulted in no billet gouging.

2. The rod extruded through a 2.910 inch die from a 1800° or 1900°F billet handled about like brass. From this information runout equipment for Weldon Spring may be designed on the basis of brass characteristics.

3. The graphite follower blocks used were partially extruded with the billet. This technique severed the extruded rod from the butt metal held up in the die. This indicates the practicability of eliminating the use of a shear or saw from the development work at Dow Chemical and the production operation at Weldon Spring. Avoidance of the need for shearing or sawing the butt obviates one source of air contamination from oxidation of a fresh unprotected sheared or sawed surface.

4. The dies were inspected after each push for wear. The inlet of the first die was grooved from the die face to the land after four purshes. The second die was used for

seventeen extrusions and on removal was found to be grooved in the same manner as the first. The third die used with glass lubricants was in good condition at the end of 8 pushes but one further push without glass started grooves on the inlet radius.

5. Some evidence was given that glass lubricants decrease the extrusion constant "K". The gauge being used at the present time to read the ram thrust cannot be read accurately at the low thrusts used to extrude uranium in the gamma phase. A strain gauge will be attached to the ram for the next program, to make possible more accurate measurement of the ram thrust.

6. Table I stipulates the cases when the "Dag" lubricant was applied to the liner and die before extrusion. There was no noticeable difference in the extrusion constant "K", the surface quality of the extruded rod, or the amount of die wear when "Dag" was used. One explanation for this may be that since "Dag" is a powdered graphite product which can adhere to steel, it could affect the operation for several pushes after its application.

7. There was no noticeable difference in behavior between the various glass lubricants used. These glass were purchased by BBC from the Thomas C. Thomas Company, Highland Park, Illinois. The compositions of these glasses are shown below:

Type	Purchase Number	% P_2O_5	% Al_2O_3	% Na_2O	% K_2O	% ZnO	% PbO	% BaO
2	TCT-1852-Y2	42.11	26.32	15.79	11.58	4.21	- - -	- - -
3	TCT-1852-Y3	40.0	25.0	15.0	11.0	4.0	5.0	- - -
4	TCT-1852-Y4	40.0	25.0	15.0	11.0	4.0	- - -	5.0

The glass, over which the billets were rolled, was ground to -100 mesh. The shaped glass pad for the nose was formed by mixing 10% by weight waterglass with glass ground to -20, +100 mesh and then drying for 24 hours.

Future Work

The purpose of the next program is to determine the effect of glass lubricants on die life. Six dies of the same design and material will be used. Three of these dies will be used with glass lubricants until failure. The other three dies will be used without glass lubricants until failure. One billet will be pushed every 10 to 15 minutes throughout this experiment. In addition to these variations the following factors will be kept constant:

1. Maximum ram speed.
2. 1800°F billet and follower block temperature.
3. Graphite follower block which will be partially extruded.
4. Die material will be Rex AA high speed steel or an equal material.
5. Flow dies of the same design as the fourth program will be used.

UO_2 FUEL ELEMENTS

by

R. B. Wrinkle
C. M. Henderson

I. Summary

Further tests on MCW UO_2 and UO_3 were made in a rubber-lined Micronizer in order to obtain more of these materials for evaluation studies of impurity pickup and fuel element powder quality. On the basis of these grinding tests it appeared that the pickup of impurities in micronizing UO_3 can be held within the WAPD UO_2 chemical specifications. Carbon, from the rubber lining of the Micronizer, was the major impurity picked up during micronizing of MCW UO_2. The Ni content of Micronized UO_2 exceeded the WAPD limits by 5 ppm, but it is expected that more complete coating of the Micronizer unit will reduce the pickup of this impurity to an acceptable level.

Uranium dioxide made from micronized UO_3 was fabricated into pellets by cold compacting at 100tsi and sintering at 1680°C for 17 hours under hydrogen to yield high sintered densities (94.5% of theoretical). Micronized UO_2 was fabricated into rods and tubes by extruding at ram pressures below 2.5tsi and sintering under the same conditions as the pellets to yield sintered densities of 95% (rods) and 87% (tubes) of theoretical.

II. Introduction

The possible beneficial influence of high fuel element density on the fission gas retention properties of UO_2 fuel elements continues to be of interest. The dependence of final density on the physical and chemical properties of the starting UO_2 powder provides the incentive for continued exploration of various means of modifying present MCW production processes to yield more sinterable powders. An added advantage of this program derives from the fact that it could lead to development of improved methods for producing uranium metal.

III. Experimental Results and Discussion

A. Powder Preparation Studies

As reported previously[1] UO_2 and UO_3 have been ground in an 8-inch stainless steel micronizer and an 8-inch rubber-lined Micronizer. The powders produced in these two tests were evaluated in fuel element fabrication studies which revealed that they were quite sinterable. In addition, these powders were found to be highly reactive. Accordingly, they were used up rather rapidly in evaluation studies at MCW and other sites. To replenish the supply of micronized UO_2, more grinding tests were run. Both an 8-inch and a 15-inch rubber-lined Micronizer were used in these tests to supply powders for further evaluation and to determine what production rates could be expected for Micronizers larger than 8 inches in diameter.

An effort was also made to reduce impurity pickup by substituting rubber hose and rubber-coated pipe for stainless steel pipe in most of the system where abrasion seemed likely to occur. The data from these micronizer tests are presented in Table I, Figure 1, and Figure 2. The chemical compositions of the micronized powders are presented in Tables II and III.

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[1] Henderson, C. M., Wrinkle R. B., *Process Development Quarterly Report, Part II,* Mallinckrodt Chemical Works, *MCW-1400,* (February 1, 1957) p. 130.

Table I

Run Data from Grinding Tests on Uranium Oxides in 8-inch and 15-inch Rubber-Lined Micronizer Units

Test No.	Material	Total Weight Ground lbs.	Grinding Rate lbs/hr	Particle Size[a] microns	Tap Density g/cc	Micronizer Size[b] inches
1	UO_3	79	105	0.61	2.1	15
2	UO_3	48.5	315	0.78	2.4	15
3	UO_2	11	52	0.77	3.5	15
4	UO_2	13	64	0.80	3.6	15
5	UO_2	57	85	0.83	3.7	15
6	UO_2	57	185	1.08	4.1	15
7	UO_2	10	30	0.70	- - -	8
8	UO_2	134	38	0.75	3.5	8
9	UO_2	7.5	43	0.79	- - -	8
10	UO_2	8.4	67	0.85	- - -	8

[a] Apparent average particle size as determined by a Fisher Sub-Sieve Sizer

[b] This is the diameter of the attrition chamber of the Micronizer.

FIGURE I

PARTICLE SIZE CURVE FOR UO_2
GROUND IN A 15 INCH MICRONIZER
AT VARYING RATES

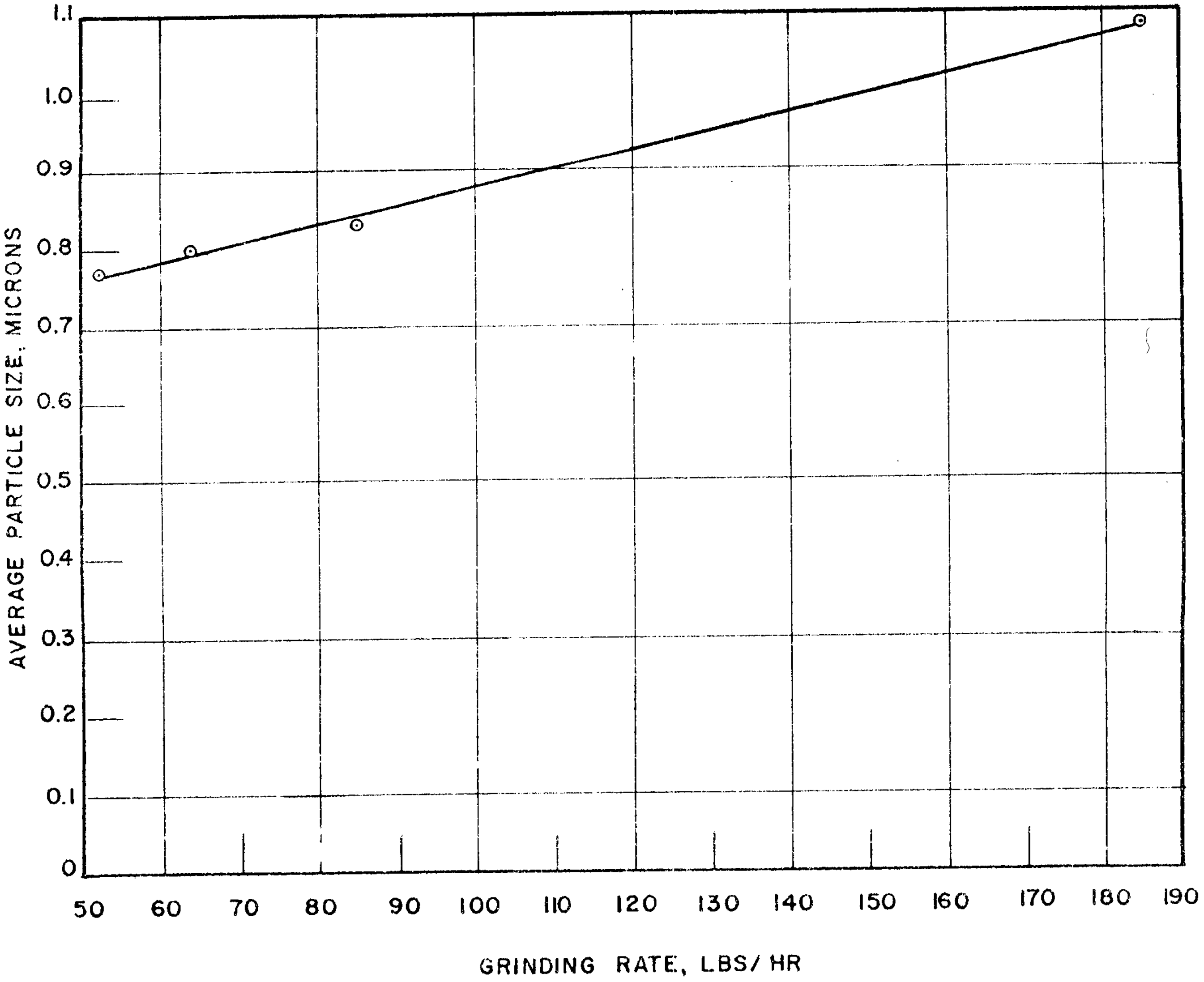

FIGURE 2
PARTICLE SIZE CURVE FOR UO_2
GROUND IN AN 8 INCH MICRONIZER
AT VARYING RATES

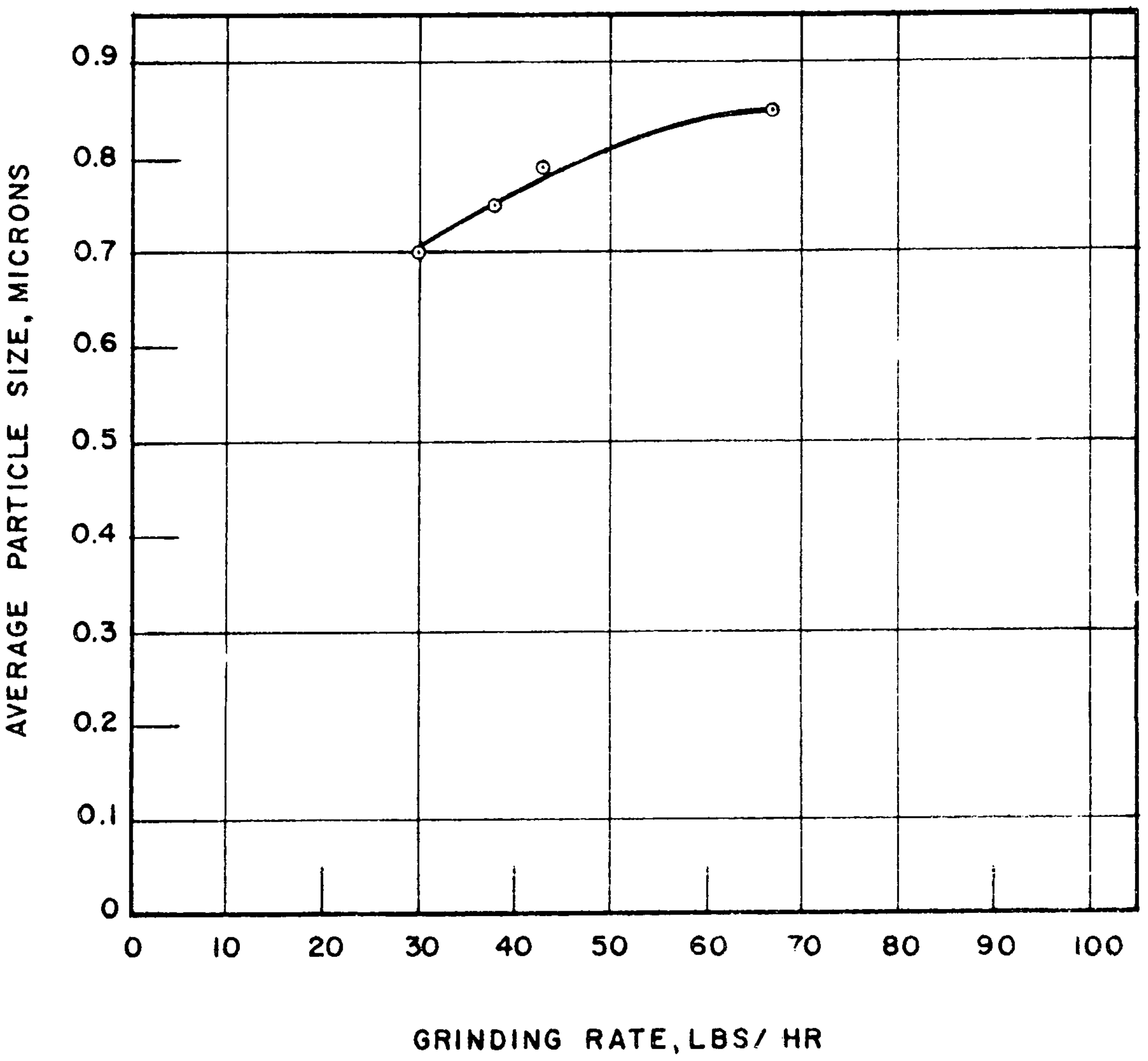

Table II

Results from 15-inch Rubber-Lined Micronizer Unit in Grinding Uranium Oxides, Chemical Composition, ppm

Element ppm	WAPD Limits for UO_2	Source UO_2	UO_2 from Test No. 3	UO_2 from Test No. 4	UO_2 from Test No. 5	UO_2 from Test No. 6	Source UO_3	UO_3 from Test No. 1	UO_3 from Test No. 2
Ag		<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Al		<10.	<10.	10.	15.	10.	<10	10.	10.
As		<10.	<10.	<10.	<10.	<10.	<10.	<10.	<10.
B	0.15	0.14	0.13	0.15	0.14	0.13	0.15	0.15	0.15
Be		<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Bi		<1.	<1.	<1.	<1.	<1.	<1.	<1.	<1.
C	115.	14.	1220.	1030.	840.	350.	- - -	- - -	- - -
Cd	0.5	- - -	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Co		<1.	2.	<1.	1.	3.	<1.	2.	2.
Cr	10.	10.	5.	6.	7.	7.	2.	2.	3.
Cu	4.	1.	3.	4.	2.	2.	<1.	3.	1.
Fe	30.	40.	30.	40.	30.	30.	15.	15.	15.
F	30.	- - -	- - -	- - -	- - -	- - -	- - -	- - -	- - -
In		0.1	0.3	0.2	0.2	0.3	0.3	0.2	0.2
Mg		40.	30.	50.	50.	70.	<10.	10.	10.
Mn		<10.	<10.	<10.	<10.	<10.	<10.	<10.	<10.
Mo	1.	0.9	<10.^{a}	<10.^{a}	<10.^{a}	<10.^{a}	<10.^{a}	<10.^{a}	<10.^{a}
Ni.	15.	20.	20.	20.	20.	20.	3	2	3
P		<50	<50	<50	50	50	<50	50	50
Pb	1.	<1.	<1.	<1.	<1.	<1.	3	<1.	<1.
Sb		<1.	<1.	<1.	<1.	<1.	<0.1	<1.	<1.

Table II (cont.)

Element ppm	WAPD Limits for UO_2	Source UO_2	UO_2 from Test No.3	UO_2 from Test No. 4	UO_2 from Test No. 5	UO_2 from Test No. 6	Source UO_3	UO_3 from Test No. 1	UO_3 from Test No. 2
Si	45.	<15.	30.	30.	30.	30.	20.	20.	20.
Sn	4.	<1.	<1.	<1.	<1.	<1.	<1.	<1.	<1.
V		<10.	<10.	<10.	<10.	<10.	<10.	<10.	<10.
Zn		<10.	50.	50.	50.	60.	20.	60.	50.

[a] A more sensitive analytical method should be used for these analyses.

Table III

Results from 8 inch Rubber-Lined Micronizer Unit in Grinding Uranium Oxides, Chemical Composition, ppm

Element ppm	WAPD Limits for UO_2	Source UO_2	Micronized UO_2 from Test No. 8 of Table I
Ag		<0.1	<0.1
Al		<10.	<10.
As		<10.	<10.
B	0.15	0.14	0.14
Be		<0.1	<0.1
Bi		<1.	<1.
C	115.	16.	480.
Cd	0.5	- - -	- - -
Co		<1	<1.
Cr	10	8.	15.
Cu	4.	1.	2.
Fe	30.	30.	100.
F	30.	- - -	- - -
In		0.1	0.1
Mg		70.	20.
Mn		<10.	<10.
Mo	1.	0.8	0.9
Ni	15.	15.	20.
P		<50.	<50.
Pb	1.	<1.	<1.
Sb		<1.	<1.
Si	45.	<15.	15.
Sn	4.	<1.	<1.
V		<10.	<10.
Zn		<10.	<10.

In Table I, it may be seen that UO_3 was more readily ground to small particle sizes than UO_2. The UO_3 particle size obtained at a grinding rate of 315 lbs/hr was still quite small. The grinding rate *vs* particle size data of Figures 1 and 2 show that particle size was not greatly affected within the grinding rate ranges tested. Further tests on both 8-inch and 15-inch units will be run in order to determine the maximum capacity of these Micronizers and to gather data to permit extrapolation of capacity to larger units. Further sinterability tests of powders of various particle sizes will be needed to determine the point beyond which further fineness in size will be of no benefit.

It may be noted from the test results of the 15-inch Micronizer presented in Table II that the UO_2 samples from Tests 3, 5, and 6 were within the WAPD limits for everything except Ni and C. The UO_2 sample from Test 4 was over the limits for these and also for Fe. The analysis for the source UO_2 showed that it failed on Fe and Ni before the grinding operation, so only the failure to meet the C limit can be attributed to the grinding. The C content of UO_2 decreased in Test 3, 4, 5, and 6 as the grinding rate increased. This decrease in C content could be the result of less contact time between the UO_2 and rubber lining in the case of the increased grinding rates. It is also possible that the rubber lining was worn more rapidly during the initial grinding tests than in subsequent tests. The UO_3 samples from Tests 1 and 2 of Table II were within the WAPD limits. The fact that UO_3 was not polluted as much as UO_2 indicates that UO_3 is not as abrasive as UO_2. The UO_2 sample from Test 8 was not within the WAPD limits for C, Cr, Fe and Ni, as may be seen from the analyses in Table III. A comparison of the analyses in Tables II and III show that in general fewer impurities were picked-up in the 15-inch Micronizer than in the 8-inch unit.

The use of larger Micronizer units and higher grinding rates seems to offer means by which the composition of micronized UO_2 could be held within WAPD purity limits. On the basis of the results obtained with the 15-inch Micronizer, it appeared that most WAPD purity limits could be met with UO_2 made from micronized MCW UO_3. Carbon pickup during micronizing may prove to be difficult to eliminate.

B. Powder Evaluation by Fabrication Studies

1. Compacting Studies

Studies of the fabricating properties of several types of UO_2 powders were presented in the preceding Quarterly[2]. At that time, all powder evaluation was carried out with 1. w/o polyvinyl alcohol and 0.8 w/o Sterotex, an animal fat lubricant. Based on the belief that a reduction in the Sterotex addition level might benefit the fired densities of pellets, a comparison of several types of UO_2 powders was made at two Sterotex addition levels to determine the effect of this lubricant on the densities of pellets made by the cold compaction method. Polyvinyl alcohol was added in quantities of 1 w/o to the various UO_2 powders to simulate the WAPD fuel element fabrication practices. All of the pellets were pressed at 100 tsi in a tungsten carbide die with flat-faced rams. The average green pellet weight was 5.5 grams, the nominal diameter was 0.4 inches and the nominal length was 0.4 inches. All of the pellets were sintered simultaneously in a G. E. Molybdenum Resistor Furnace for 17 hours at 1680°C using a hydrogen atmosphere. Table IV shows the pellet densities obtained with the different types of UO_2 powder at two lubricant addition levels.

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[2] *Ibid.*, p. 147

Table IV

Comparison of Pellet Densities for UO_2 Powders at Different Lubricant Addition Levels

(Compacted at 100 tsi and sintered at 1680°C for 17 hours)

	Pellet Densities,[a] Percent of Theoretical					
	Lubricant: 0.2 w/o Sterotex			Lubricant: 0.8 w/o Sterotex		
UO_2 History	Unfired	Fired	Difference	Unfired	Fired	Diffetence
1. Fuel element grade UO_2 that was then ground in a rubber-lined Micronizer.	66.9	92.4	25.5	64.6	91.3	26.7
2. Produced from UO_3 that had been ground in a rubber-lined Micronizer.	65.1	94.5	29.4	65.0	91.6	26.6
3. Produced from ammonium diuranate	65.1	92.6	27.5	64.2	90.6	26.4
4. Produced from cold hydrated UO_3.	64.8	93.2	28.4	62.5	89.6	27.1
5. MCW fuel element grade UO_2 as supplied to WAPD (control)	68.2	88.7	20.5	66.7	86.8	20.1

[a] Densities were calculated by dividing the weight of each pellet by its volume as determined by micrometer measurements.

As shown in Table IV, the highest sintered pellet density of 94.5% was obtained with 0.2 w/o Sterotex from UO_2 made from micronized MCW UO_3. In-all cases the use of 0.2 w/o Sterotex produced pellets of higher fired densities than did 0.8 w/o Sterotex. The difference in densities attributed to the lower addition of Sterotex ranged from 1.1% to 3.6% of the theoretical density of UO_2.

It is interesting to note that all four of the special UO_2 powders tested yielded higher sintered pellet densities than the control powder (normal MCW produced WAPD type UO_2). The UO_2 made from micronized UO_3 producted pellets with the highest sintered densities (94.5% of theoretical) that have been made to date at MCW. It is also interesting that the higher sintered densities of the special UO_2 powders were achieved without significant changes in the green densities.

2. Extrusion Studies:

Continued studies in extrusion were concerned with attempts at fabrication of various UO_2 powders into prototype fuel elements without sacrifice in sintered densities or surface quality.

Both WAPD type UO_2 and micronized UO_2 were extruded into rods and tubes. Rods of ½-inch diameter were extruded in lengths of a foot or more and then cut into lengths of 5 inches or less. Tubes of ⅝inch O.D. and ⅜-inch I.D. were extruded and cut into lengths up to about 5 inches. The extruded samples were allowed to dry in air for at least one night and were then faced off at the ends. The densities of the green samples were caculated by dividing the weight of each sample by its volume as determined by micrometer measurements. Some of the extruded samples were sintered at 1680°C for 17 hours in hydrogen and the sintered densities of the samples were determined by a mercury displacement method. Examples of extruded rods and tubes are illustrated in Figures 3 and 4. The extrusion data and the densities of some extruded samples are presented in Table. V.

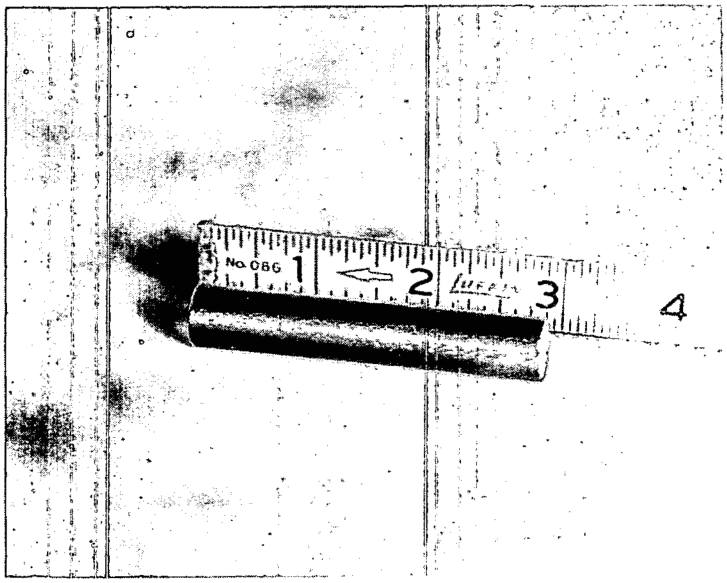

Figure 3

Extruded UO_2 Rod after sintering. (Micronized UO_2 was used with 8.5 w/o of 1.35 w/o Methyl Cellulose solution. Sintered density = 95.% of theoretical)

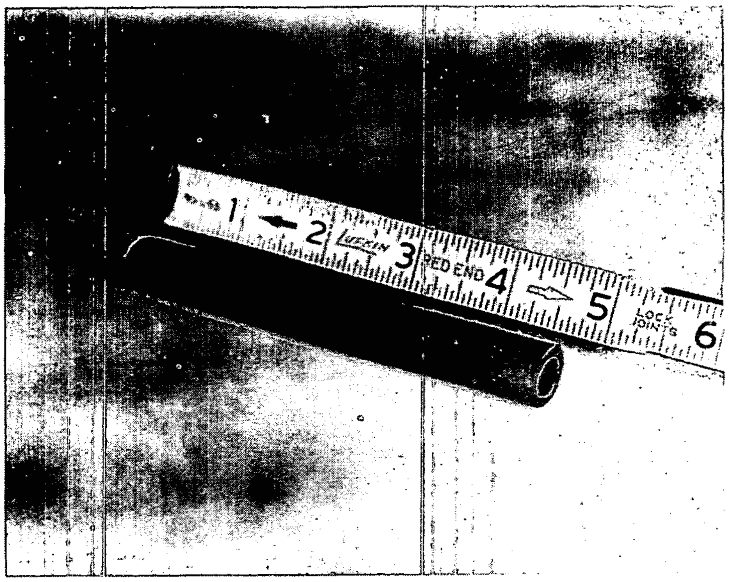

Figure 4

Extruded UO_2 Tube after Sintering. (Micronized UO_2 was used with 16.0 w/o of 15.0 w/o acrylic resin solution. Sintered density = 87.% of theoretical)

Table V

Extrusion of Micronized UO_2 Powders Using Various Plasticizers

(Sintered at 1680°C for 17 Hours)

Mix No.	UO_2 History	Plasticizer Added	Ram[a] Pressure psi	Type of Sample	Quality of Sample	Densities, Percent of Theoretical		
						Unfired	Fired	Difference
1.	Fuel-element-grade MCW UO_2 ground in a rubber-lined Micronizer to 0.83μ average particle size.	8.5 w/o of a 2.7 w/o methyl cellulose-H_2O solution[b]	1,000.	½ inch diameter rod	Medium to good surfaces, good green strength	49.	94.	45.
2	Fuel-element-grade MCW UO_2 ground in a rubber-lined Micronizer to 0.83μ average particle size.	8.5 w/o of a 1.35 w/o methyl cellulose-H_2O solution	4,700.	½ inch diameter rod	Good surface, good green strength	49.	95.	46.
3	Fuel-element-grade MCW UO_2 ground in a rubber-lined Micronizer to 0.83μ average particle size.	10.0 w/o of 12.5 w/o acrylic resin[c] H_2O solution	750.	½ inch diameter rod	Medium surface, fair green strength	50.	92.	42.
4.	Fuel-element-grade MCW UO_2 ground in a rubber-lined Micronizer to 0.60μ average particle size	16.0 w/o of 15.0 w/o acrylic resin-[d] H_2O solution	1,800.	⅝ inch O.D. ⅜ inch I.D. tube	Fair surfaces, good green strength	---	87.	---

[a] Ram Pressure = Ram thrust, lbs divided by the ram area, sq. in.

[b] Plus 0.1 w/o Sterotex, an animal fat lubricant used to improve extrudability.

[c] Acrylic resin plasticizer CB35, manufactured by the B. F. Goodrich Chemical Company.

[d] Acrylic resin plasticizer K707, manufactured by the B. F. Goodrich Chemical Company.

It may be seen from mixes 1 and 2 in Table V that high density (up to 95.% of theoretical) UO_2 rods with good surface quality and good green strength can be extruded from micronized UO_2 mixes containing methyl cellulose plasticizer solutions. These densities, which were obtained on rods extruded at ram pressures under 5,000 psi (2.5 tsi), are equal to or better than any densities obtained at MCW by cold compaction at die pressures up to 100. tsi. Best results were obtained when 8.5 w/o of a methyl cellulose plasticizer (1.35 w/o methyl cellulose in aqueous solution) was used. The rod produced from mix 3, which contained an acrylic resin plasticizer, was lower both in sintered density and in green strength. The density of the tube from mix 4 was materially lower than that of the rods from the other mixes but this may have resulted from an unfavorable die design. Additional work has been planned employing an improved die design.

In the past, three die designs were evaluated on an exploratory basis in an effort to determine the effect of die contour on extruded rod quality. One die had a 40° included lead-in angle joining a land ½ inch in diameter by one inch long. A second die had a 50° included lead-in angle joining a land ⅝ inch in diameter by four inches long. This second die was later modified to make the third die by providing a 4° relief angle and shortening the land to ¾ inch length. It was found that the die with the 40° lead-in angle was the only one which consistently yielded rods with satisfactory surfaces. Further work on die design will be done in order to determine the effect of lead-in angle on surface quality when all other variables are held constant.

IV. Program

On the basis of our experiences of this quarter, it is planned to proceed along the following lines during the next quarter:

1. Continue to investigate the possibilities of producing more sinterable UO_2 powders.
2. Investigate the possibilities of lowering the impurity pickup from fluid-jet type grinding mills through the use of linings with lower metallic impurities and higher resistance to abrasion.
3. Continue studies to develop an optimum die design for the extrusion of maximum density UO_2 fuel elements.
4. Investigate the effect of plasticizers, and plasticizer solvents other than water, in powder fabrication studies.

HYDROGEN CONTENT OF DERBY AND INGOT METAL

by

C. R. Lepper
B. J. Buntz

I. Summary

1. The average derby hydrogen for approximately 50 Production Plant derbies was found to be 3.5 ppm. and ranged from 1.0 - 5.3 ppm.

2. The 36 heats poured and tested gave an average ingot hydrogen value of 0.76 ppm. From the experiment we see that derby hydrogen level does not have any effect on ingot hydrogen.

3. The testing of an unpoured melt shows that the derby hydrogen is outgassed before the melt is poured.

4. The crucible and mold dressing are not factors that affect the hydrogen content of the ingot.

5. For values of vacuum at pour from 13 - 300 microns Hg, it has been found that the ingot hydrogen content shows no correlation but remains within the limits observed, that is 0.46 - 1.50 ppm.

II. Introduction

An investigation was conducted to determine the hydrogen content in present production derbies, and the effect, if any, that this value has on the hydrogen content of the finished ingot. Further than the direct effect of derby hydrogen, other factors such as mold and crucible dressing, vacuum at pour, and hydrogen content and distribution of the melt in the crucibles were studied.

In order to eliminate the possible variables from different graphite sources all heats were poured in a single type mold.

III. Results and Discussion

A. Normal Heats

Approximately 50 Production Plant derbies were sampled by removing a ⅛ inch center slice from each derby. A smaller center sample was removed from this slice and analyzed for hydrogen. The average hydrogen value for these derbies was found to be 3.5 ppm and ranged from 1.0 - 5.3 ppm.

These derbies along with pilot plant dingot and derby metal was charged according to hydrogen content. These heats were melted in furnaces 9 and 10, because of the extremely good vacuums obtained in this set of furnaces. Also, these heats were poured in International, type 7572 graphite, vertically split molds. The resulting ingots were sampled at the top and bottom and were analyzed for hydrogen.

The data for the sixteen heats of known hydrogen value, using pilot plant dingot or derby metal and the Production plant derbies can be seen in Table I.

Table I

Ingot Hydrogen *vs* Hydrogen in Charge and Vacuum at Pour

Heat No.	H_2 Charged ppm	Ingot H_2 ppm	Vacuum at Pour microns Hg	Material Source
9402	1.1	0.81	56	Pilot Plant
9601	1.5	0.90	6	Pilot Plant
9711	2.0	0.77	9	Pilot Plant
9720	2.1	0.55	30	Pilot Plant
9724	2.1	0.46	8	Pilot Plant
9506	2.4	0.55	6	Production Plant
9729	2.4	0.60	18	Pilot Plant
9513	2.4	0.55	13	Pilot Plant
9521	2.7	1.00	13	Production Plant
9679	3.0	0.77	18	Pilot Plant
9540	3.0	0.60	8	Production Plant
9622	3.2	0.59	12	Pilot Plant
9626	3.2	0.74	8	Pilot Plant
9516	3.9	0.85	10	Production Plant
9530	4.3	0.90	12	Production Plant
9525	4.9	1.20	10	Production Plant
Average	2.8	0.74	18	
Range	1.1 - 4.9	0.46 - 1.20	6 - 56	

The results here show no direct correlation between derby hydrogen content and the hydrogen content of the ingot produced.

B. The Effect of Molds and Mold Dressings

Twelve heats were cast in new International molds which were outgassed and painted as normal. The resulting ingots were again sampled at the top and bottom and analyzed for hydrogen. In order to obtain data of higher vacuums at pour no special furnaces were specified for this test. The results are shown in Table II.

Table II

Hydrogen in Ingot from Outgassed and Painted Molds

Heat No.	Ingot H_2 ppm	Vacuum at Pour microns
9349	0.88	68
9350	0.73	13
9351	0.79	150
9354	0.72	58
9355	0.81	38
9356	0.95	110
9359	0.74	160
9360	0.68	54
9361	0.84	49
9363	0.56	56
9364	0.69	80
9365	0.66	200
Average	0.76	86
Range	0.56 - 0.88	13 - 200

Six of the molds used above were outgassed a second time but were used without the benefits of a new mold dressing. These heats were cast in any furnace, were sampled at the top and bottom, and were analyzed for hydrogen. The results of these heats are tabulated in Table III.

Table III

Hydrogen in Ingots Poured in Molds with no Second Dressing

Heat No.	Ingot H_2 ppm	Vacuum at Pour microns
9377	0.59	100
9378	0.67	48
9379	0.66	28
9382	0.84	42
9383	1.2	290
9384	0.74	38
Average	0.78	91
Range	0.59 - 1.2	28 - 290

From the values shown in Tables II and III it seems evident that the mold dressing has no effect on ingot hydrogen.

C. Unpoured Melt

To evaluate the concentrations of hydrogen in the melt, a furnace slug was deliberately formed. The charged crucible was taken through a complete heating cycle as perscribed by standard operating procedure; however, the melt was not poured but allowed to solidify in the crucible. A ⅛ inch center slice was removed from this furnace slug and the hydrogen samples removed from the slice. This slug was sampled and the data obtained is shown in Table IV.

Table IV

Hydrogen in the Melt

Positions	H_2 ppm
Top side	0.84
Center side	0.84
Bottom side	0.75
Bottom Cone	0.85
Average	0.82

From Table IV it appears that the hydrogen has been outgassed before the melt is poured. The results also indicate that the remaining hydrogen is evenly dispersed. However, more values, especially internal values, would have to be available to give a positive answer.

D. Crucible Dressings

Two heats were poured using other than standard crucible dressings:

a) One crucible was used without any dressing.

b) Another crucible was used incorporating a hand painted dressing, since these dressings are thinner than those applied by spraying. Both dressings had essentially the same composition which is a water slurry of MgO.

The two heats were once again sampled at the top and bottom and were analyzed, The data are shown in Table V.

Table V

Hydrogen in Ingots Produced with Thin or No Crucible Dressing

Heat No.	Conditions	Ingot H_2 ppm	Vacuum at Pour microns
8891	unpainted crucible	0.63	140
8892	hand painted crucible thin dressing	0.97	80

Since these values fell within the range of hydrogen values found for normal painted molds, one can say that the manner of application or thickness of crucible dressings does not have any effect on the resulting hydrogen content of the ingot.

E. Conclusion

The 36 heats involved in these tests produced an average hydrogen value of 0.76 ppm. This average is less than that found on 26 heats reported in September, 1955, (0.89 ppm) however, the range is the same (0.5-1.5 ppm).

A study of the vacuum at pour for the heats obtained in these tests shows that between 13 and 300 microns there is no direct correlation to the resulting ingot hydrogen value. See Tables I, II, III, and V for complete breakdown.

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Glossary of Specialized Terms

billet	- a bar of forged dingot uranium suitable for subsequent rolling
black oxide	- U_3O_8
brown oxide	- UO_2
derby	- the uranium metal product of the nominal 300, 100 and 50 lb. reduction bombs which is subsequently recast
dingot	- (direct ingot) the uranium metal product of 1400 and 3300 lb. reduction bombs. This metal not recast.
DMFL	- dingot magnesium fluoride liner
ESU	- easily soluble uranium
green salt	- UF_4
I & E slug	- (hollow) internally and externally cooled slug
ingot	- recast uranium metal
MFL	- magnesium fluoride liner
NOK	- a uranyl nitrate liquor which is fed to the neutral ether system for final purification
OK - liquor	- the uranyl nitrate liquor of highest purity used as a feed to the denitration pots
orange oxide	- UO_3
P - D	- pumper decanter
RMF	- reject magnesium fluoride
rod	- cylindrical length of uranium produced by rolling or extruding uranium billets and ingots
shotgun	- a measure of neutron adsorbing impurities in uranium

(continued on next page)

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Glossary continued

slag	- magnesium fluoride, containing small quantities of uranium and magnesium, formed in the thermite bomb reaction
slug	- rods of uranium machined to specific diameter and lengths. Slugs, when canned are used as fuel elements
soda - salt	- sodium diuranate; usually applied to raw materials of that composition
UNH	- uranyl nitrate hexahydrate
U-Con	- a product of the physical separations plant consisting of a mixture of fine metal particles, uranium oxides, and magnesium fluoride, screened to -10 mesh and assaying 70 - 75% uranium
U-Mag	- an intermediate product of the physical separations plant consisting of the +10 mesh oversize from the screening of ground RMF. It is further separated to 701-metal and C-701
701 metal	- the metal concentrate product of the physical separations plant consisting of uranium metal particles ranging in size from +10 mesh to ½ inch and assaying 95% uranium
C-701	- the reject product of the physical separations plant consisting chiefly of finely ground magnesium fluoride

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