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U.S. ATOMIC ENERGY COMMISSION

# PROCESS DEVELOPMENT QUARTERLY REPORT

## Part II - Pilot Plant Work

August 1, 1959

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# PROCESS DEVELOPMENT QUARTERLY REPORT
## PART II - PILOT PLANT WORK

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This is a progress report on current work and is issued as promptly as possible at the end of the quarter. As a result, it is subject to inaccuracies.

Mallinckrodt Chemical Works
St. Louis, Missouri

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## GENERAL SUMMARY

Work was continued during this quarter on pumper-decanter efficiency studies, thorium decontamination, solvent recovery, fluid-bed denitration, and fluid-bed reduction. Results are reported on the use of the HF-$H_2O$ azeotrope in green salt production, and on the production of dingot metal from Canadian green salt.

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

II. Efficiency of the pilot plant pumper-decanters was greatly improved by the maintenance of interfaces.

The low efficiency of the D-3 pumper-decanter in the plant could be substantially raised by an interface to prevent backmixing.

III. A review of refinery performance, based on a correlation of wash raffinate density with extract uranium saturation, showed that high-thorium product resulted from low extract saturation.

IV. Tributyl phosphate recovery by hexane stripping of raffinate can be greatly improved through the use of a pumper-decanter in place of the present open column.

V. The pilot plant fluid-bed denitrator has been operated at production rates as high as 500 lb $UO_3$/hr-sq ft using high feed concentrations.

Correlations of previous particle size and heat transfer data are presented.

VI. A pilot plant fluid-bed reduction reactor with a tapered internal mandrel has been placed in service. The equipment has performed well in preliminary runs.

VII. Equipment to convert low concentration HF to 38% HF by distillation has been installed. Runs have been made in the green salt reactors in order to simulate the conditions whereby the 38% HF will be utilized. These runs demonstrate the ability to produce high-quality $UF_4$ utilizing 38% HF to the "A" reactor tube.

VIII. Laboratory analysis of green salt produced at Port Hope, Canada, indicated the green salt to be approximately comparable to Weldon Spring material, with the exception of hydrogen content, which was about twice the level found in Weldon Spring green salt. Metal from 3300-lb dingots, produced from this green salt by the long-soak technique, had hydrogen levels of 3.9 ppm and 3.4 ppm, which are higher than is normally found in metal produced by the long-soak technique.

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

# PUMPER-DECANTER EFFICIENCY

by

J. T. Krieg
D. A. Novak
S. Simecek

## I. Summary

A study was made to determine what could be done to increase the efficiency of the refinery extraction system. It was found that the efficiency could be increased by any one or combination of the following modifications:

1. Establishment of organic-aqueous interfaces in all decanters.
2. Pretreatment of the organic feed to remove all traces of uranium.
3. Filtration of the aqueous feed.

The above items are listed in order of increasing complexity and expense.

## II. Introduction

Uranium is extracted from feed materials at Weldon Spring in a series of five pumper-decanters using a 30 per cent (V/V) TBP-hexane solvent. It has been shown[1] that the efficiency of this operation could be improved, thereby resulting in a reduction of uranium loss to the raffinate and an increase in product purity. (The latter would result from an increase in the uranium saturation of the extract.)

It has been shown[2] that the establishment of interfaces in the pilot plant decanters nearly doubled extraction efficiency. However, there were several features about this test which were unique. First, the feed in both the "interface" run and the control run contained no solids. This deviation from plant practice was made to facilitate accurate soluble-uranium analysis of raffinate. Second, the interfaces were manually controlled. In normal plant practice interfaces would be controlled automatically. Third, in the interface run, extract from the previous stage was introduced into the decanters at a point immediately above the interface as shown in Figure 1A (of the current report). This enabled the extract to contact the aqueous phase countercurrently in the lower section of each decanter resulting in what is referred to as "bonus extraction."

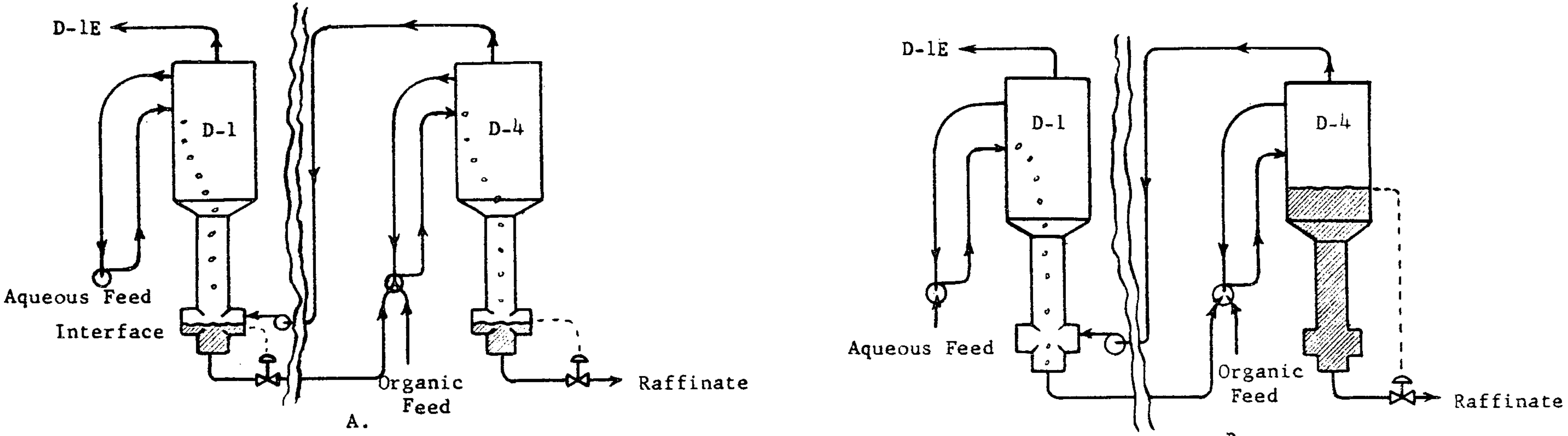
---

[1] Novak, D. A., Damerval, F. B., and Krieg, J. T., "Pumper-Decanter Efficiency Studies," *Process Development Quarterly Report, Part II*, Mallinckrodt Chemical Works, *MCW-1426* (February 2, 1959), p 25-40

[2] Novak, Damerval, and Krieg, *MCW-1426*, p 36-38

Figure 1

SCHEMATIC OF PUMPER-DECANTER OPERATIONS

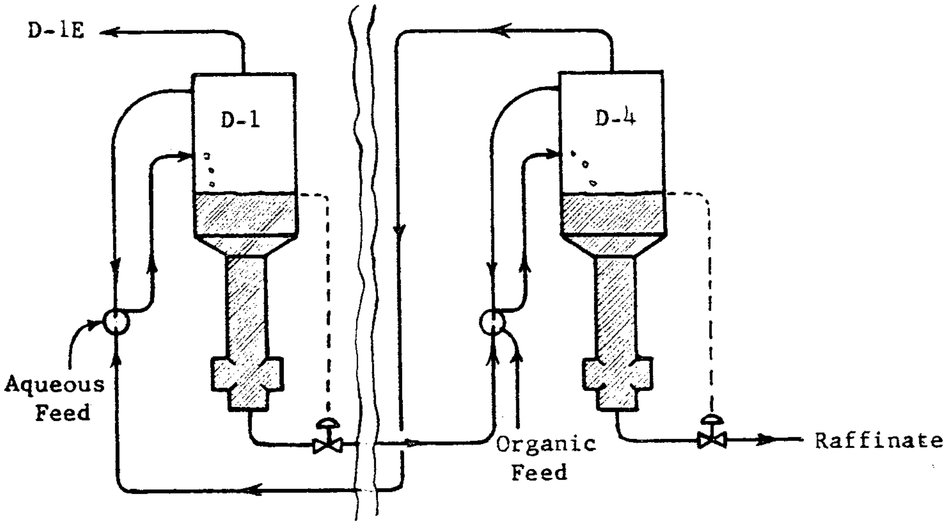


A.

Interface Plus "Bonus" Extraction
(Total of Four Units)

B.

Interface in Last Decanter Only
(Total of Four Units)



C.

Normal Interface Operation
(Total of Four Units)

As a follow-up to this study, runs were made this quarter to test operation using refinery digest slurry feeds and automatic-interface control; and to determine the effect of feeding extract from previous decanters into the mixing pump suction instead of into the decanters directly. In addition, further studies of the refinery extraction operation were made to determine the cause of their low efficiency. The results of these studies are described herein.

## III. Experimental

### A. Equipment

The pilot plant extraction equipment used in these studies consisted of four pumper-decanter units and is the same as that described previously.[3]

### B. Procedure

### 1. Pilot Plant Studies

Run 54B was a control run simulating as closely as possible normal refinery operation. An interface was held in the last decanter only as shown in Figure 1B. The organic-feed/aqueous-feed flow ratio was held constant by controlling the uranium concentration in the second decanter between 50 and 60 g/l. The feed was a refinery digest blend whose composition is shown in Table I.

Table I

Feed Composition

| Feed | Weight Per Cent |
|---|---|
| Phillips | 29.6 |
| Anaconda A | 14.1 |
| Lucky Mac | 11.2 |
| Mexican Hat | 10.8 |
| Sapiens | 7.1 |
| New Mexican Partners | 6.8 |
| Uranium Reduction | 6.7 |
| Rare Metals | 6.6 |
| Canadian Metals | 4.1 |
| Monticello | 3.0 |
| | 100.0 |

---

[3] Novak, Damervai, and Krieg, *MCW-1426*, p 26

The over-all uranium concentration was 460 g/l and the nitric acid concentration was about 1*N*.

Run 54A was made to determine the effect of interface operation in all decanters as is shown in Figure 1C. The extract feed to each decanter was fed through the mixing pumps (Figure 1C) and interfaces were controlled automatically. In other respects it was identical to the control run. The feed used in this run was from the same digest batch as the feed used in the control run.

Run 41 was identical to the preceding run (Run 54A) with the exception of the aqueous feed, which was a synthetic, solid-free solution containing 400 g U/l, and was 1*N* in $HNO_3$ and 1*N* in salt nitrate. The purpose of this run was to compare operations with slurry feed and synthetic, solid-free feed.

### 2. Plant Studies

In order to determine typical refinery performance, all streams in the extraction operation were sampled for uranium once a day for a ten-day period. A few streams were sampled hourly for composite samples.

## IV. Results and Discussion

### A. Pilot Plant Studies

Table II is a general summary of pilot plant extraction-efficiency runs. The results are plotted as McCabe-Thiele diagrams in Figure 2.

Table II

Run Summary

| Run No. | Feed | Interfaces | D-2 Control U g/l | Organic Feed U g/l | Raffinate Total U g/l | D-1E Saturation % | Physical Performance |
|---|---|---|---|---|---|---|---|
| Control (54B) | Refinery Digest | Last decanter only | 56 | 0.044 | 0.86[a] | 90 - 95 | Good |
| 54A[b] | Refinery Digest | All[c] decanters | 64 | .1 | .47[a] | 87 - 92 | Good |
| 41[b] | Synthetic feed (no solids) | All[c] decanters | 43 | .04 | .0036 | 87 - 92 | Good |

[a] Insoluble U = 0.3 ± 1 g/l.

[b] Extract feeds were introduced into the suction side of mixing pumps.

[c] Automatic control.

---

### 1. Effect of Interfaces

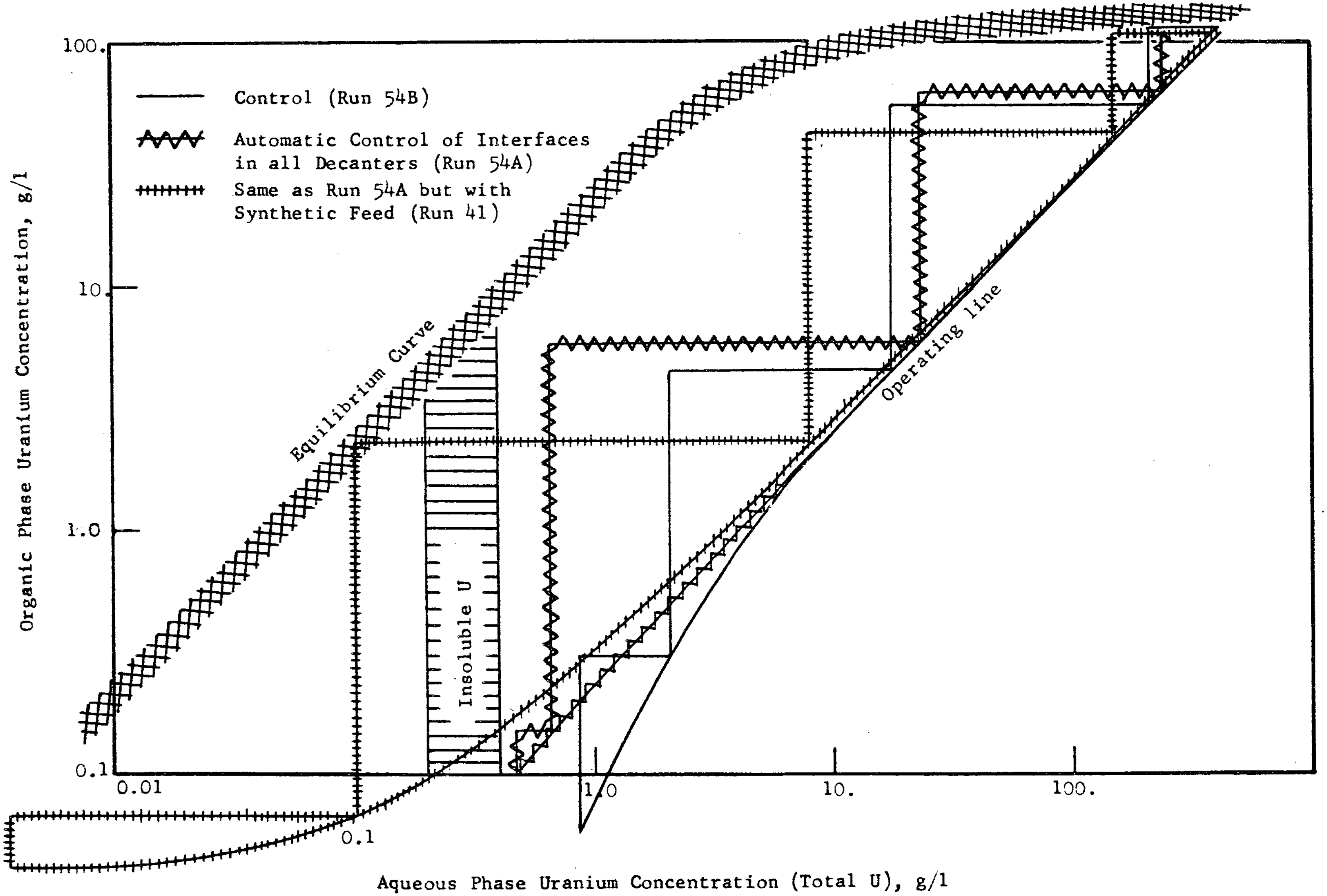
The effect of interfaces in all decanters on extraction efficiency may be seen by comparing Run 54B (control run) with Run 54A (interface run). Uranium loss to the raffinate was reduced from 0.86 g total uranium/l in the control run to 0.47 g/l in the interface run. Since 0.3 ± 1 g uranium/l was insoluble, a considerable reduction in the soluble uranium loss was accomplished. Uranium saturation in the organic extract appears to be slightly less in the interface run although saturation of the second decanter extract was greater. Physical operation of the interface control system was quite satisfactory. As shown in Figure 2, the uranium concentration in the organic feed in both the interface and control runs was negligible compared to the uranium concentration in the raffinate.

### 2. Effect of Slurry Feeds

The effect of slurry feeds on extraction performance is best illustrated in Figure 2 comparing the synthetic-feed run with slurry-feed runs. Although the phase equilibrium distribution of soluble uranium was nearly the same for both types of runs, much more uranium was extracted from the synthetic feed. Soluble uranium loss to the raffinate was reduced by a factor of ten or more by the use of solid-free feed. Uranium saturation of the extract was about the same in the slurry-feed and the synthetic-feed run (Runs 41 and 54A, respectively).

Figure 2

OPERATING DIAGRAM OF PILOT PLANT RUNS



The stage efficiencies diagrammed in Figure 2 for the synthetic-feed interface run, although good, were not as outstanding as previously reported[4] for a very similar run (Figure 3 of the current report) in which the interfaces were controlled very low in the decanter so as to encourage bonus extraction. The latter operation is depicted schematically by Figure 1A.

### 3. Effect of Uranium Concentration of the Organic Feed

The effect of uranium in the organic feed on extraction performance is shown by comparing Figure 2 (Run 41) with Figure 3 (Run 38 from a previous report[5]). Although poorer stage efficiencies were obtained in Run 41 (Figure 2), uranium loss to the raffinate was lower by several orders of magnitude when the organic feed contained less uranium.

## B. Plant Studies

The operation of the refinery extraction system, as determined by the plant sampling program, is diagrammed in Figure 4. The performance of the fifth decanter (D-5) is not diagrammed because it was inconsistent from day to day probably due to the daily variation of insoluble uranium and contaminants in feed materials. Inspection of Figure 4 shows the third decanter (D-3) to be conspicuous by its consistently poor performance. Potential causes for this deficiency, as illustrated in Figure 5, are:

1. Backmixing of organic from D-2.
2. Short circuiting of extract through the decanter.
3. Not enough recycle rate due to:
   a. Poor pump efficiency.
   b. Too much resistance in D-3 recycle line and valves.
4. Back flow of D-5E to D-3 bottom.

In order to diagnose the problem, hourly composite samples were taken around D-3 during one shift of operation. The sample results are shown in Figure 6.

Since the organic phase in D-3 bottoms contains a higher concentration of uranium than either D-3E or D-4E, it appears evident that this liquid is composed in part of organic from the discharge of the D-3 mixing pump. This flow of organic is in the wrong direction (backmixing) and is detrimental to extraction performance. The establishment of an aqueous-organic interface in the lower half of D-3 would circumvent this problem by con-

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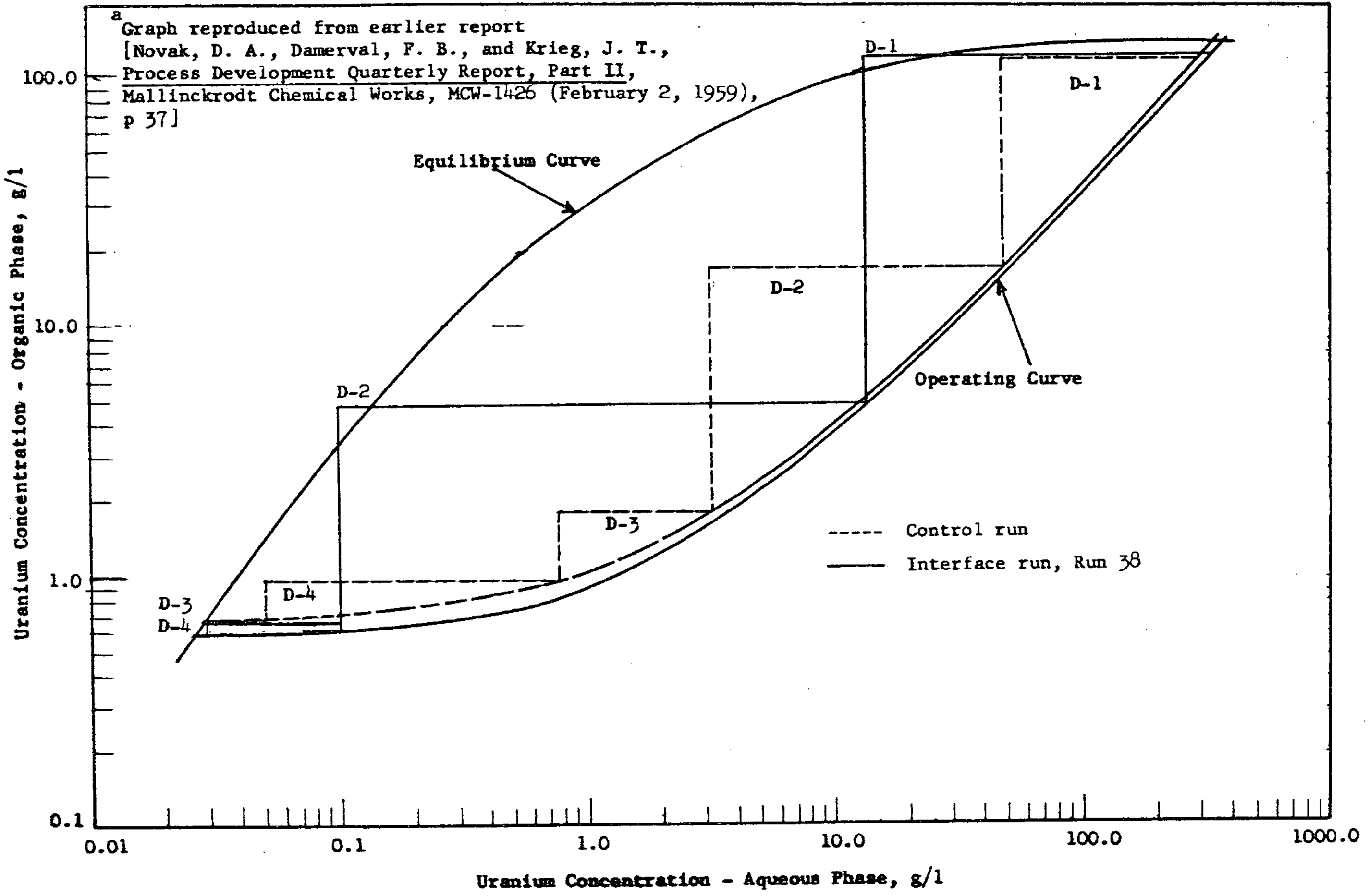
[4] Novak, Damerval, and Krieg, *MCW-1426*, p 25-40

[5] Novak, Damerval, and Krieg, *MCW-1426*, p 37

Figure 3

McCABE-THIELE DIAGRAM OF "INTERFACE" RUN WITH "BONUS" EXTRACTION[a]



[a] Graph reproduced from earlier report [Novak, D. A., Damerval, F. B., and Krieg, J. T., Process Development Quarterly Report, Part II, Mallinckrodt Chemical Works, MCW-1426 (February 2, 1959), p 37]

Figure 4

## REFINERY OPERATING DATA

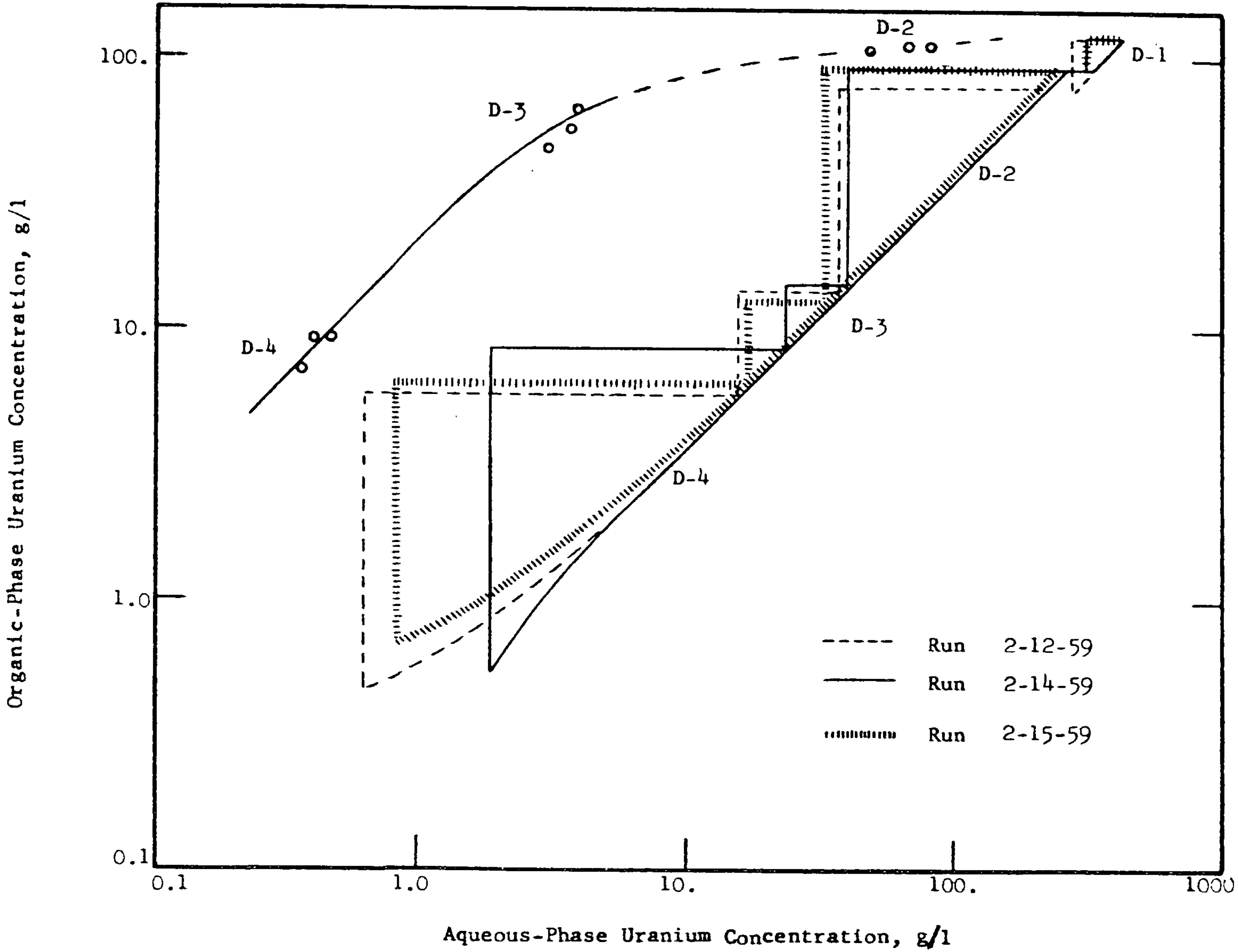


Figure 5

SCHEMATIC OF BACKMIXING IN PUMPER-DECANTER

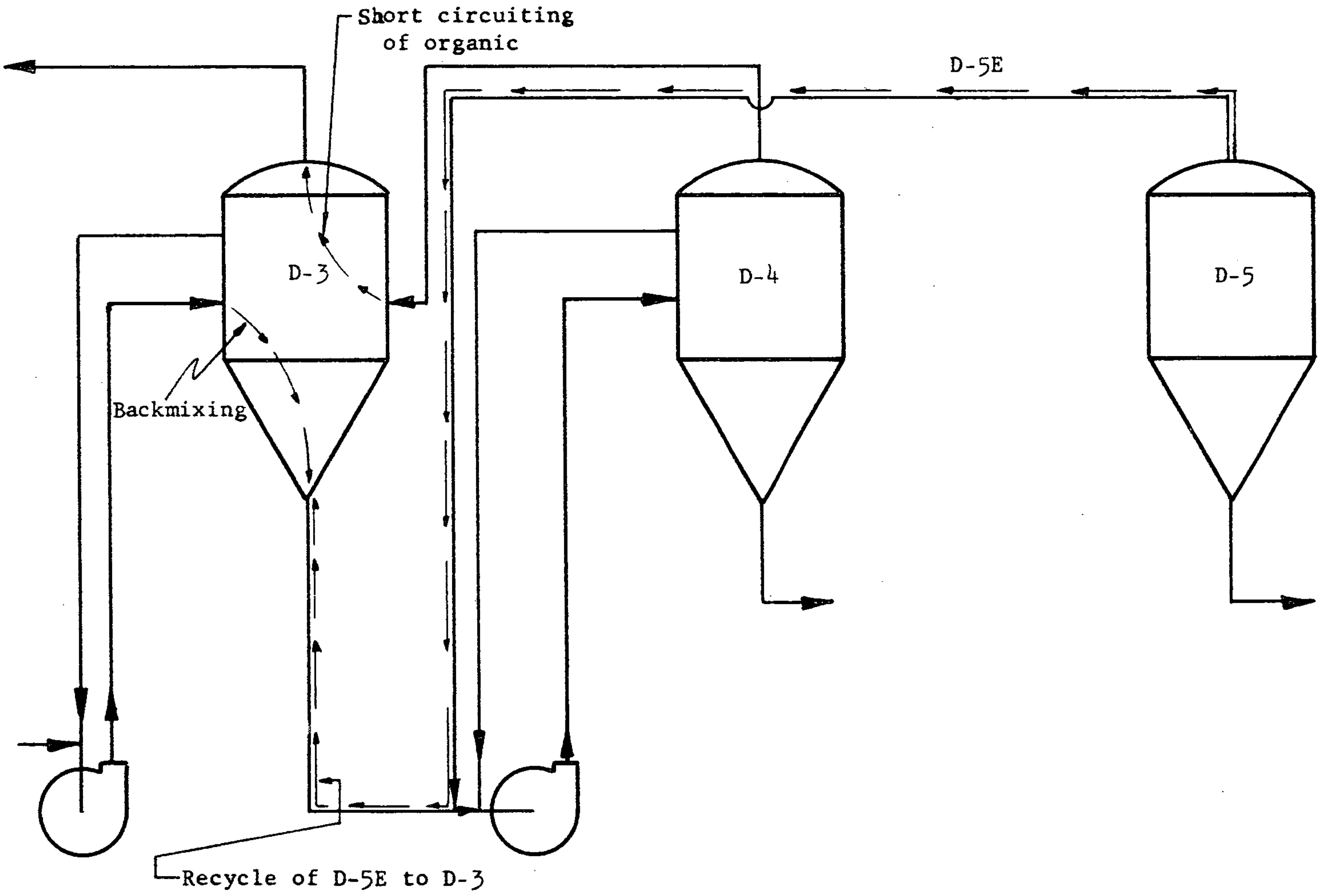
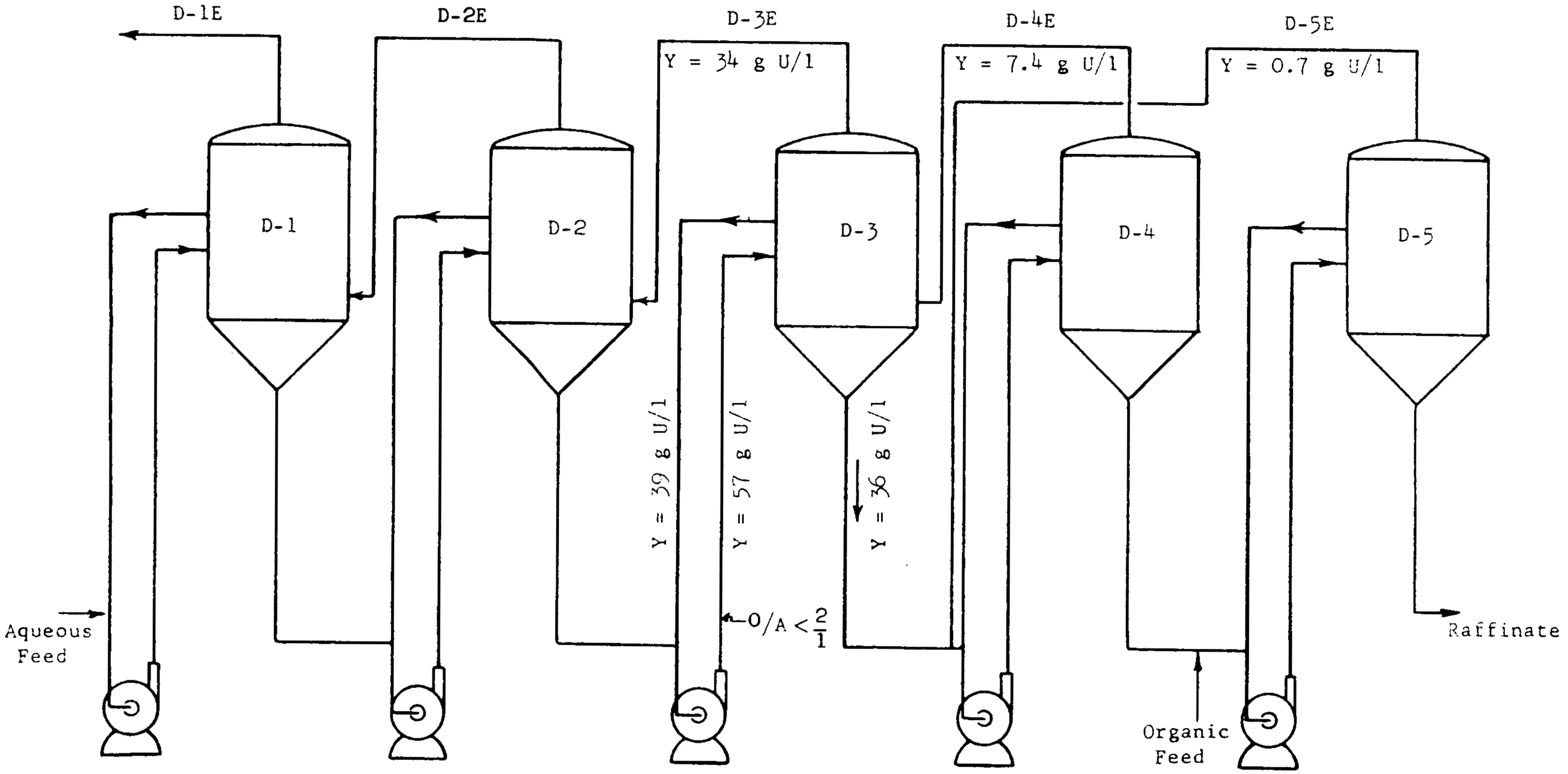


Figure 6

REFINERY D-3 OPERATION (3-25-59)



Y = organic-phase uranium concentration

O/A = organic/aqueous volume ratio

verting D-3 bottoms to straight aqueous phase. Since the uranium concentration in D-3E is nearly the same as in D-3R, there appears to be very little short circuiting of D-4E through D-3. This appears to be only a minor problem which could be solved by feeding D-4E directly to the D-3 mixing pump and would be done anyway if interfaces were installed in all decanters.

There is no evidence of D-5E backing up through D-3 bottoms.

## V. Conclusions

1. Backmixing in the refinery extraction system is partially responsible for poor extraction performance. The establishment of aqueous-organic interfaces in all refinery decanters should eliminate backmixing.
2. The establishment of automatically-controlled interfaces in all the pilot plant decanters improved extraction performance, reducing soluble uranium loss from slurry feeds by a factor of two or more.
3. Extraction performance was also improved by reducing the trace uranium concentration in organic feed and by using solid-free aqueous feed.

# THORIUM DECONTAMINATION

by

J. T. Krieg

## Summary

An investigation was made to determine the cause of occasional thorium contamination in Weldon Spring orange oxide. It was found that all high-thorium orange oxide occurred during periods when the extract uranium saturation was less than 88%. Conversely, whenever the extract saturation was less than 88% for more than one day's duration, the orange oxide contained >50 ppm thorium.

It was also found that the density of the wash raffinate stream is a useful parameter for continuously monitoring the extract saturation.

## Introduction

Thorium decontamination in the Weldon Spring refinery has usually been acceptable, but on three occasions high thorium levels have occurred in the orange oxide (>50 ppm, U basis).

An investigation was conducted to determine the cause of the high thorium contamination and to recommend preventive measures to minimize the chances of a re-occurrence. The results of this investigation are reported herein.

## Results and Discussion

It has been shown in theoretical calculations[1,2] that the refinery cannot decontaminate thorium-bearing feeds when the uranium saturation of pregnant solvent is significantly below 90%. Saturation is like a dam blocking the flow of thorium into the washed extract and backing it up into the raffinate. If the dam is raised (uranium saturation increased), several days are required before a steady-state thorium inventory is accumulated in the extraction equipment. If saturation is suddenly decreased, however, thorium is bled into the washed extract at a rapid rate until the thorium reservoir is lowered.

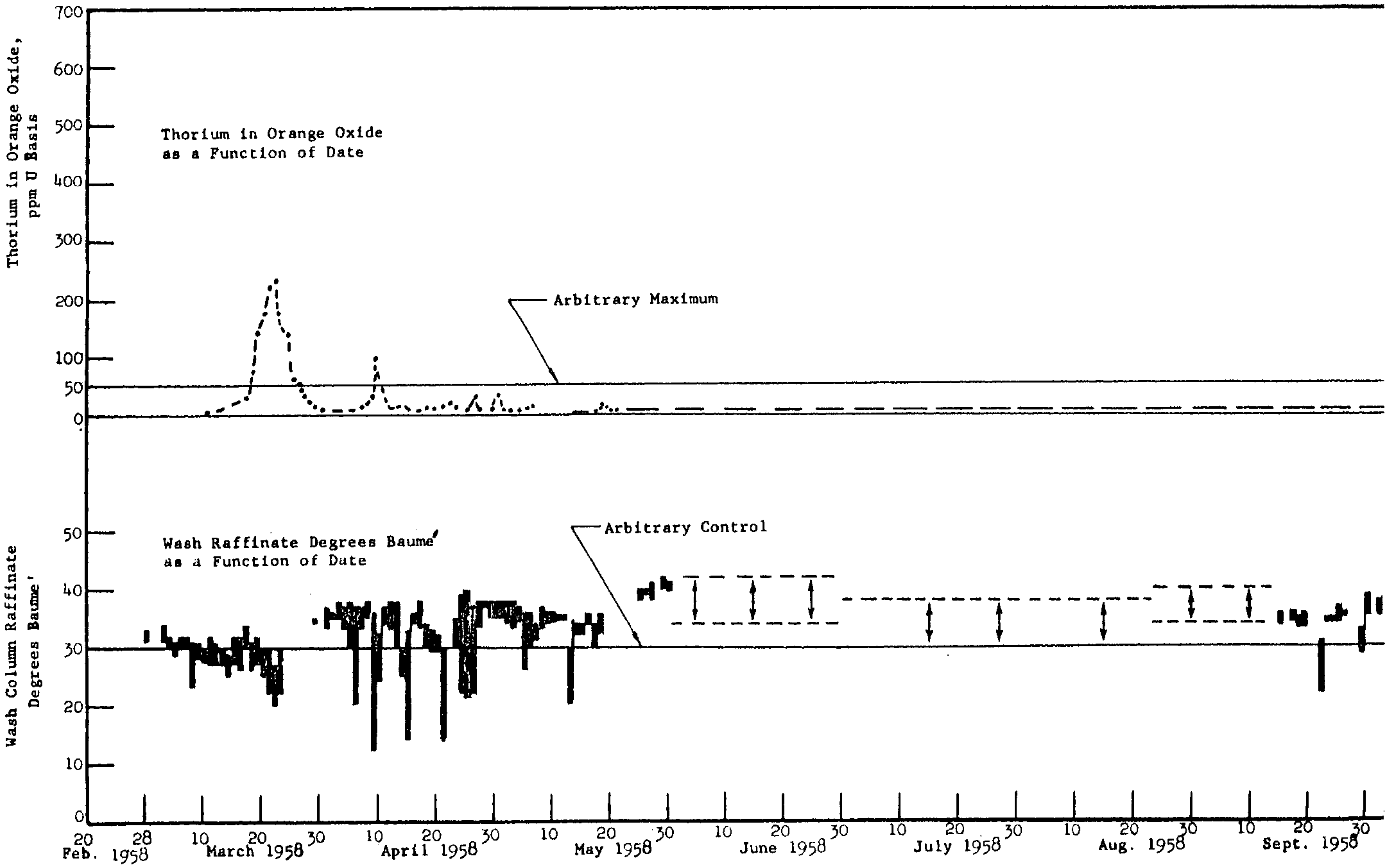
---

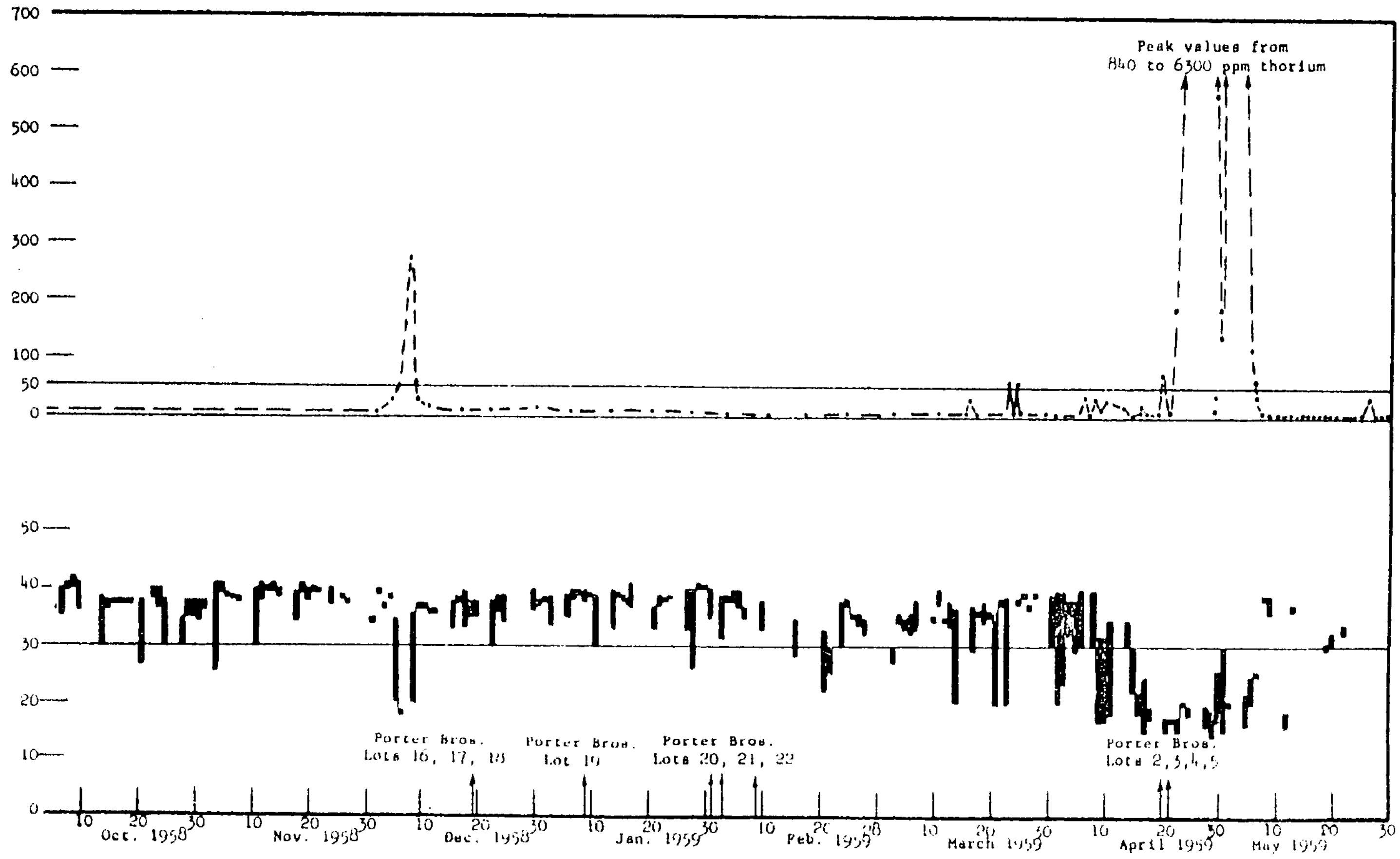
[1] Weidman, S. W., Krieg, J. T., and Lang, G. P., "The Effect of Uranium Refinery Process Variables on Predicted Thorium Decontamination," *Process Development Quarterly Report, Part I*, Mallinckrodt Chemical Works, *MCW-1415* (July 1, 1958), p 35-61

[2] Lang, G. P., and Krieg, J. T., "The Effect of Uranium Saturation on the Extraction of Elements Other than Uranium into Tributyl Phosphate," Mallinckrodt Chemical Works; a paper presented by Mr. G. P. Lang at the American Chemical Society Nuclear Technology Symposium at Boston, Massachusetts, on April 5, 1959

Figure 1

CORRELATION BETWEEN THORIUM IN ORANGE OXIDE AND THE DENSITY OF WASH RAFFINATE




700
600
500
400
300
200
100
50
0
Peak values from
840 to 6300 ppm thorium
50
40
30
20
10
0
Porter Bros.
Lots 16, 17, 18
Porter Bros.
Lot 19
Porter Bros.
Lots 20, 21, 22
Porter Bros.
Lots 2,3,4,5
10 20 30
Oct. 1958
10 20 30
Nov. 1958
10 20 30
Dec. 1958
10 20 30
Jan. 1959
10 20 30
Feb. 1959
10 20 30
March 1959
10 20 30
April 1959
10 20 30
May 1959

To determine the cause of the high-thorium orange oxide occasionally produced in the refinery during the past, a continuous record of extract saturation is necessary. Direct measurements of saturation are not available in refinery records because they were never made on a routine basis. A correlation of saturation with some easily measured property is required. The density of the wash raffinate is such a parameter, as is demonstrated in the appendix, and is routinely measured in regular refinery operation.

With this new tool the thorium contamination record in refinery orange was re-examined as far back as thorium records are available (15 months). The record is presented in Figure 1 along with a record of the wash raffinate density. It is indicated in Figure 1 that each period of high-thorium orange oxide (>50 ppm) was accompanied by an extract uranium saturation of less than 88% (30° Baumé wash raffinate). Conversely, during each period when the extract saturation was less than 88% for more than one day, high-thorium orange oxide was produced.

It should also be noted in Figure 1 that during December, January, and February of 1959 five lots of Porter Brothers (average Th ~ 8%, $U_3O_8$ basis) were processed in the refinery with no rise in thorium content of the orange oxide. During this period high uranium saturations were being maintained (93% - 96%). In contrast, four lots of Porter Brothers feed with similar thorium concentrations were processed during a short period in April when saturations were as low as 72%. During this period the orange oxide was very high in thorium.

## Conclusions and Recommendations

1. Low uranium saturation of the extract appears to be the cause of the high-thorium orange oxide produced in the refinery.

2. It is recommended that the refinery use the density of the wash raffinate stream as a measure of extract saturation. The recommended operating range is between 35° and 40° Baumé (representing 92 to 96% saturation).

# APPENDIX

As shown below, the density of the wash raffinate is a parameter for extract uranium saturation in practice as well as in theory. Since the wash raffinate is essentially in equilibrium with the pumper-decanter extract, a small difference in saturation shows up as a large difference in wash-raffinate uranium concentration, as shown in Figure 2.

The TBP in the extract not complexed by uranium is complexed by nitric acid as $HNO_3 \cdot TBP$. On washing, the complex breaks down and the acid is transferred to the wash raffinate. Thus, a high uranium and low nitric acid level in the wash raffinate indicate high uranium saturation of the extract, while low uranium and high nitric acid indicate low extract saturation. Since uranium and nitric acid concentrations in wash raffinate are related as shown in Figure 3, a density measurement of the wash raffinate will indicate these concentrations, and hence the uranium saturation level of the extract.

The relationship between extract uranium saturation and wash raffinate density is shown in Figure 4, which was derived from the data of Figure 3 and the TBP-uranium-nitric acid-water equilibrium data. The points are analytical checks of the extract saturation at several wash raffinate densities.

Figure 2

THE EFFECT OF ORGANIC-PHASE URANIUM SATURATION ON THE CONCENTRATION OF AQUEOUS-PHASE URANIUM AT EQUILIBRIUM

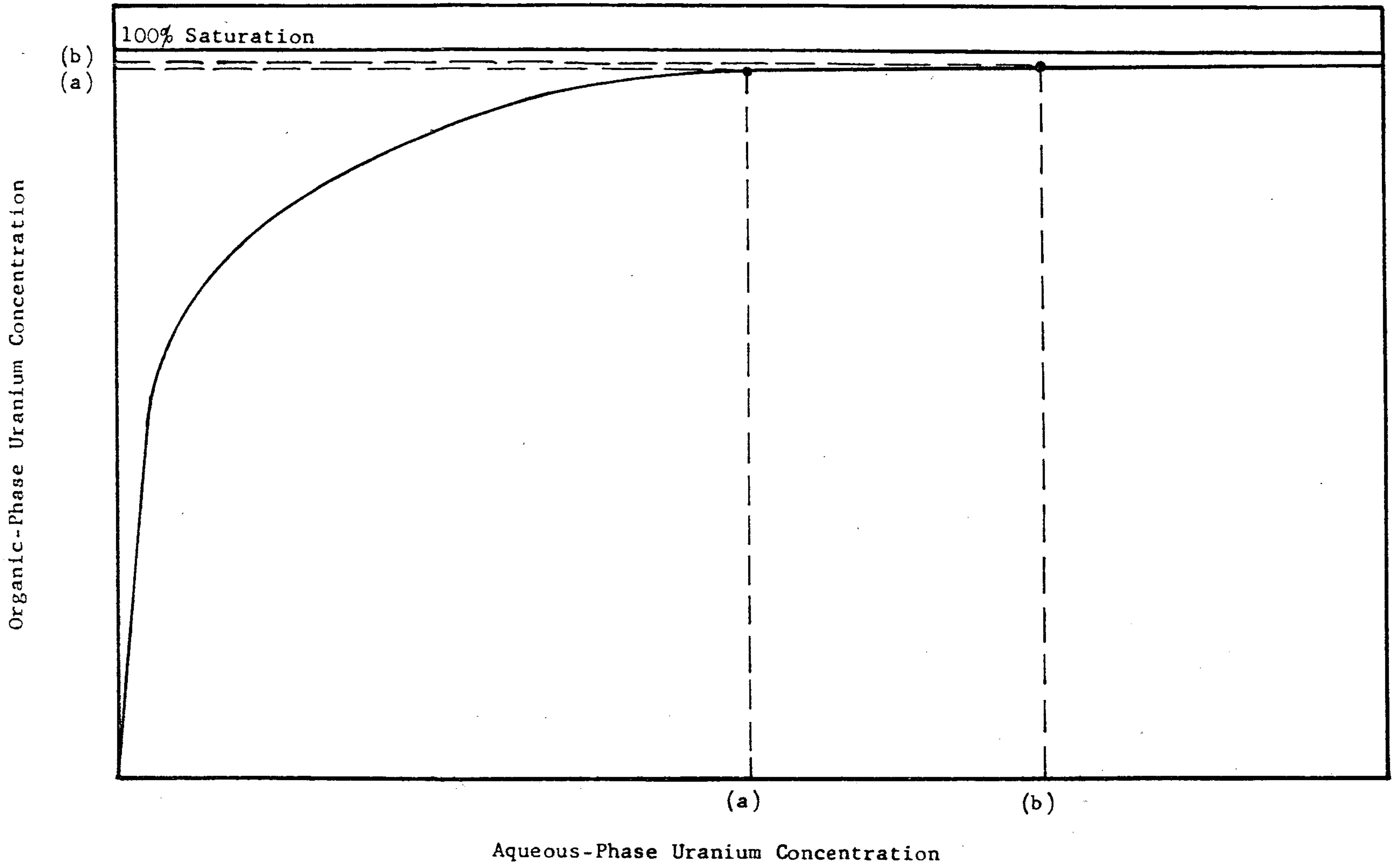


Figure 3

CORRELATION BETWEEN URANIUM AND NITRIC ACID CONCENTRATIONS IN REFINERY WASH RAFFINATE

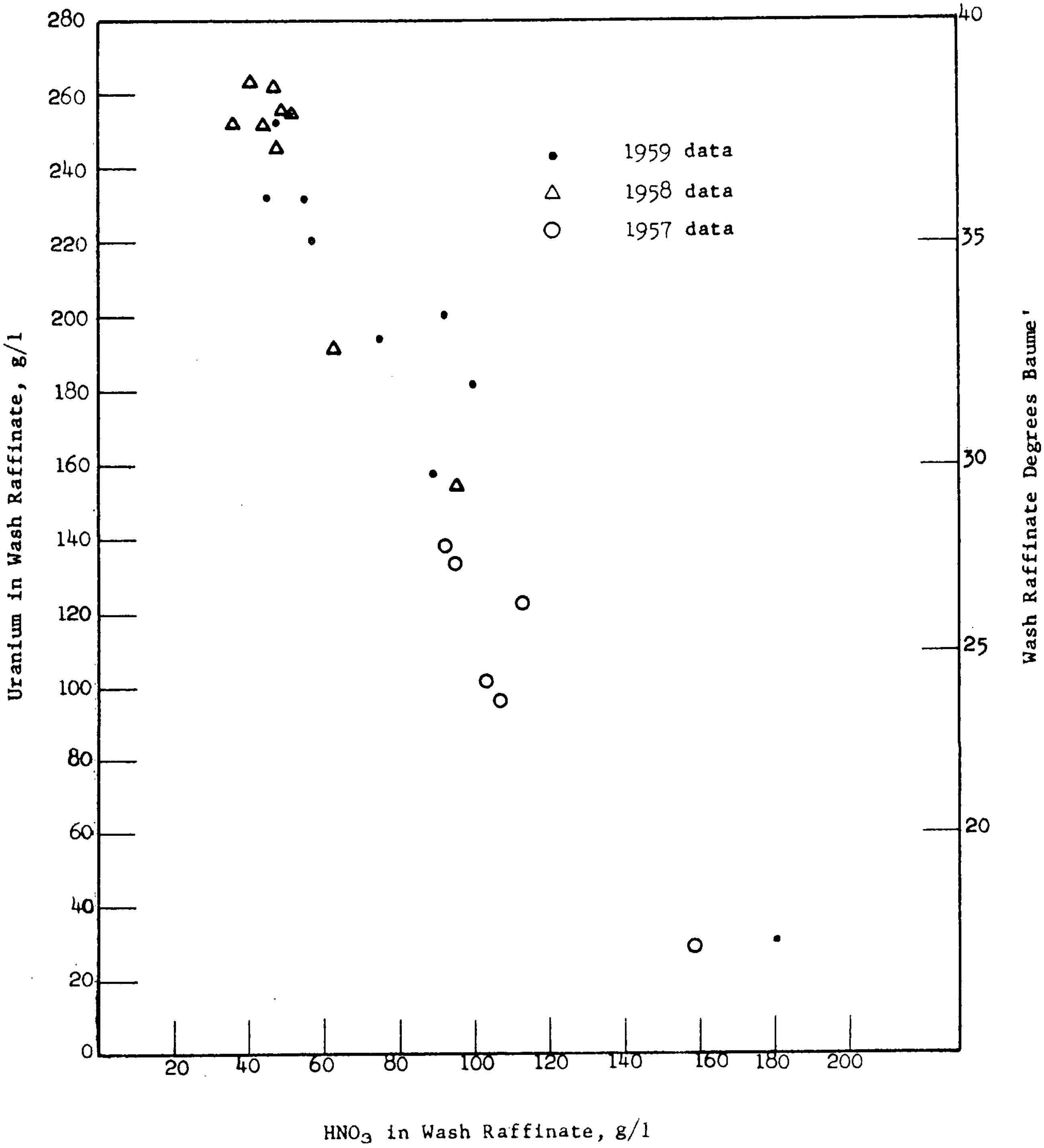
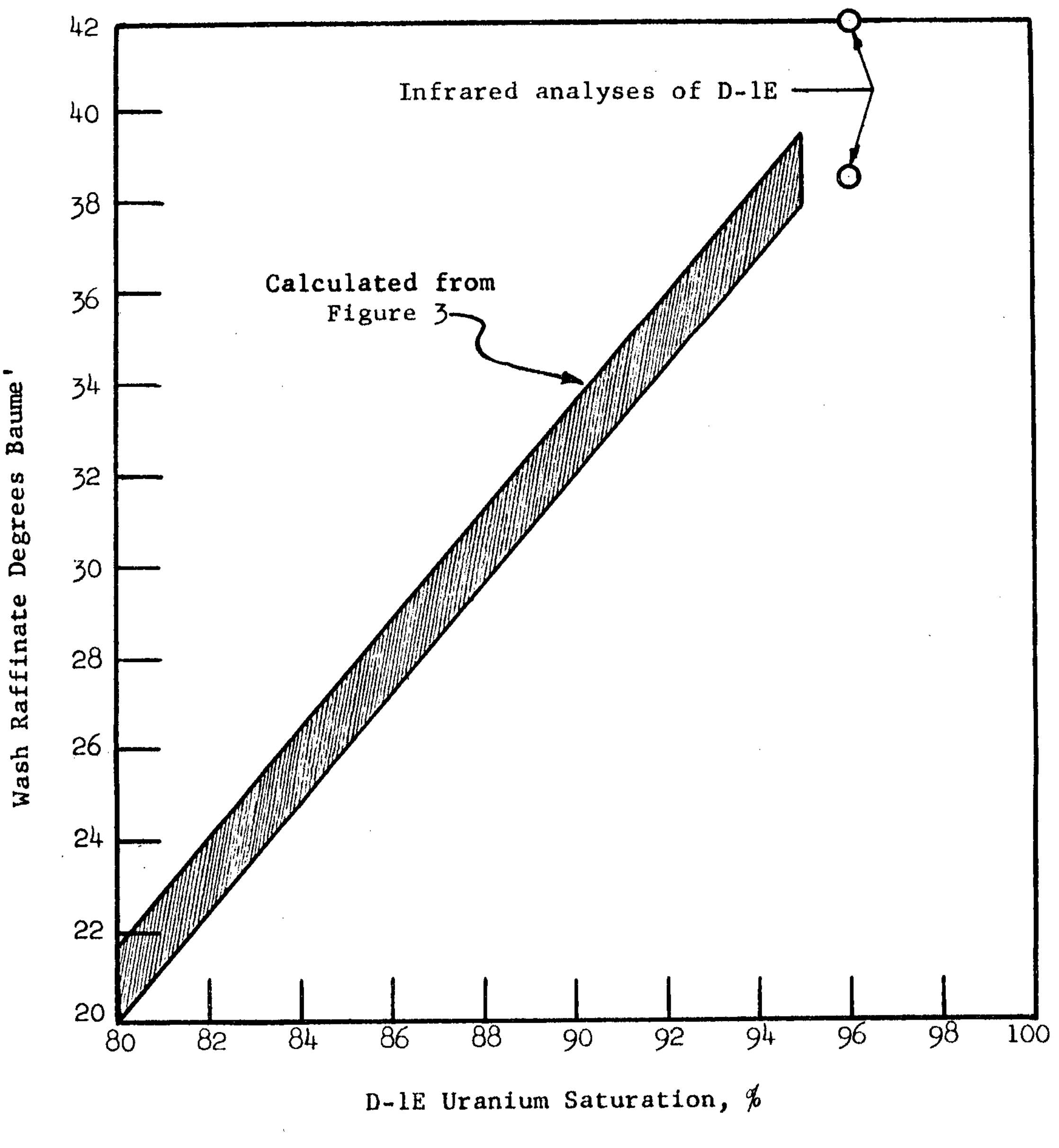


Figure 4

THE EFFECT OF D-1E URANIUM SATURATION ON WASH RAFFINATE DENSITY



# FURTHER STUDIES ON IMPROVING RECOVERY OF TRIBUTYL PHOSPHATE FROM PUMPER-DECANTER RAFFINATE

by

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## Summary

Further pilot plant studies indicate that more efficient tributyl phosphate recovery from pumper-decanter raffinate can be achieved by contacting aqueous raffinate with hexane in a mixing pump. Data are presented for raffinate scrubbing using countercurrent wash column operation, mix-pump column operation, and pumper-decanter operation. Pumper-decanter operation appears to be the most effective.

## Introduction

Previously reported pilot plant studies[1] indicated that the Weldon Spring refinery could achieve more effective tributyl phosphate (TBP) removal from pumper-decanter raffinate by modifying the existing system to a series wash operation. Following installation and operation of a series wash column system, it was found that the TBP losses were still considerable. An analytical check of the hexane effluent from both columns showed that the TBP removed from the raffinate by the second column was equal to the amount removed in the first column. Thus, recovery had been doubled, but the TBP loss was still too high to be neglected. It should be noted that following the pilot plant study, refinery rates were increased, suggesting the possibility that perhaps the scrub columns were flooding at the increased rates. An alternative was that efficient aqueous-organic contacting may have been lost in the scale-up of pilot plant data.

With these two factors in mind, further study was initiated in the pilot plant, with the following objectives:

1. Determine the effects of more vigorous contacting of aqueous and organic.
2. Obtain capacity data for various types of equipment operation.

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[1] Simecek, S., "Improving Removal of Tributyl Phosphate from Pumper-Decanter Raffinate by Series Washing," *Process Development Quarterly Report, Part II*, Mallinckrodt Chemical Works, *MCW-1429* (May 1, 1959), p 15-21

## Experimental

A schematic diagram of the pilot plant column is shown in Figure 1. The equipment shown is that described earlier,[2] modified so that hexane was injected into the raffinate line, instead of of the bottom of the column as in normal operation. The hexane and raffinate were then mixed in a pump as in pumper-decanter operation. The mixture was pumped to the top of the scrub column, where separation took place with the raffinate settling to the bottom of the column, and the hexane overflowing from the top to be recycled.

Two runs were made; a control run using a simple countercurrent wash column operation and a run using the equipment depicted in Figure 1. Due to the limitations of the flow metering equipment, refinery rates could not be simulated in the pilot plant mix-pump column equipment. A raffinate flow rate of 20 gallons per minute was used with an organic-aqueous volume ratio (O/A) of 5/1, whereas the plant columns are currently handling 30 gallons per minute. Later studies showed that had it been possible to run at refinery rates using the mix-pump column, flooding of the column would have occurred. Countercurrent wash column operation appeared to be stable at refinery rates.

Because of the limitations of the column accessories, studies were continued using the pilot plant pumper-decanters. A schematic diagram of this system is shown in Figure 2. When using the pumper-decanter equipment, it was possible to bleed fresh hexane into the system simulating a proposed continuous refinery scrubbing operation.

The raffinate used in all cases came directly from the refinery pumper-decanters.

## Results and Discussion

The results of the mix-pump column run compared to countercurrent wash column operation are shown in Table I. Flow rates in both cases were similar with a volume ratio (O/A) of 5/1.

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[2] Simecek, *MCW-1429*, p 16

Figure 1

SCHEMATIC OF MIX-PUMP COLUMN

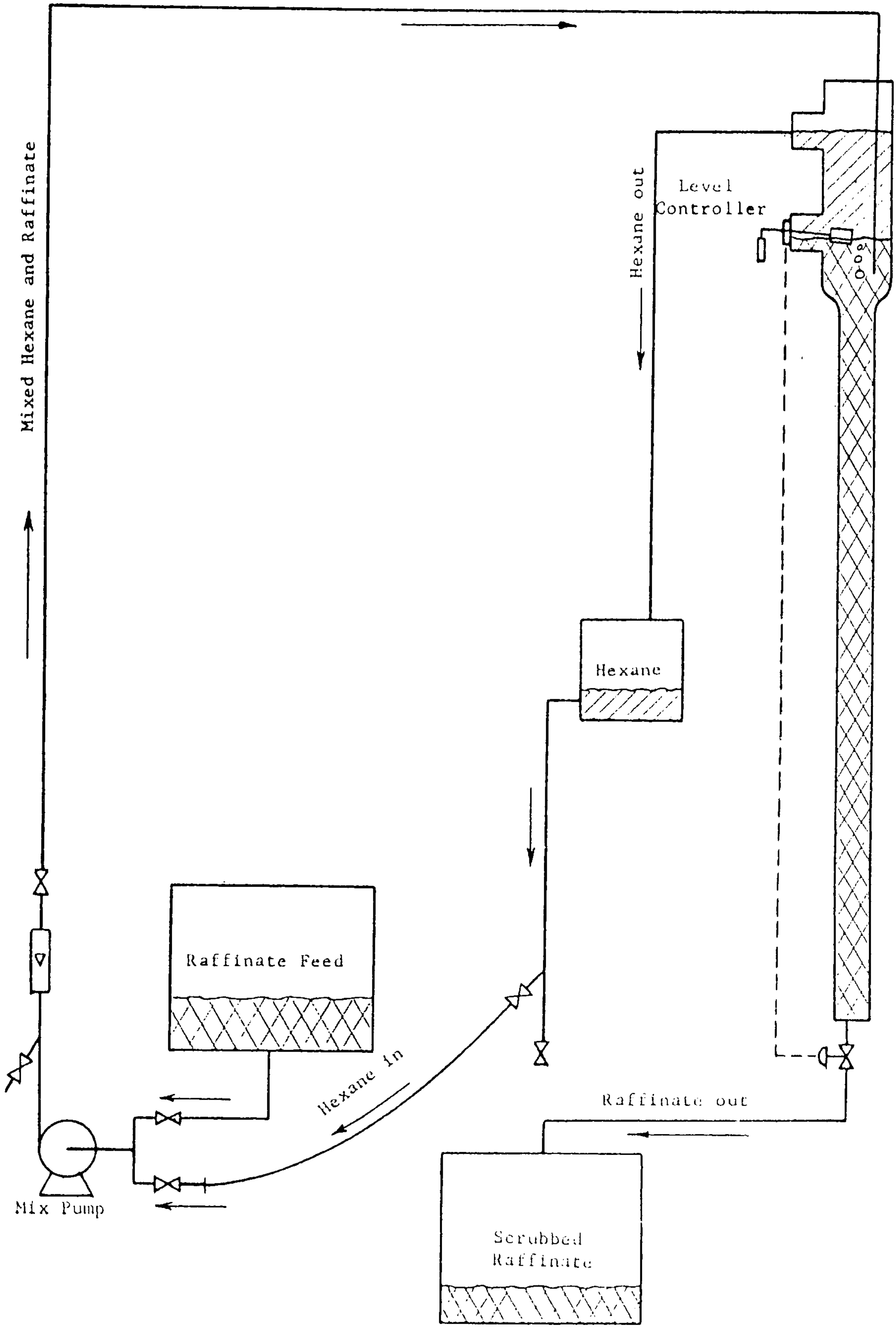
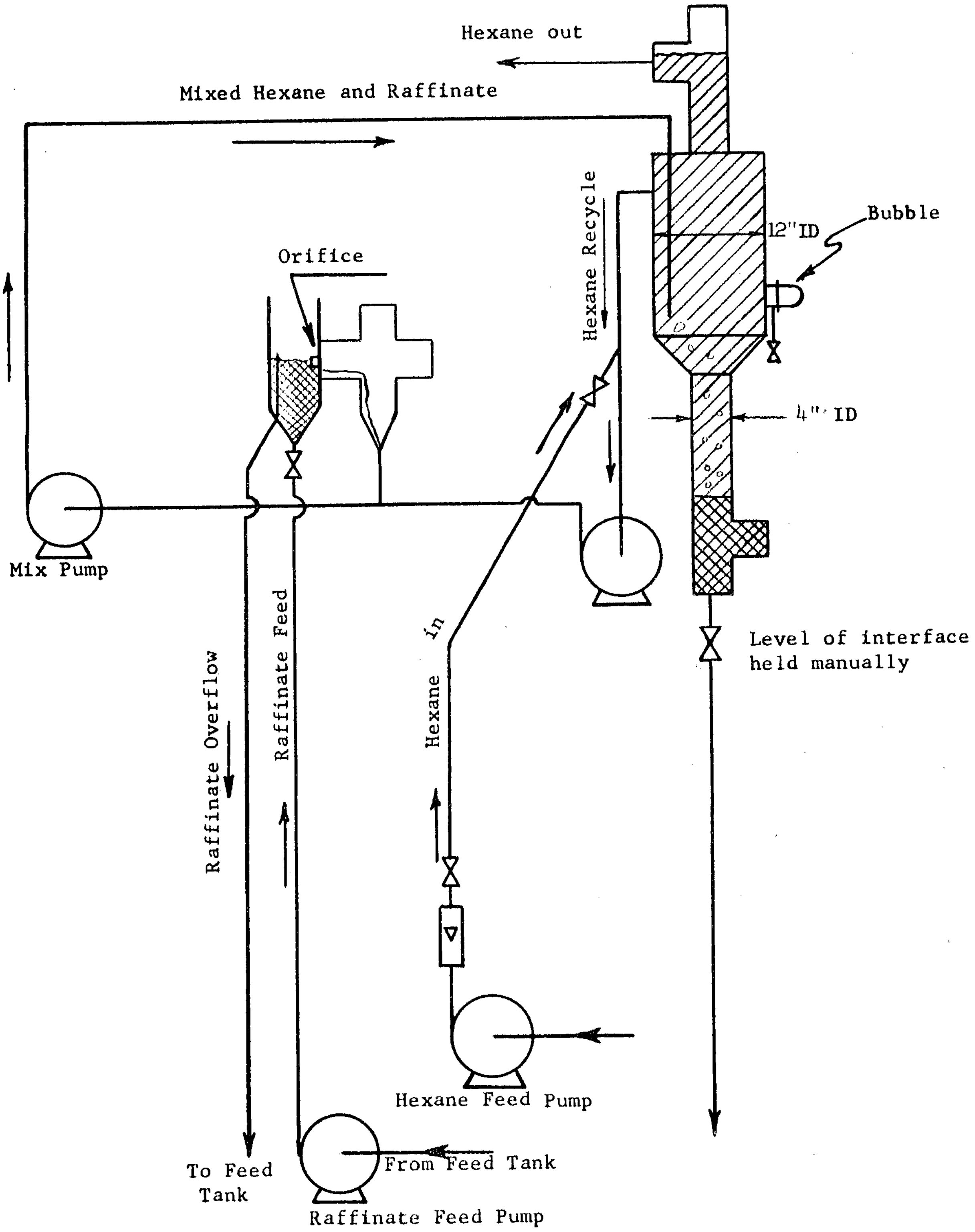


Figure 2

SCHEMATIC OF PUMPER-DECANTER OPERATION



## Table I

## Summary of Analytical Results for Column Runs

### Control Run (Countercurrent Column Operation)

| Sample | TBP % (V/V) |
|---|---|
| Raffinate In | 0.08 |
| Raffinate Out | 0.07 |
| Hexane In | 5.06 |
| Hexane Out | 5.93 |

### Mix-Pump Column Operation

| Sample | TBP % (V/V) |
|---|---|
| Raffinate In | 0.09 |
| Raffinate Out | 0.01 |
| Hexane In | 4.92 |
| Hexane Out | 6.03 |

The conditions and the results for the pumper-decanter runs are shown in Tables II and III, respectively. The data underlined are questionable.

## Table II

### Summary of Operating Conditions in Pumper-Decanter Runs

| Condition | Run Number 61A | Run Number 61B | Run Number 61C |
|---|---|---|---|
| Raffinate Feed Rate, gph | 43 | 43 | 22 |
| Hexane Recycle Rate, gph | 240 | 240 | 240 |
| Hexane Feed Rate, gph | 3.7 | 1.9 | 1.9 |
| Over-all O/A Volume Ratio (nominal) | 0.086 | 0.044 | 0.086 |
| Recycle O/A Volume Ratio | 5.58 | 5.58 | 10.9 |

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## Table III

### Analytical Results[a,b] from Pumper-Decanter Runs

| Sample | TBP % (V/V) Run 61A | TBP % (V/V) Run 61B | TBP % (V/V) Run 61C |
|---|---|---|---|
| Raffinate in Feed Tank | 0.80 | 0.56[c] | 0.56[c] |
| Raffinate Feed at Orifice (composite) | 0.02 | 0.44 | 0.17 |
| Hexane in Feed Tank | 0.28 | 0.28 | 0.28 |
| Hexane Feed at Feed Pump (composite) | 0.25 | 0.27 | 0.19 |
| Hexane at Bubble (composite) | 0.49 | >1.0 | 0.89 |
| Hexane Out (composite) | 0.64 | 1.16 | 1.16 |
| Raffinate Out (composite) | 0.09 | 0.03 | 0.01 |

[a] Analysis by infrared methods except as noted.

[b] Underlined data are questionable.

[c] Analysis for "total organic" made by contacting aqueous phase with hexane, separating aqueous and organic phases, distilling off hexane from organic phase, and measuring residue.

It can be seen by comparing the difference between the "raffinate in" and the "raffinate out" that better scrubbing of the raffinate was obtained using pump mixing (either in the pumper-decanter or in the pump-mix column system) as opposed to open column operation. This observation indicates that poor contacting is a problem in the refinery, efficient contacting not being achieved in an open column.

While operating the decanters for raffinate scrubbing, it was noted that flooding occurred in the 4-inch-ID section, but that a stable interface was maintained in the 12-inch section. Since flooding in a pumper-decanter is a function of O/A volume ratio in the mix pump as well as cross-sectional area, O/A ratios varying from 5/1 to 30/1 were tried to ascertain whether a stable interface could be maintained in the 4-inch section at refinery flow rates corresponding to a 30-gallon-per-minute aqueous through-put. Emulsification, however, occurred in all cases, showing that it is impractical for the refinery to contemplate mix-pump column operation with the existing columns.

A scale-up of the 12-inch-ID section based on flow rate per unit cross section showed that a pumper-decanter for scrubbing raffinate would require a 6.46-foot diameter at a raffinate flow rate of 30-gallons per minute. This figure compares more favorably with the 6-foot diameter of the present refinery decanters than with the 2-foot-7-inch diameter of the scrub column disengaging section.

## Conclusions

The conclusions drawn from the results obtained in this study were:

1. Flooding is not a problem in the operation of an open column at refinery rates.
2. With open column operation at refinery rates, the contact necessary to remove effectively TBP from raffinate cannot be achieved.
3. Better contacting of aqueous and organic phases can be accomplished with a mixing pump than with an open column.
4. The use of a pump for mixing and the existing scrub column for settling would result in flooding of the column.
5. The use of a pump for mixing and a decanter for settling would result in stable operation and most efficient scrubbing.

# FLUID-BED DENITRATION

by

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## I. Summary

The fluid-bed denitrator has been operated at rates up to 500-lb $UO_3$/hr-sq ft utilizing uranyl nitrate feed concentrations up to 11.8 lb U/gal with satisfactory particle size control. Heat transfer film coefficients from 37 to 47 Btu/hr-sq ft-°F and apparent vertical thermal conductivities well in excess of 20,000 Btu-ft/hr-sq ft-°F were calculated for runs made at the above conditions.

Correlations were developed indicating the effects of uranyl nitrate feed concentration, operating temperature, spray nozzle air-to-liquid volume ratio, and production rate on particle size. Another correlation was evolved which relates the average particle size, uranyl nitrate feed composition, operating temperature and production rate to the heat transfer film coefficient within the reactor.

## II. Introduction

Investigation of a fluid-bed process for the thermal decomposition of refined uranyl nitrate has continued during the past 21 months. Included in this period is the six-month interval which marked the installation of new equipment at the Weldon Spring site. One aim of these studies was the generation of chemical and engineering data necessary for the design of the optimum production-scale fluid-bed denitrator which would serve in place of the familiar denitration pots with their associated maintenance costs and variable product. A second objective of the fluid-bed denitration program is the production of uranium trioxide with physical properties suitable for use in the pilot plant fluid-bed reduction and hydrofluorination units.

Fluid-bed denitration is achieved by continuously atomizing uranyl nitrate solution into a heated fluid-bed of uranium trioxide particles, where evaporation and thermal decomposition occur. Detailed discussions of the operations involved and the equipment employed have been presented in previous reports.[1,2,3] The investigation of primary operating variables and the effects thereof have also been reported.[4,5] This report contains a description of the operation of the denitrator during the past quarter and a detailed presentation of the correlations evolved.

## III. Experimental

### A. Equipment

The operation of the fluid-bed denitrator and the equipment under study have been described previously.[6,7]

### B. Procedure

Six runs have been made since the last report.[8] The general operating procedure is as follows: With air passing through the spray nozzles and fluidizing air distribution plate, the reactor is charged with approximately 300 lb of $UO_3$. The bed is heated to operating temperature by the circulation of molten salt through the internal bayonet heaters. When the bed reaches operating temperature, water is introduced into the spray nozzle. After feeding water through the nozzle for a short period to cool it, the flow of uranyl nitrate solution is started. The feed rate and atomizing air flow are then adjusted to the desired values. A brief description of the completed runs is given below. Detailed operating conditions for each run are summarized in Table I.

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[1] Sanders, E. F., and Robinson, S. N., *Process Development Quarterly Report, Part II*, Mallinckrodt Chemical Works, *MCW-1409* (November 1, 1957), p 33-39

[2] Sanders, E. F., *et al.*, *Process Development Quarterly Report, Part II*, Mallinckrodt Chemical Works, *MCW-1411* (February 1, 1958), p 49-61

[3] Damerval, F. B., *et al.*, *Process Development Quarterly Report, Part II*, Mallinckrodt Chemical Works, *MCW-1421* (November 1, 1958), p 67-76

[4] Damerval, F. B., *et al.*, *Process Development Quarterly Report, Part II*, Mallinckrodt Chemical Works, *MCW-1426*, (February 2, 1959), p 57-65

[5] Damerval, F. B., *et al.*, *Process Development Quarterly Report, Part II*, Mallinckrodt Chemical Works, *MCW-1429* (May 1, 1959), p 41-55

[6] Sanders and Robinson, *MCW-1409*, p 34-37

[7] Damerval, *et al.*, *MCW-1421*, p 68-74

[8] Damerval, *et al.*, *MCW-1429*, p 41-55

<u>Table I</u>

<u>Fluid-Bed Denitrator Operating Conditions</u>

| Condition | Run Number<br>60 | 61 | 62 | 63 | 64 | 65A | 65B | 65C |
|---|---|---|---|---|---|---|---|---|
| 1. UNH Feed Rate, gal/hr | 7.4 | 7.8 | 8.4 | 9.7 | 11.0 | 14.0 | 15.4 | 17.3 |
| 2. Feed Concentration, lb U/gal | 9.3 | 9.75 | 9.75 | 11.7 | 11.5 | 11.8 | 11.8 | 11.8 |
| 3. Sulfate Added, ppm (U basis) | 1500 | 2500 | 2500 | 2500 | 2500 | 2500 | 2500 | 2500 |
| 4. Average Production Rate, lb $UO_3$/hr | 85 | 98 | 120 | 136 | 152 | 198 | 218 | 245 |
| 5. Fluidizing Velocity, ft/sec | 1.9 | 1.9 | 1.9 | 1.9 | 1.9 | 1.9 | 1.9 | 1.9 |
| 6. Fluidizing Gas Flow, std cu ft/min | 19 | 20 | 20 | 20 | 20 | 20 | 20 | 20 |
| 7. Average Bed Temperature | | | | | | | | |
| (a) Heater Area, °F | 650 | 630 | 650 | 605 | 608 | 604 | 603 | 606 |
| (b) Nozzle Area, °F | 610 | 605 | 615 | 590 | 595 | 594 | 592 | 586 |
| 8. Fluidizing Gas Temperature, °F | 620 | 610 | 610 | 630 | 620 | 620 | 620 | 620 |
| 9. Salt Temperature, °F | 980 | 720 | 800 | 745 | 765 | 800 | 817 | 850 |
| 10. Average Salt Temperature Drop, °F | 25 | 14 | 16 | 15 | 21 | 20 | 24 | 26 |
| 11. Salt Flow, gal/min | – | 24 | 24 | 23 | 23 | 18 | 19 | 20 |
| 12. Number of Nozzles Used | 2 | 1 | 1 | 1 | 1 | 1 | 1 | 1 |
| 13. Atomizing Air Pressure, psig | 60 | 50 | 50 | 50 | 56 | 32 | 35 | 42 |
| 14. Atomizing Air Flow, std cu ft/min | 1.4 | 1.0 | 1.3 | 3.6 | 0.8 | 0.7 | 0.7 | 0.8 |
| 15. Total Hours of Operation | 37 | 24 | 9.5 | 15 | 23.5 | 3.5 | 1.0 | 4.0 |
| 16. Per Cent On-Stream | 76 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |

## Run 60

This run was made at a relatively high feed rate using 98% UNH (9.3 lb U/gal). For a period of several hours a rate of 130 - 140 lb $UO_3$/hr was maintained. The downtime experienced and the eventual shutdown were due to repeated dust refeed plugging, which caused varying amounts of bed caking.

## Run 61

Run 61 marked the first successful use of 100% UNH (9.75 lb U/gal) as feed liquor. Production was maintained at 100 lb $UO_3$ per hour (200 lb/hr-sq ft) for a 24-hour period.

## Run 62

Run 62 was a continuation of Run 61 but with production at 120 lb $UO_3$/hr. The run proceeded smoothly for nine hours, at which time the gaskets in the spray nozzle failed, forcing a shutdown.

## Run 63

Run 63 was the first of three runs made with a highly concentrated feed. The concentration was estimated to be 11.7 lb U/gal from the boiling point (278°F) and the specific gravity (2.75). The run continued smoothly for 15 hours at a feed rate calculated to produce 136 lb $UO_3$/hr. At this time the uranyl nitrate crystallized in the feed line forcing a shutdown.

## Runs 64 and 65

The feed employed in these runs was the same as that used for Run 63. Operation at 150 lb $UO_3$/hr proceeded for 23.5 hours without incident. Vertical heat transfer was excellent. Run 65A was initiated when the feed rate was increased to an equivalent of 200 lb $UO_3$/hr, a rate which was maintained for 3.5 hours. The rate was then increased to 218 lb $UO_3$/hr for an additional hour (Run 65B). At this time the rate was again increased to 250-lb $UO_3$/hr (500 lb $UO_3$/hr-sq-ft) and maintained at this level for 4 hours. The vertical heat transfer continued to be excellent until refeed plugging forced a shutdown.

Several unsuccessful attempts were then made to operate using a set of metallic filter elements in the top of the reactor as a means of returning fines to the bed. Excessive pressures were experienced in the reactor and efforts were temporarily discontinued. An adequate filter system is being designed and will be installed during the next quarter.

## IV. Results

The chemical analyses of the uranium trioxide produced are found in Table II. The over-all heat transfer coefficients from the molten salt to the fluid bed and the film coefficients from the molten salt tubes to the bed, for the runs described, are summarized in Table III. Also included are apparent vertical thermal conductivity values from the lower portion of the reactor to the nozzle zone. Table IV contains a typical particle size analysis for each run described.

### Table II

### Chemical Analysis of $UO_3$ Produced in the Fluid-Bed Denitrator

| | Run Number | | | |
|---|---|---|---|---|
| | 60 | 61 | 62 | 63 |
| $UO_3$, % | 99.48 | 99.10 | 99.07 | 99.06 |
| Nitrate, % (sample basis) | 0.78 | 0.97 | 0.81 | 0.95 |
| $H_2O$, % (sample basis) | 0.13 | 0.16 | 0.22 | 0.19 |
| Sulfate, ppm (sample basis) | 900. | 1200. | 1250. | 1300. |

### Table III

### Heat Transfer Data

| Run No. | Over-All Coefficient, $U_T$ Btu/hr-sq ft-°F | Gas Film Coefficient, $h_o$ Btu/hr-sq ft-°F | Vertical Thermal Conductivity Btu-ft/hr-sq ft-°F |
|---|---|---|---|
| 61 | 53.5 | 70.5 | 21,000 |
| 62 | 43.2 | 53.8 | 18,000 |
| 63 | 38.4 | 47.0 | 36,000 |
| 64 | 34.0 | 43.1 | 52,000 |
| 65 | 31.8 | 39.0 | 45,000 |

## Table IV

## Typical Particle Size Analyses of Fluid-Bed Denitrator Product

| Sieve Fraction mesh | Run Number | | | |
|---|---|---|---|---|
| | 61 | 62 | 63 | 64 |
| +20, % | 15.6 | 11.7 | 12.2 | 14.0 |
| -20 +35, % | 17.9 | 15.9 | - | - |
| -20 +40, % | - | - | 16.9 | 25.2 |
| -35 +50, % | 14.1 | 13.6 | - | - |
| -40 +70, % | - | - | 15.2 | 19.1 |
| -50 +80, % | 9.6 | 10.4 | - | - |
| -70 +140, % | - | - | 12.0 | 11.7 |
| -80 +140, % | 7.5 | 9.8 | - | - |
| -140 +200, % | 3.1 | 4.8 | 4.3 | 3.8 |
| -200 +270, % | 4.3 | 5.7 | 6.4 | 5.0 |
| -270 +325, % | 4.7 | 3.4 | 2.1 | 1.7 |
| -325 , % | 23.1 | 24.7 | 30.8 | 19.4 |

## V. Discussion of Results

The heat transfer coefficients and chemical purity of the $UO_3$ produced have continued at approximately the same levels previously reported. Even at the very high production rates apparent vertical thermal conductivity continued to be high.

Major emphasis during the past quarter has been placed on developing correlations relating reactor operating conditions to particle size and heat transfer. These correlations, based on data presented previously,[9] are presented in Figures 1 through 8.

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[9] Dameryal, *et al.*, *MCW-1429*, p 42-47

Figure 1

BULK DENSITY VERSUS $UO_3$ PRODUCTION RATE

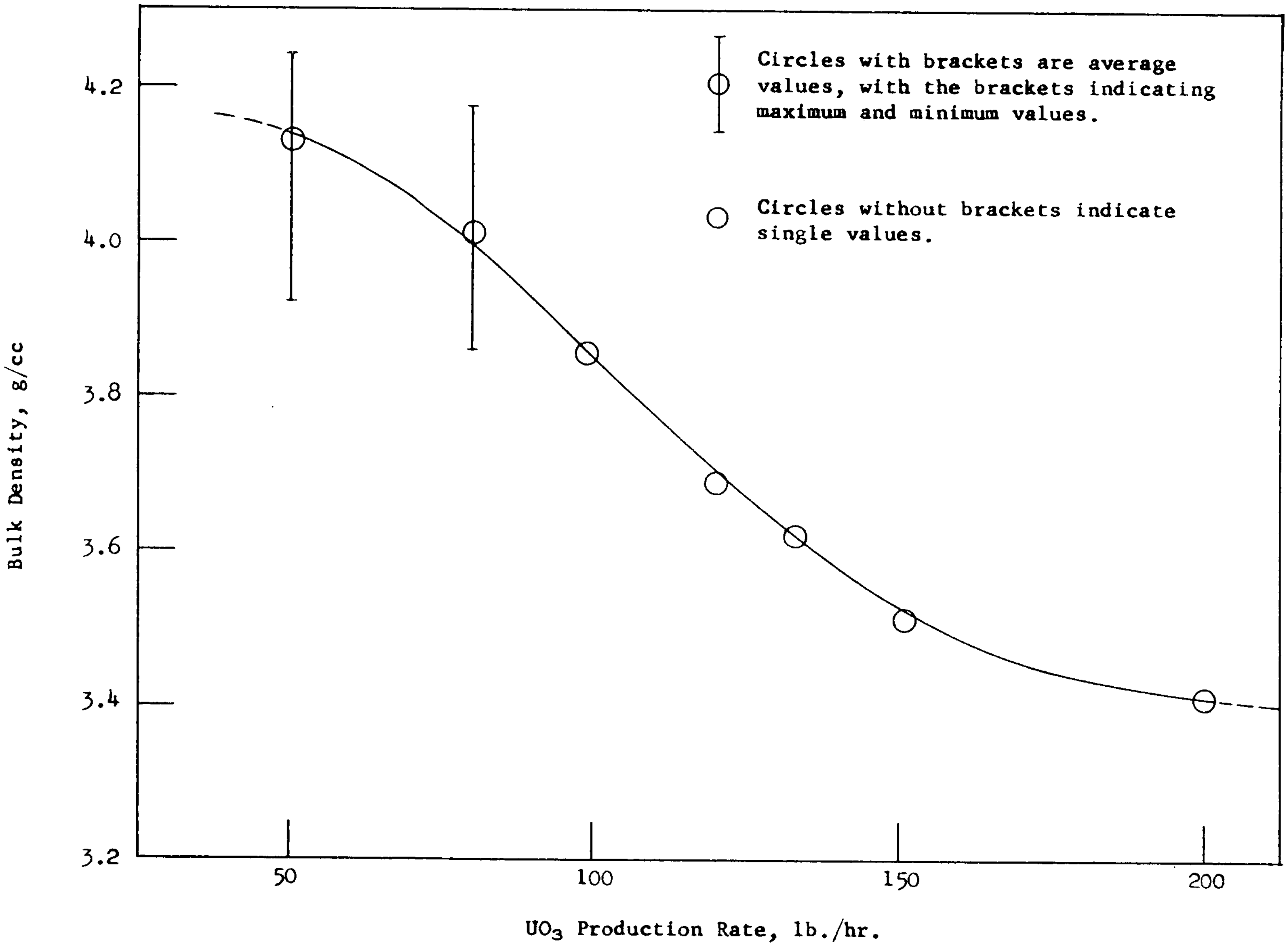


Figure 2

EFFECT OF NOMINAL OPERATING TEMPERATURE ON AVERAGE PARTICLE DIAMETER

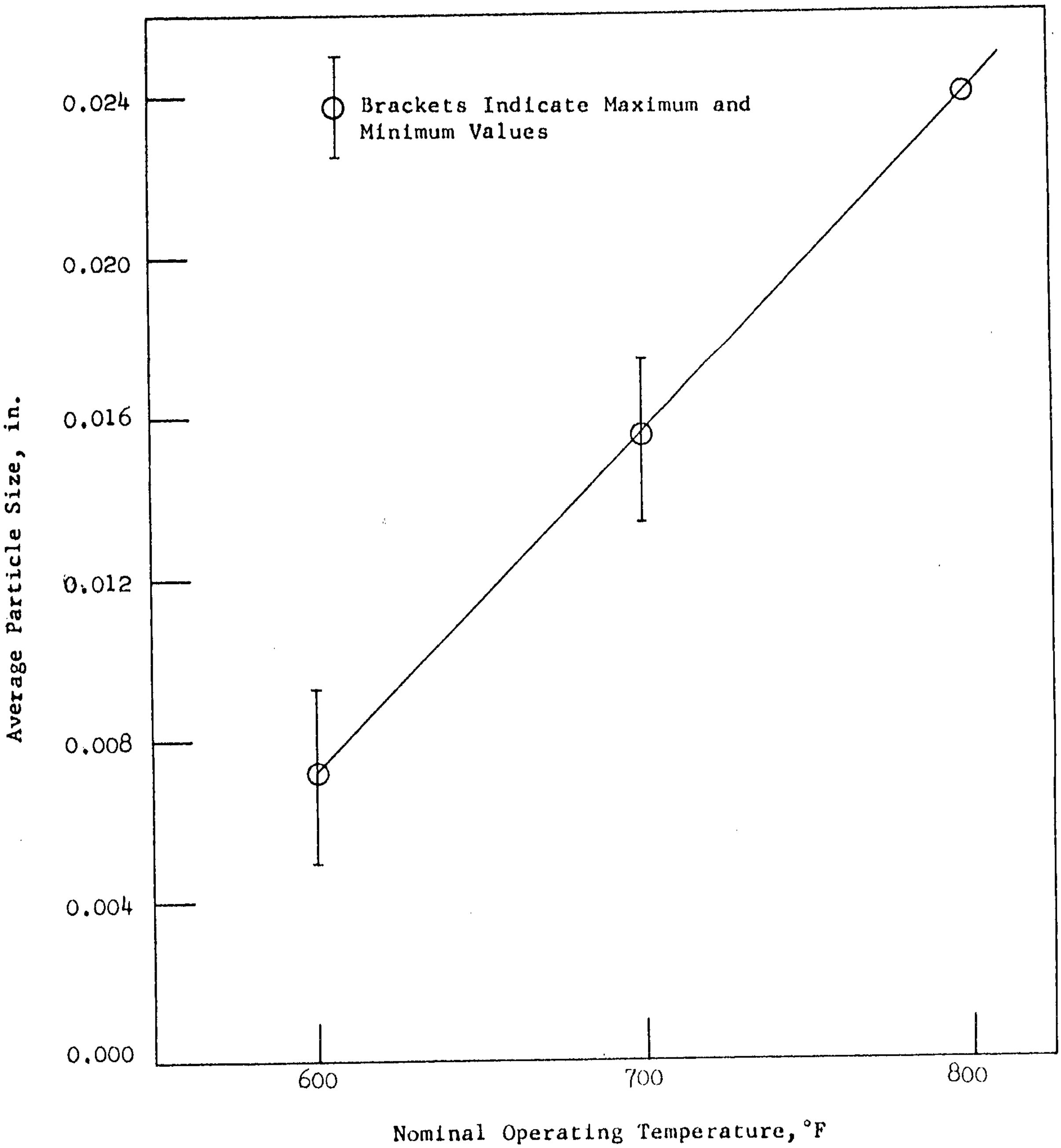


Figure 3

EFFECT OF FEED COMPOSITION ON AVERAGE PARTICLE DIAMETER

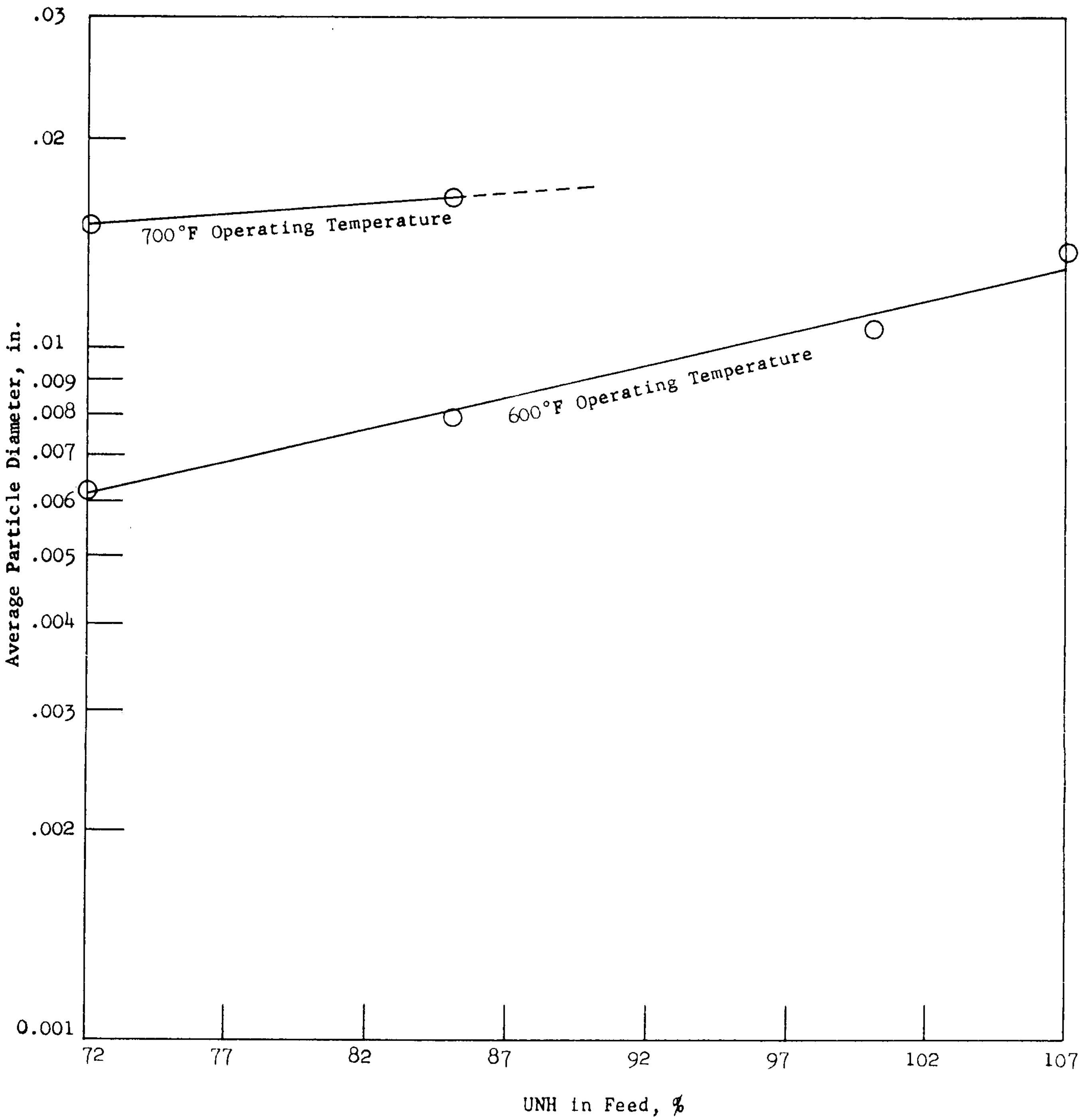


Figure 4

EFFECT OF THE NOZZLE AIR-TO-LIQUID
VOLUME RATIO ON AVERAGE PARTICLE DIAMETER

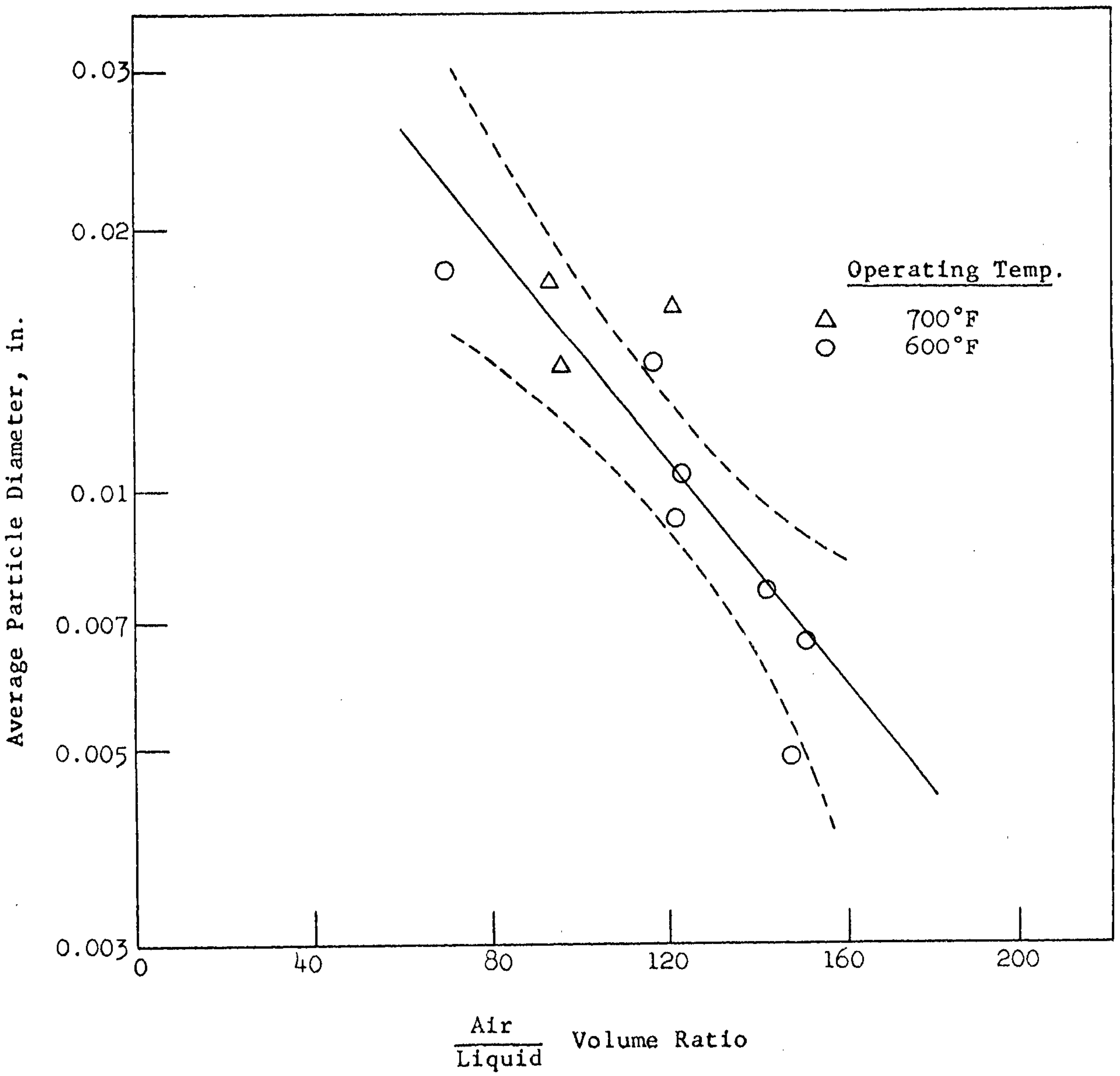


Figure 5

EFFECT OF $V_g$ [(a)] ON THE AVERAGE PARTICLE DIAMETER

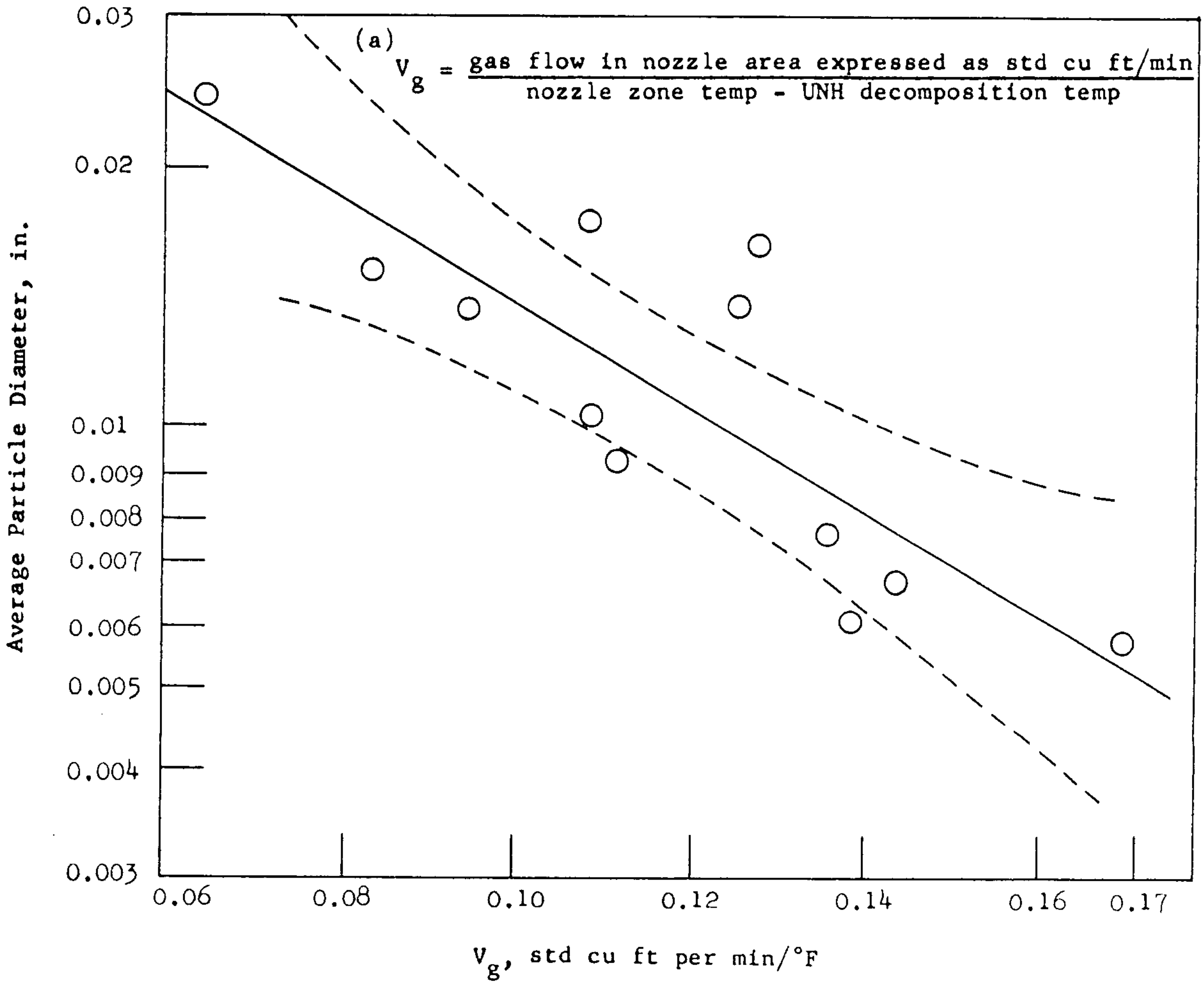


Figure 6

CORRELATION OF HEAT TRANSFER COEFFICIENT, $h_o$, WITH AVERAGE PARTICLE DIAMETER AND $V_g$

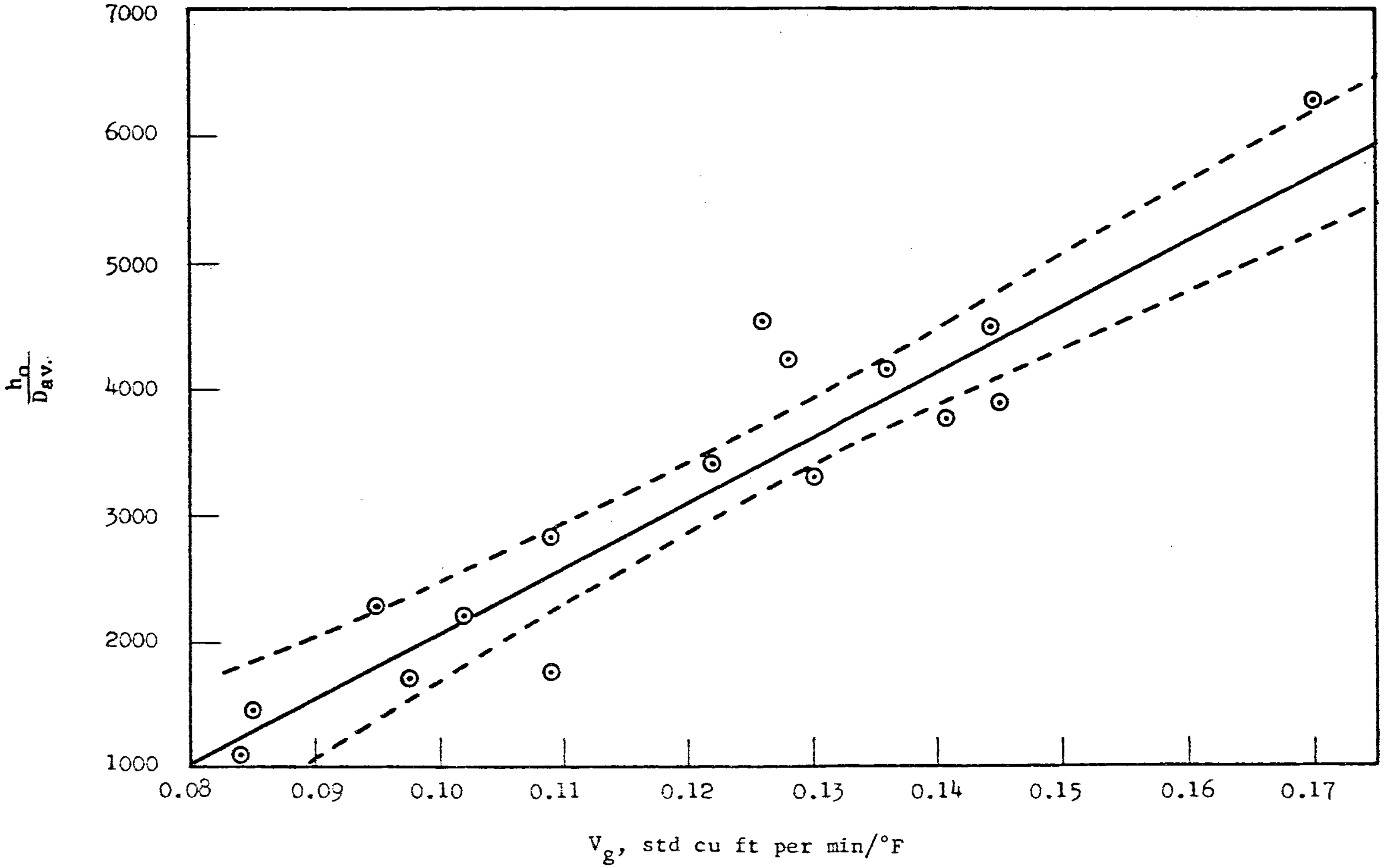
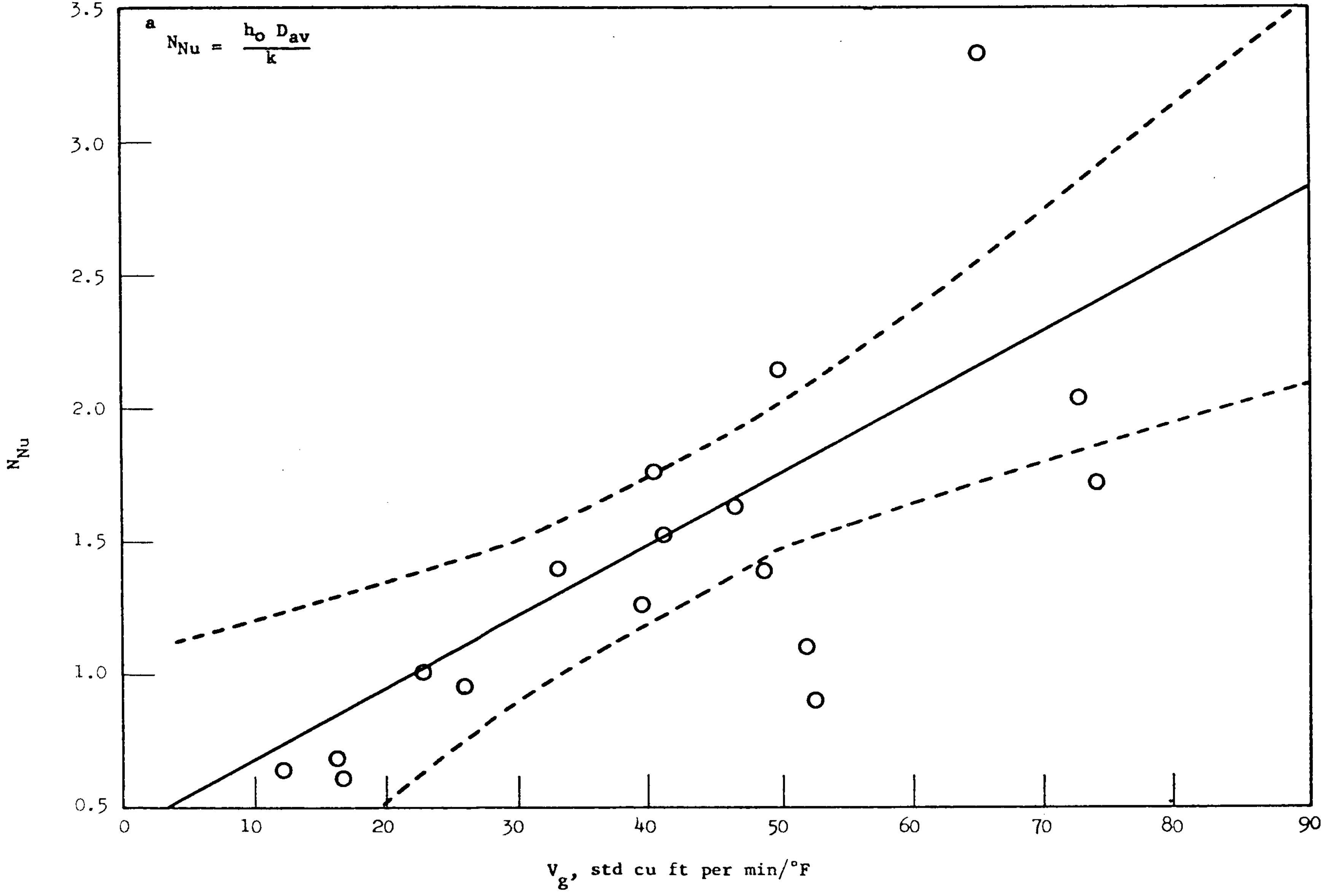


Figure 7

CORRELATION OF THE PARTICLE NUSSELT NUMBER, $N_{Nu}$,[a] WITH PARTICLE SURFACE AREA AND $V_g$



[a] $N_{Nu} = \frac{h_o D_{av}}{k}$

Figure 8

EFFECT OF AVERAGE PARTICLE DIAMETER ON THE HEAT TRANSFER COEFFICIENT, $h_o$

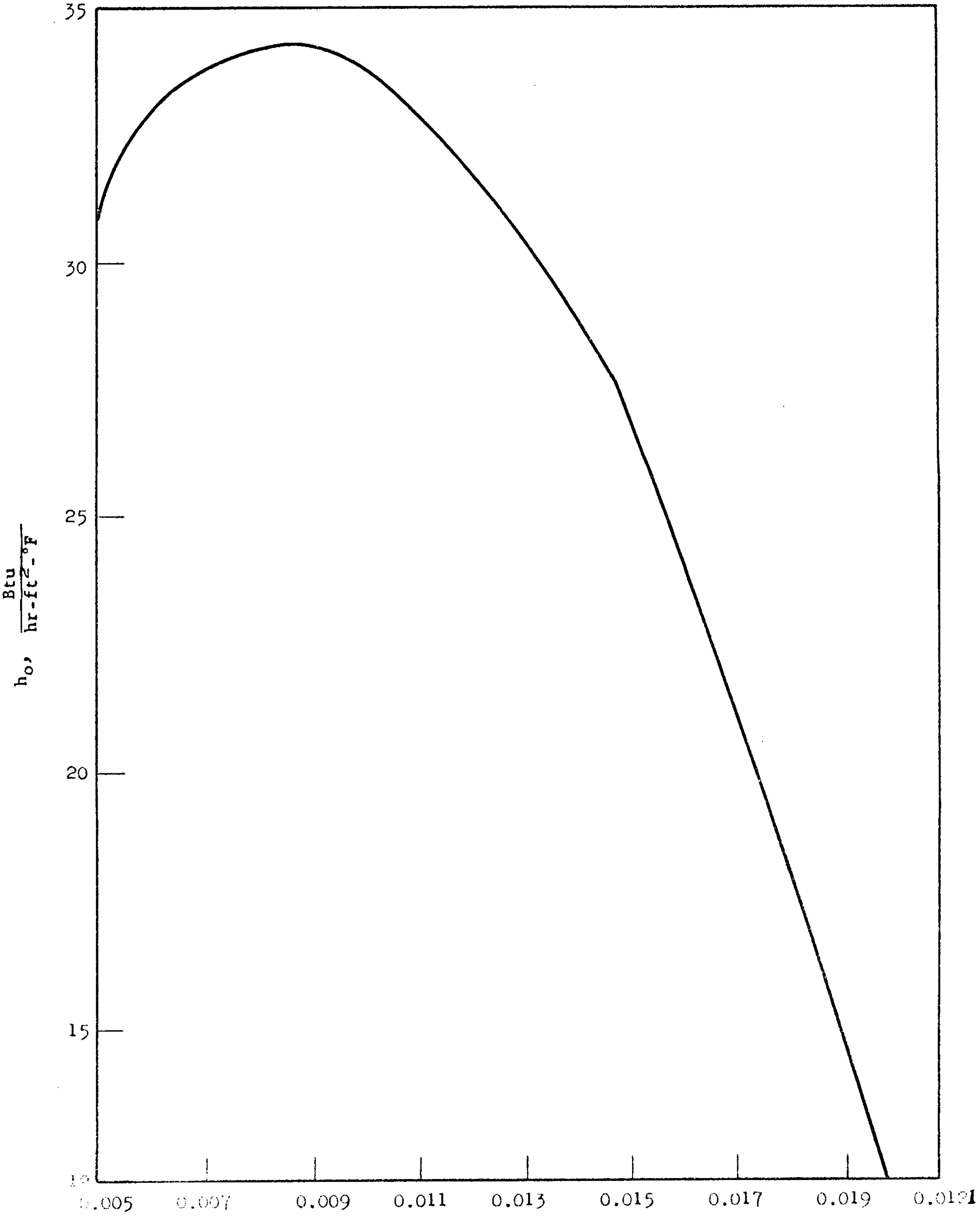


Figure 1 shows the effect of the production rate on the product bulk density. It should be stressed that the data employed to develop this curve were not gathered at a constant feed composition; during operation at the higher rates, a considerably higher feed concentration was employed than at the lower rates. The higher rates and/or feed concentrations may result in increased voidage within the particles produced and consequently a lower bulk density. Particle size distributions were almost identical at different production rates in a number of cases, indicating that the distribution is not a factor in the bulk density change.

Figure 2 shows the effect of operating temperature on the average particle diameter of the product. The average particle diameter is defined as:

$$D_{av} = \sum_{1}^{n} W\, d_f,$$

where n is the number of fractions into which the material is separated, W is the weight fraction of material of nominal diameter $d_f$, and $d_f = \sqrt{d_1\, d_2}$, where $d_1$ and $d_2$ are the openings of the adjacent U.S. Standard sieves (in inches) used in separating the corresponding fraction. Only particle size data for runs with 72 to 86% UNH feed were used for this curve. While operation at higher feed concentrations yields a product with a somewhat larger particle size, it is believed that the trend indicated by Figure 2 remains.

The average particle diameter of the product is plotted against the uranyl nitrate feed composition in Figure 3. At both the 600°F and 700°F bed-temperature levels a positive slope is indicated.

Figure 4 indicates the effect of the air-to-liquid volume ratio, employed in the spray nozzle, upon the average particle diameter of the product. The dashed lines indicate the limit of error (at the 95% confidence level) which would be anticipated for a series of runs at a given nozzle air-to-liquid volume ratio.

Figure 5 presents a correlation of the average particle diameter of the product with the total gas flow and temperature in the spray zone as represented by the total gas flow in the nozzle area (atomizing air, fluidizing air, and denitration gas) in standard cubic feet per minute divided by [the reactor temperature minus the UNH decomposition temperature (arbitrarily taken as 300°F)]. This expression, designated "$V_g$," represents the thermal driving force for denitration and the turbulence and void fraction in the spray zone. Since average particle diameter is affected by both the nozzle air-to-liquid volume ratio and $V_g$, the scatter of points in Figures 4 and 5 is somewhat to be expected.

The molten salt tube-to-bed heat transfer coefficient, $h_o$, has been correlated with average particle diameter of the product and the expression "$V_g$" to give the equation:

$$\frac{h_o}{D_{av}} = 54{,}000\ V_g - 3340,$$

where $h_o$ = outside film coefficient, Btu/hr-sq ft-°F,

$D_{av}$ = average particle diameter, inches, and

$V_g$ = gas flow/temperature driving force, std cu ft per min/°F.

This correlation is shown in Figure 6.

These data have also been evaluated in terms of the Nusselt number to yield the equation:

$$N_{Nu} = 0.0315\ V_g S + 0.122,$$

as shown in Figure 7, where

$N_{Nu}$ = Nusselt number = $\frac{h_o\ D_{av}}{k}$

$V_g$ = gas flow/temperature driving force, std cu ft per min/°F,

$S$ = particle surface area based on $D_{av}$, sq ft, and

$k$ = thermal conductivity of gas phase, Btu-in./hr-sq ft-°F

Figure 8 illustrates the relationship of average particle diameter to heat transfer. This relationship was derived from the correlations shown in Figures 5 and 6. The curve is included to indicate the general effect of particle size on heat transfer. The negative slope of the curve at the larger average particle diameters is in accordance with the findings of other investigators. The positive slope with the small average particle diameters may be attributed to the use of a fluidizing velocity much greater than that required for incipient fluidization. This excess velocity could result in a void fraction great enough to affect adversely the heat transfer.

Future runs will be made to test the various correlations developed for validity and general usefulness. It is believed that by the introduction of additional equilibrium data and refinement of the correlations evolved, the operation of the fluid-bed denitrator will become calculable and reproducible.

## VI. Conclusions

The successful operation of the fluid-bed denitrator at production rates up to 250 lb $UO_3$/hr (500 lb $UO_3$/hr-sq ft) with feed concentrations of 11.8 lb U/gal has greatly broadened the previously conceived limitations placed on fluid-bed denitration equipment. The fact that this rate was achieved with only one spray nozzle indicates that the limit for a single nozzle is as yet unknown. There is no reason to believe that higher feed concentrations could not be employed if suitable pumping and metering equipment were installed.

The correlations presented for particle size and heat transfer have placed the operation of the denitrator on a much sounder theoretical basis. It should now be possible to select operating conditions which will yield a desired product and a predictable heat transfer coefficient. The development of these correlations has also served to explain a number of puzzling observations made earlier. For example, the factorial experiment previously reported[10] indicated that an improved heat transfer coefficient was obtained with more dilute UNH at a given uranium feed rate. Since this situation involved a variation in $V_g$, examination of Figures 3 and 6 now indicates that such an effect should be anticipated.

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[10] Damerval, *et al.*, *MCW-1429*, p 48-49

# PILOT PLANT FLUID-BED REDUCTION

by

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## I. Summary

A fluid-bed reduction reactor employing an internal tapered mandrel has been installed in the pilot plant. To date three runs yielding useful data have been made.

## II. Introduction

A fluid-bed reactor designed for the reduction of fluid-bed-denitrated $UO_3$ to $UO_2$ has been installed in the pilot plant and is now in operation. This reactor utilizes an internal tapered mandrel designed according to a theory described in detail elsewhere.[1] Briefly, the mandrel is tapered to provide a constant superficial gas velocity throughout any vertical plane in the reactor bed. By virtue of the constant velocity, provided the velocity is not too far above that required for incipient fluidization, it is believed that a close approach to "piston flow" of the solids can be achieved. Yet, since the particles are fluidized, the advantages of a fluid bed, particularly the asset of good heat transfer, can still be maintained.

"Piston flow" is considered advantageous because it assures that no particles fed to the reactor short-circuit to the product line before being completely reduced. Thus, a given production rate can be achieved in one piston flow reactor, whereas several stages would be required if conventional, well-mixed fluid beds were employed.

## III. Equipment Description

An isometric view of the fluid-bed reactor and its auxiliaries is shown in Figure 1. The reactor is a 5-inch diameter by 5-foot,-9-inch long schedule-40 pipe fabricated of 347 stainless steel. Centered inside this pipe is a tapered mandrel, 53 inches long with a bottom diameter of 2.89 inches tapering to a top diameter of 0.63 inch. This mandrel, shown in Figure 2, has been described in more detail in an earlier report.[2]

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[1] Robinson, S. N., Smith, W. J. S., and Zimmerman, B. E., *Process Development Quarterly Report, Part II*, Mallinckrodt Chemical Works, *MCW-1416* (August 1, 1958), p 17-26

[2] Damerval, F. B., *et al.*, *Process Development Quarterly Report, Part II*, Mallinckrodt Chemical Works, *MCW-1429* (May 1, 1959), p 49

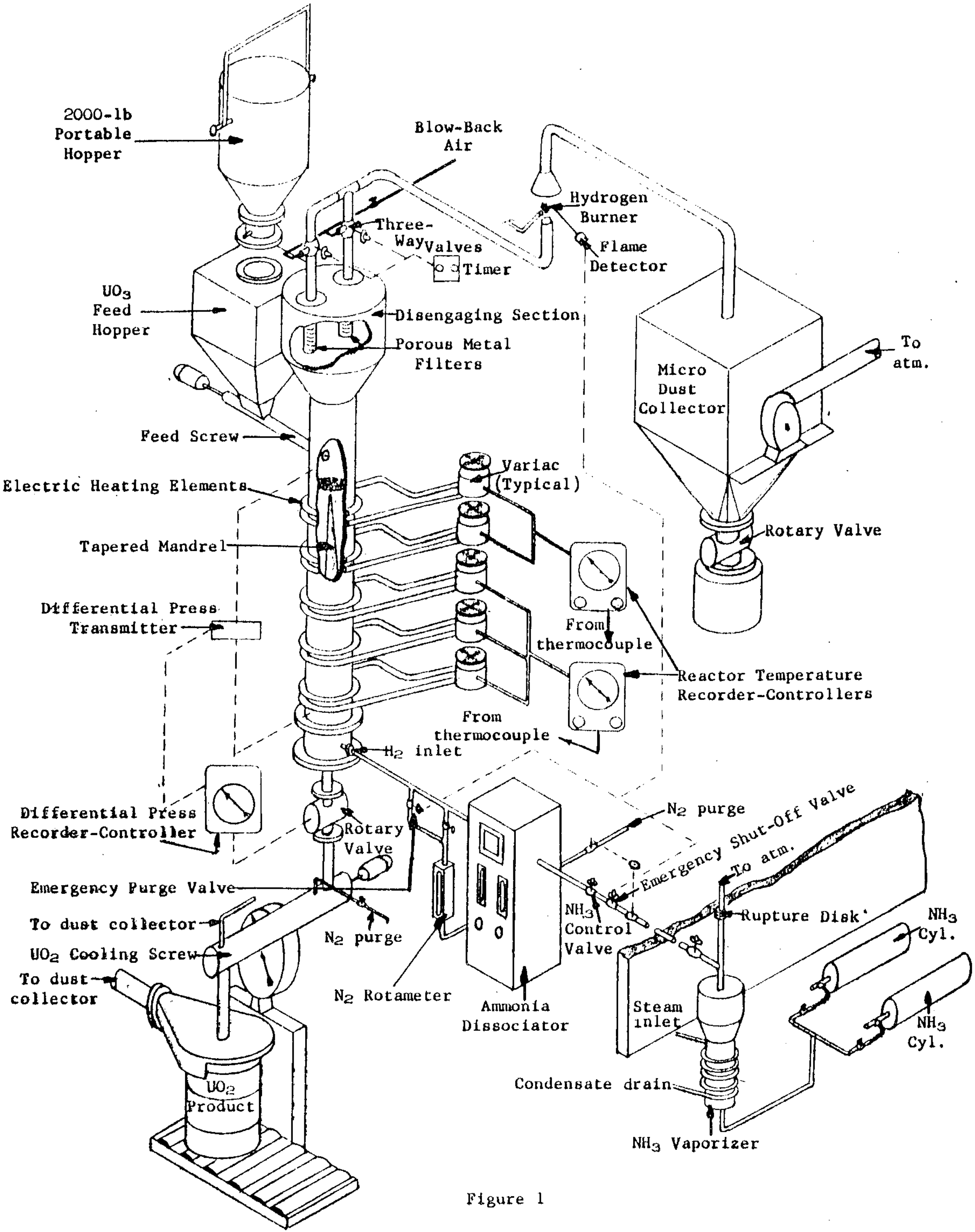
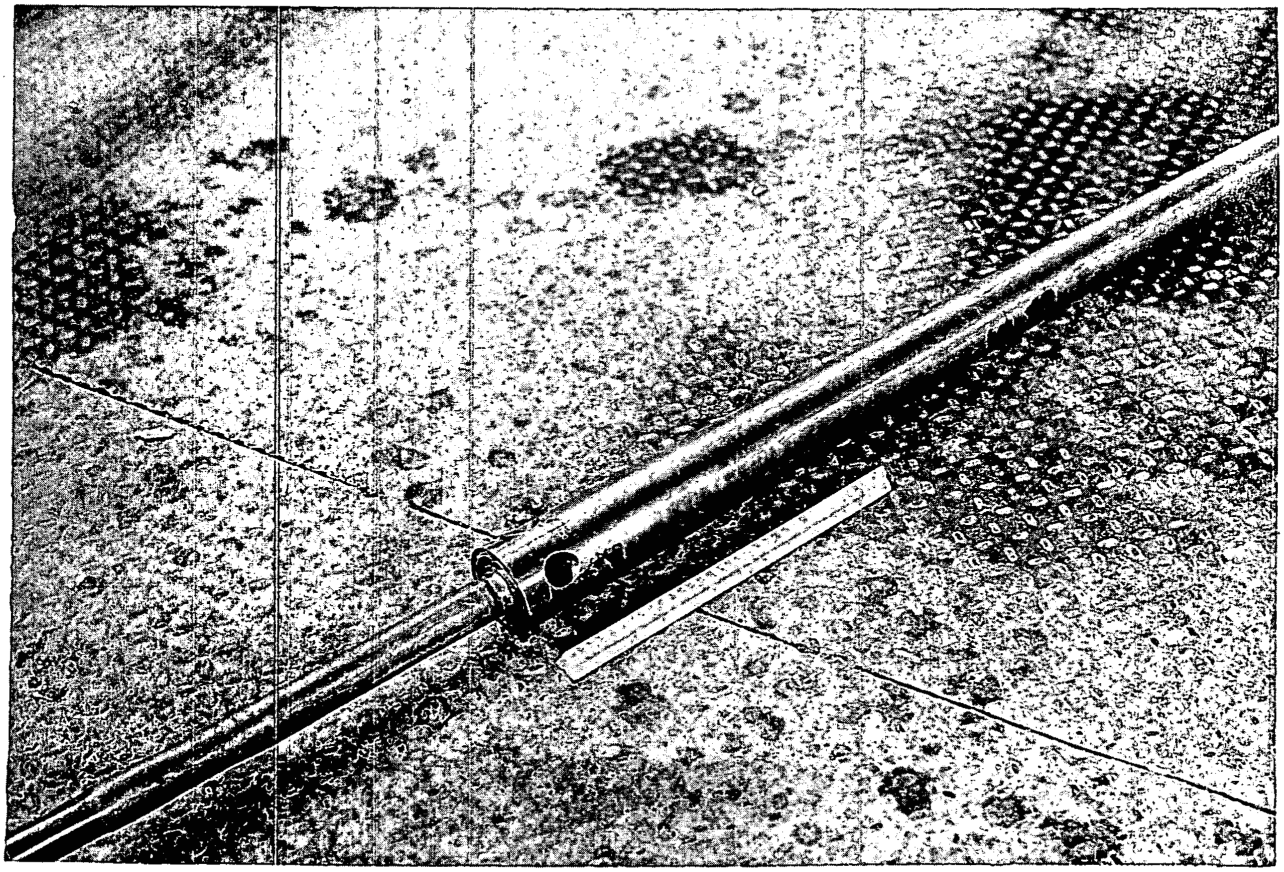


Figure 1

FLUID-BED REDUCTION UNIT

Figure 2

Tapered Mandrel for Fluid-Bed-Reduction Reactor



Dissociated ammonia ($3H_2 + N_2$) is metered into the spool piece and through a Metal-Edge wire gas distribution plate into the bottom of the reactor. The distribution plate is pictured in Figure 3. Figure 4 shows the various parts assembled.

The off-gases leave the top of the reactor through a 16-inch diameter by 2-foot-long disengaging section. Two 2½-inch diameter by 8-inch long, Metal-Edge filters with a total filtering area of about 56 square inches are located in this section, and space is provided for the addition of a third filter, if necessary. A pneumatically-operated three-way valve is provided on top of each filter. Powder entrained in the off-gases is collected on the filters and is periodically returned to the bed by reversing the position of one of the three-way valves, allowing a surge of nitrogen to flow back through the filter. The top of the disengaging section is shown in Figure 5. The off-gases then pass through a propane pilot flame for combustion of the excess hydrogen, through a bag-type dust collector, and are finally discharged to the atmosphere.

Orange oxide is discharged from a 2000-pound-capacity portable hopper into the reactor feed hopper whence it is fed to the top of the bed by a 2-inch-diameter feed screw. Uranium dioxide leaves the bottom of the reactor through three 1-inch-diameter holes which slant towards the one-inch-diameter downcomer welded to the bottom of the mandrel. The powder passes from the downcomer through a 2-inch-diameter expansion bellows and a rotary valve to a nitrogen-purged cooling screw and a drumming station. (A gas seal is provided by the rotary valve and the 2-foot head of powder above it. A screw-type sampler is provided at the cooling screw discharge for sampling the $UO_2$ product.)

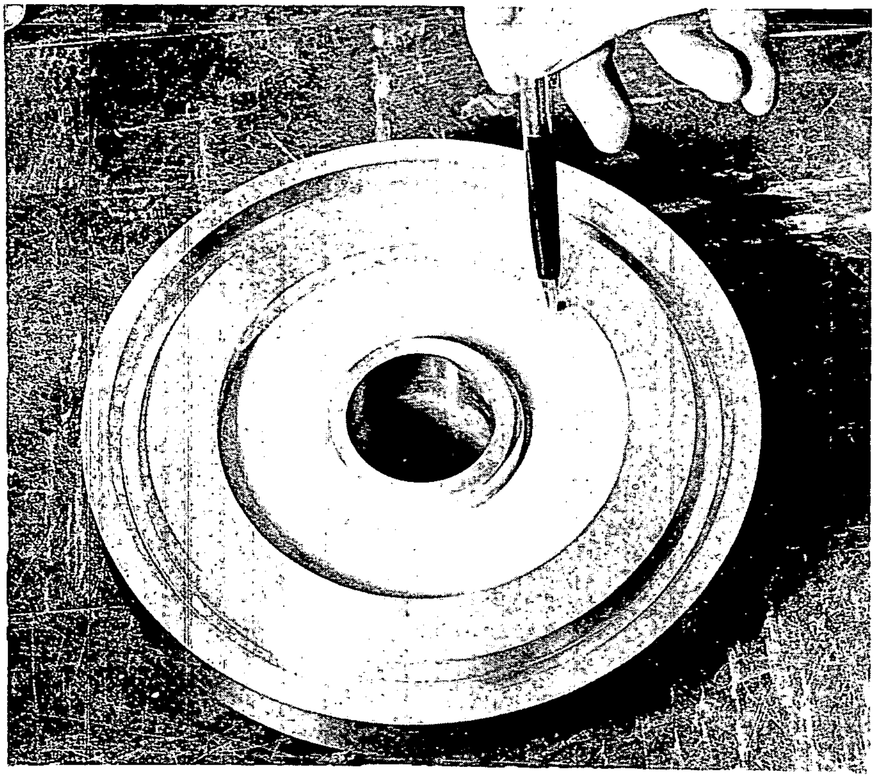
Heat is supplied to the reactor by Calrod electrical heating elements clamped to the reactor shell. These elements supply a total of 9 kw to the reactor and are divided into five heating zones, each provided with a Powerstat. The top two zones are controlled by one temperature controller, and the bottom three zones operate from a second temperature controller. The reactor shell is encased in removable insulation cans.

Thermocouples are provided in the dissociated ammonia inlet to the reactor, in the bottom of the reactor, in each of the five heating zones, in the disengaging section, and at the hydrogen burner. Pressure taps are located in the gas spool piece below the reactor, in the reactor bed five inches above the gas distribution plate, and in the disengaging section above the bed. The pressure taps in the gas expansion chamber and in the disengaging section are connected to a differential pressure controller that controls the speed of the product rotary valve. A tachometer measures the speed of the manually set variable speed drive on the $UO_3$ feed screw. A flame detection device at the hydrogen burner stops hydrogen flow to the reactor in the event of a flame failure.

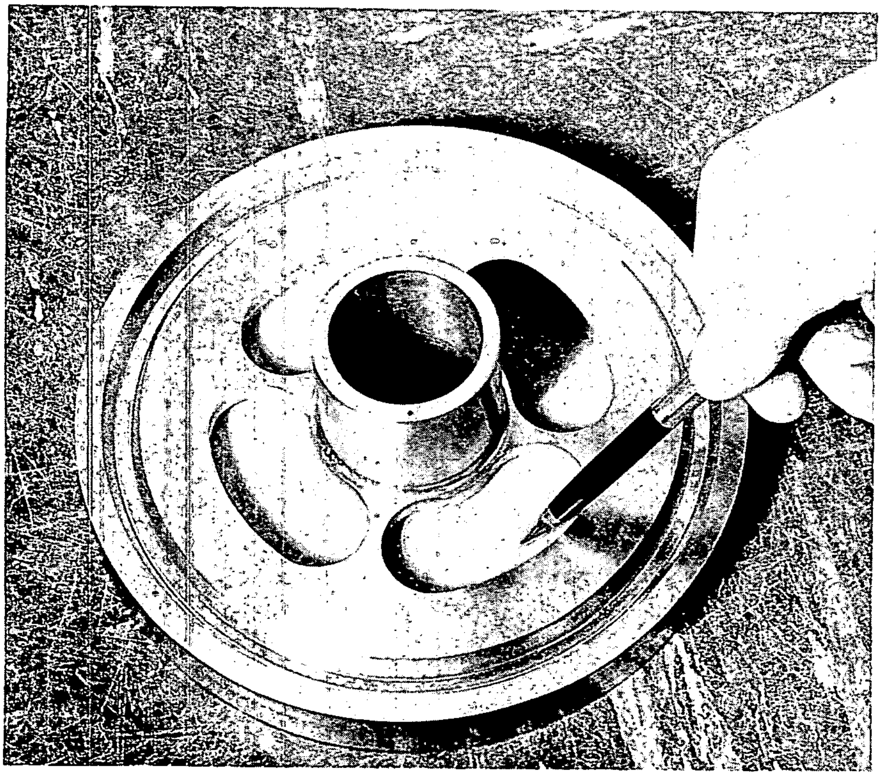
Figure 3

Gas Distributor Plate for Fluid-Bed-Reduction Reactor

Top View



Bottom View



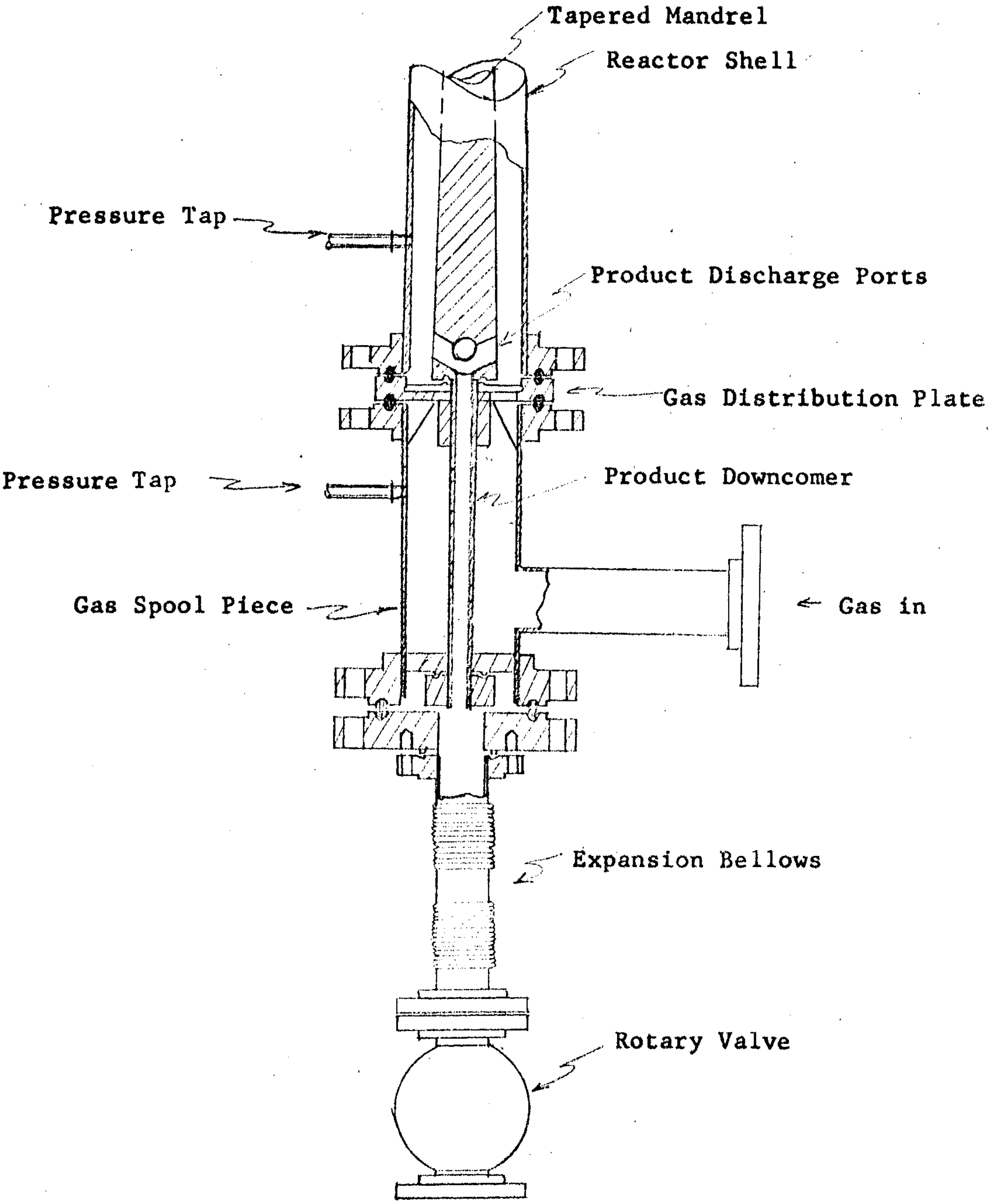
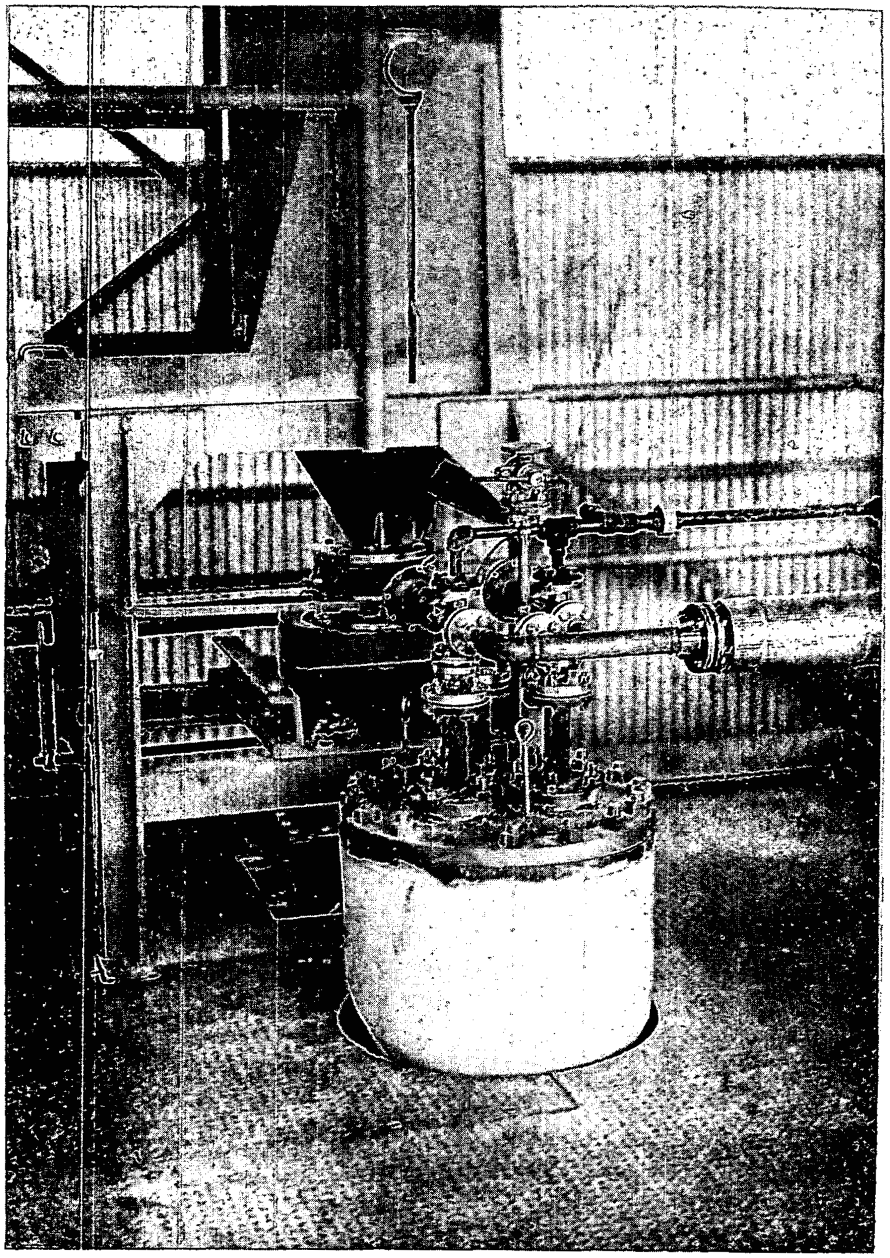


Figure 4

DETAIL OF BOTTOM OF FLUID-BED REDUCTION REACTOR

Figure 5

Fluid-Bed-Reduction Reactor
Disengaging Section and Off-Gas Piping



## IV. Experimental Procedure

Three runs have been made in the reduction fluid-bed. The operating conditions for these runs are presented in Table I. The feed consisted of $UO_3$, produced in the fluid-bed denitrator, screened so that more than 75% of the particles were minus 40 mesh and plus 70 mesh. The feed rate was chosen to allow a hold-up time in the reactor of approximately two hours, and the dissociated ammonia flow was set to maintain, as nearly as possible, incipient fluidization. The heaters were set to hold a bed temperature of approximately 1000-1100°F.

Table I

Fluid-Bed Reduction
Operating Data

| Condition | Run Number<br>FBR-2 | <br>FBR-4 | <br>FBR-5 |
|---|---|---|---|
| Average Production Rate, lbs $UO_2$/hr | 34 | 41 | 35 |
| Average Bed Height, inches | 36 | 39 | 46 |
| Average Solids Residence Time, hrs | 1.7 | 1.8 | 2.4 |
| Average Cracked Ammonia Flow, scfh | 153 | 108 | 154 |
| Average Number × Theory of $H_2$ | 2.9 | 1.4 | 2.5 |
| Average Superficial Gas Velocity, ft/sec | | | |
| Bottom of Bed | 0.98 | 0.80 | 1.08 |
| Top of Bed | 0.96 | 0.81 | 1.04 |
| Average Gas Pressure at Bottom of Bed, psig | 3.9 | 4.7 | 5.3 |
| Average Bed Temperature, °F | 990 | 1120 | 1085 |
| Range of Average Bed Temperature Measurements, °F | 890-1040 | 1090-1140 | 1025-1155 |
| Total Duration, hrs | 4.8 | 15.25 | 16 |
| Duration at Steady State, hrs | --- | 10.33[a] | 8[a] |

[a] All average operation conditions are calculated for steady-state operation.

Runs FBR-4 and FBR-5 were both good runs from the standpoint of stability of equipment performance and constancy of operating data. FBR-2, however, had to be terminated after a short period of operation due to a hydrogen leak.

## V. Experimental Results

The chemical and physical properties of the $UO_2$ product are presented in Table II. These data are averages of the analyses of samples taken during steady-state operation. The chemical analyses are based on the assumption that all the uranium was present as $UO_2$ or $UO_3$, although the intermediate $U_3O_8$ was present in the samples. Table III shows the $UO_2$ content of the product at the various operating conditions of the three runs.

Table II

Fluid-Bed Reduction
Feed and Product Analyses

| | Run Number | | | | | |
|---|---|---|---|---|---|---|
| | FBR-2 | | FBR-4 | | FBR-5 | |
| | Feed[a] | Product[b] | Feed[a] | Product[b] | Feed[a] | Product[b] |
| Average Bulk Density, g/cc | 2.97 | 3.23 | 3.31 | 3.43 | 3.16 | 3.16 |
| Average Tap Density, g/cc | 3.07 | 3.52 | 3.59 | 3.63 | 3.34 | 3.32 |
| Nominal Sieve Cut, U. S. Mesh | -40 +70 | | -40 +70 | | -40 +70 | |
| Mean Particle Diameter, inches[c] | 0.0095 | 0.0078 | 0.0079 | 0.0072 | 0.0096 | 0.0097 |
| Average $UO_3$ in product, w/o | | 42.2 | | 34.9 | | 29.7 |
| Average $UO_2$ in product, w/o | | 57.4 | | 65.1 | | 70.2 |

[a] All feed material was produced in the pilot plant fluid-bed denitrator.

[b] Data are averages of analyses of samples taken during steady-state operation.

[c] Mean volume - surface equivalent diameter [Damerval, F. B., *et al.*, *MCW-1429*, p 49].

## Table III

### Fluid-Bed Reduction
### Run Conditions and Product Analysis

| | Run Number | | |
|---|---|---|---|
| | FBR-2 | FBR-4 | FBR-5 |
| Solids Residence Time, hrs | 1.7 | 1.8 | 2.4 |
| Fluidizing Gas Velocity, ft/sec | 0.98 | 0.80 | 1.08 |
| Average Bed Temperature, °F | 990 | 1120 | 1085 |
| Percent $UO_2$ | 57.4 | 65.1 | 70.2 |

## VI. Discussion of Results

The conversion of $UO_3$ to $UO_2$ achieved in all three runs is less than desired; however, these first runs are in the nature of shake-down runs and the results are not necessarily representative of the ultimate efficiency of the reactor. The data do indicate the effect of higher temperature and longer residence time. Table III indicates that the conversion was higher during FBR-4 than during FBR-2, FBR-4 being carried out at an average temperature of 1120°F versus 990°F for FBR-2. While higher reduction temperatures do benefit the conversion rate, they may have an adverse effect on the subsequent hydrofluorination step. It is also desired to make the range of bed temperatures considerably smaller. There are relatively cold spots at the bottom of the bed and in the middle of the reactor where the support gussets are located. Elimination of these low temperature spots should enhance the degree of conversion.

The nominal residence time during FBR-5 was 0.6 hour greater than that during FBR-4, with consequent greater conversion. The average solids residence time may be increased by raising the bed level or by decreasing the production rate, the latter being the less desirable method.

Attrition of the feed does not appear to be a problem. For RunsFBR-4 and FBR-5 the mean particle diameters of the product and feed were essentially the same. The difference determined for Run FBR-2 is probably due to non-representative sampling.

# THE USE OF THE HF-$H_2O$ AZEOTROPE IN GREEN SALT PRODUCTION

by

G. Kerr
L. Weber

## I. Summary

Experimental equipment and operating conditions are described for the initial runs in which green salt was produced from $UO_2$ by hydrofluorination with HF-$H_2O$ azeotrope. Excellent reactor operation was obtained when an azeotrope ratio of 0.135 lb of 38% HF per lb of green salt was used at an overall HF rate of 1.2 times the stoichiometric amount.

## II. Introduction

In the past, screw reactors for the production of green salt from $UO_2$ have operated on the "70% flowsheet." Under this plan, enough anhydrous HF was fed to the counter-current reactor to convert the $UO_2$ to $UF_4$, and the HF in the discharge gas stream formed a 70% acid solution with the water of reaction.

It is now practical to operate green salt reactors at much lower excesses of HF than the 2.3 times the theoretical amount which was routinely used to produce 70% HF in the offgas. The cost of HF is high enough to encourage this route for continued production use. The theoretical limit to such reductions in excess of reagents is the stoichiometric amount (1.0 × theory). However, high quality green salt cannot be produced with an absolute minimum of reagent in currently used industrial equipment.

Operation of green salt reactors with excesses of 20 - 30% has been demonstrated at this and other AEC sites. To minimize reagent excesses as much as possible, the concept of recovering and recycling the 38% HF-$H_2O$ azeotrope to the reactors was proposed. The problem of handling and recovering this azeotrope is difficult because of the very corrosive nature of dilute HF solutions. A recovery system was designed and constructed, and it is in the pre-operational testing phases. A future report will describe the startup of this system. The scope of the present report is limited to a description of experimental operation of a green salt reactor using a simulated recycle of 38% HF-$H_2O$ mixture to the upper tube. With this recycle imposed on the reactor, it is expected that successful operation at an overall HF consumption approaching 1.0 will be both possible and practical.

The azeotrope recovery system consists essentially of a distillation column, a vaporizer, and a metering station. The distillation column will accept mixtures of HF and $H_2O$ that are below

38% HF and will produce 38% HF and water. The water is discarded while the 38% HF is recycled back to the reactor in the vapor state. Therefore, the offgas being fed to the azeotrope recovery system must necessarily be below the azeotrope composition. In this system, the economy of operation increases as the overall HF consumption is reduced.

## III. Experimental

### A. Reactor Operation Using an Azeotrope Recycle Stream

Three screw reactors operating in cascade are designated as the "A", "B", and "C" reactors. Each reactor is agitated by a long screw, which is driven at one end and discharges powder at the other end. The HF flows countercurrent to the $UO_2$ through all three tubes.

$UO_2$ is fed to the drive end of the "A" reactor, and anhydrous HF is fed to the discharge end of the "C" reactor. The azeotrope recycle stream is fed to the discharge end of the "A" reactor where it mixes with the partially reacted HF flowing from the "B" reactor.

After the HF leaves the "A" reactor, it is filtered to remove green salt dust, condensed, and then reconcentrated to 38% HF in a Karbate distillation column. This reconcentrated acid may then be recycled to the "A" reactor. The overheads from the still, which consist of the water generated in the reaction of HF with $UO_2$ and a small amount of HF, are neutralized and discarded.

### B. Method of Simulation of Azeotrope Recycle

To determine the proper operating conditions for running a reactor on azeotrope recycle, it was necessary to devise a way of making the azeotrope artificially and metering it into the "A" reactor accurately. By the use of an installed anhydrous HF flowmeter, together with its controls, a method of metering steam and mixing the two streams prior to entering the reactor was provided to simulate the recycle of azeotrope. This arrangement for metering HF and steam separately provides great flexibility for testing the various run conditions.

## IV. Discussion

### A. Choice of Experimental Conditions

The choice of run conditions is dependent on two factors: cost and production of high-quality $UF_4$. The condition of minimum cost is not necessarily one of good operability. The objective of this work was to develop a set of conditions under which the reactor will operate at the lowest possible cost. This means operating with the lowest possible overall HF excess, and secondarily, with the lowest possible amount of azeotrope recycle.

## B. The Role of HF Concentration Profile in Operability

The operability of a reactor depends on several factors: HF concentration profile, temperature profile, and total volume of gas flowing through the reactor system.

The most practical place to consider HF concentration is at the point where it leaves the "A" reactor. This is referred to as "offgas" since it leaves the reactor system here.

Under conditions of 1.3 × theory of HF flow the offgas composition will be about 40% HF. If the overall HF excess is gradually lowered from 1.3 to 1.0 the offgas composition will drop from about 40% HF to 0% HF (assuming 100% conversion). If, while running at an overall HF rate of 1.0 × theory, the recycle of azeotrope is then started at some low rate and gradually increased to a rate of 0.356 pound azeotrope per pound $UF_4$, the reactor offgas concentration will increase from 0% HF to 28% HF, at which point the pressure drop in the present offgas system limits the operation.

It is possible, theoretically, to operate the reactor with any combination of HF and azeotrope feed rates between these extremes; however, not all of these combinations are economical, nor are all of them possible under present conditions.

## C. Offgas Volume Relations

The volume of reactor offgas varies over a wide range, depending on the particular combination of overall HF rate and the azeotrope recycle rate being fed to the "A" reactor. If AHF is fed to the reactor at an overall rate of 1.0 × theory with no azeotrope recycle, the reactor offgas volume will be 3.5 $ft^3$/pound $UF_4$ (at 400°F and 17 psia). At 1.3 × theory, 5.6 $ft^3$/pound $UF_4$ is obtained under the same conditions. With azeotrope recycle conditions of 1.0 × theory AHF and 0.356 pounds azeotrope per pound $UF_4$ (28% HF offgas), the volume is 13.8 $ft^3$/pound $UF_4$. At high azeotrope rates, the available pressure drop for offgas filtration appears to limit operations.

## V. Results

The results of reactor operation using azeotrope recycle into the "A" reactor are shown in Table I. The experimental work was started using a 1.0 overall AHF rate with sufficient azeotrope flow to the "A" reactor tube to produce a 20% offgas. Since this condition resulted in poor reactor operation, attempts were made to improve reactor operation by increasing the amount of azeotrope flow. This resulted in conditions under which reactor operation was impossible because of the large volume of offgas and the resulting back pressure. At this time air cooling was instituted on the "B" tube, and further attempts to improve reactor performance were made by using slightly more than the theoretical 1.0 overall HF rate and by "bypassing" some anhydrous HF into the "A" reactor along with the azeotrope.

## Table I

## Azeotrope Recycle Experiment

|  |  |  |  | Average Product Quality |  |  |  |  |  |  |  | Offgas Flow Rate cfh[b] |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  | "A" |  | "B" |  | "C" |  |  |  |  |  |  |  |
| Run | AHF Stoich. Ratio | Azeotrope Rate lbs 38% HF per lb $UF_4$ | Calc. Offgas Concn. w/o HF | No.[a] | Assay | No.[a] | Assay | No.[a] | Assay | A.O.I. | W.S. | Total | Azeo. Recycle Alone[c] | Reactor Performance | Comments |
| 1 | 1.0 | 0.135 | 20 | 9 | 33.9 | 11 | 87.0 | 27 | 96.5 | 0.8 | 2.7 | 6,260 | 3320 | Overriding of "B" temperatures - severe Caking in B and C tubes |  |
| 2 | 1.0 | 0.135 | 20 | 3 | 35.5 | 6 | 69.9 | 7 | 86.2 | 5.3 | 7.7 | 6,260 | 3320 | Same as Run 1 | Adjusted "A" tube temps. but poor control |
| 3 | 1.0 | 0.188 | 23 | 4 | 40.0 | 5 | 80.9 | 7 | 96.7 | 1.3 | 1.9 | 7,570 | 4630 | Small improvement over Run 1 |  |
| 4 | 1.0 | 0.356 | 28 | 2 | 35.5 | 2 | 86.8 | 1 | 96.7 | 0.1 | 3.2 | 11,700 | 8780 | Frequent shutdown of HF flow a/c high reactor inlet pressure | Improved control of temps. in "A" tube |
|  |  | (Air cooling of "B" tube instituted at this time.) |  |  |  |  |  |  |  |  |  |  |  |  |  |
| 5 | 1.0 | 0.239 | 25 | 5 | 23.7 | 5 | 78.0 | 4 | 95.6 | 1.3 | 3.0 | 8,810 | 5870 | Some shutdowns of HF flow a/c high reactor inlet pressure - large improvement in operation of "B" reactor - some caking in "C" tube |  |
| 6 | 1.1 | 0.239 | 30 | 15 | 43.1 | 15 | 86.3 | 14 | 96.7 | 0.7 | 2.7 | 9,390 | 5870 | More frequent shutdown of HF flow a/c high reactor inlet pressure - severe caking in "C" tube |  |
| 7 | 1.3 Bypassed 0.1 to "A" | 0.135 | 34 | 13 | 44.0 | 13 | 88.0 | 21 | 96.0 | 0.9 | 2.9 | 8,000 | 3320 | Good reactor operation comparable to normal operation with high excess HF |  |
| 8 | 1.2 Bypassed 0.1 to "A" | 0.135 | 27 | – | – | 3 | 86.6 | 8 | 97.4 | 0.4 | 2.5 | 7,420 | 3320 | Same as Run 7 |  |

[a] Indicates number of individual samples included in the average.

[b] Volumes calculated at 400°F 17 psia.

[c] Volumes calculated from 38% HF rate assuming it to pass through the reactor unchanged. Difference between total volume and this volume represents water of reaction plus any amount of HF above stoichiometric.

The last condition shown in the table, an azeotrope ratio of 0.135 lbs 38% HF/lb $UF_4$ and an overall HF rate of 1.2 times the stoichiometric amount, gave excellent reactor operation, comparable to the normal operation of a reactor on high excess HF operation.

Additional work aimed at continued good reactor performance, production of high-quality $UF_4$ and a decreasing overall HF consumption is planned. It is expected that this work will proceed concurrently with the initial process startup of the azeotrope recovery and recycle equipment.

# PRODUCTION OF DINGOT METAL FROM CANADIAN GREEN SALT

by

R. W. Becker

## Summary

Green salt, produced at Port Hope, Canada, was evaluated in the laboratory and then used in producing four 3300-pound dingots by the long-soak technique. Laboratory analysis indicated the green salt to be of uniform composition and to be approximately comparable to Weldon Spring material, with the exception of hydrogen content. The latter was about twice the level found in Weldon Spring green salt. Two of the bombs ignited prematurely; the remaining two were electrically ignited after 30 hours of heating. Metal from the long-soak bombs was analyzed and found to be comparable to Weldon Spring dingots except in hydrogen content. The hydrogen levels of 3.9 and 3.4 ppm were higher than is normally found in metal produced by the long-soak technique.

## Introduction

As part of an exchange program between Mallinckrodt Chemical Works and the Port Hope Refinery, green salt produced at one site was evaluated by the other. The objective of the program was to compare the material on the basis of chemical and screen analysis, behavior in the reduction reaction, and composition and yields of the metal produced.

## Experimental and Results

Enough green salt to produce four 3300-pound dingots was blended and packaged according to the usual procedure. (The remainder of the material was submitted to the laboratory for evaluation in small-scale bombs.) A sample of the material taken during packaging gave the analysis shown in Table I.

## Table I

### Analysis of Green Salt Produced by the Port Hope Refinery

| | |
|---|---|
| Uranium | 75.86% |
| $UF_4$ | 98.96% |
| AOI[a] | 0.58% |
| $UO_2F_2$ | 0.41% |
| Ni | 30 ppm |
| Fe | 35 ppm |

[a] Ammonium Oxalate Insoluble.

Thief-samples were taken from two of the packaged hoppers and subjected to analysis for hydrogen and for mesh size. Table II gives the results of these analyses. The number of the dingot produced from each hopper is shown at the top of the columns.

## Table II

### Hydrogen and Screen Analyses of Port Hope Green Salt

| | Dingot Number | |
|---|---|---|
| | 1814 | 1838 |
| Hydrogen, as $H_2O$ and/or HF, ppm | 56 | 61 |
| + 20 mesh, % | 1.0 | 0.7 |
| - 20 + 70, % | 5.9 | 5.8 |
| - 70 +100, % | 4.4 | 4.3 |
| -100 +200, % | 12.6 | 12.8 |
| -200 +325, % | 14.7 | 14.4 |
| -325, % | 60.7 | 61.2 |

Liners for the four bombs were jolted on the No. 1 (Hermann) jolter. They were of good quality in both appearance and green hardness. The hardness of all four liners was of the order of 85.

The Port Hope green salt appeared to be of lower density than Weldon Spring material, filling the hoppers completely and filling the lined shells to a level higher than normal. There were no problems encountered in charging the material to the blenders blending or in charging the lined shells. The charges were tamped with the concrete vibrator to give a 5-inch cap for one bomb and 3-inch caps for the other three. It was necessary to remove 42 pounds of blend from charge No. 1838.

The magnesium excess was 1% for all bombs

Two thermocouples were placed in each charge, one in the center of the charge and the other at the radius of gyration 19.5 inches below the top

All four bombs were heated by the long soak furnace cycle:

| | | |
|---|---|---|
| Furnace bottom and middle zone | 1150°F | 6 hours |
| Furnace bottom zone | 800°F | 24 hours |

Bombs 1813 and 1814 fired prematurely at 16.00 and 11.40 hours, respectively; bombs 1836 and 1838 were ignited electrically after 30 hours of heating. The charge heating curves for the bombs are shown in Figure 1 and the maximum center temperatures attained are given in Table III. The heating curves are comparable to those obtained for Weldon Spring material.

Table III

Heating and Yield Data for Dingot Metal Made from Canadian Green Salt

| Dingot Number | Firing Time hr:min | Charge Center Temperature °F | Temperature at Radius[a] of Gyration °F | Crude Yield % | Machined Yield % | Hydrogen ppm |
|---|---|---|---|---|---|---|
| 1813 | 16:00 | 300 | 580 | 97.4[b] | 82.0 | 5.6 |
| 1814 | 11:40 | 190 | 550 | 90.9[c] | 70.8 | 5.0 |
| 1836 | 29:40 | 560 | 670 | 89.7 | 76.4 | 3.9 |
| 1838 | 29:45 | 540 | 670 | 95.6 | 80.3 | 3.4 |

[a] Equivalent to the average charge temperature.

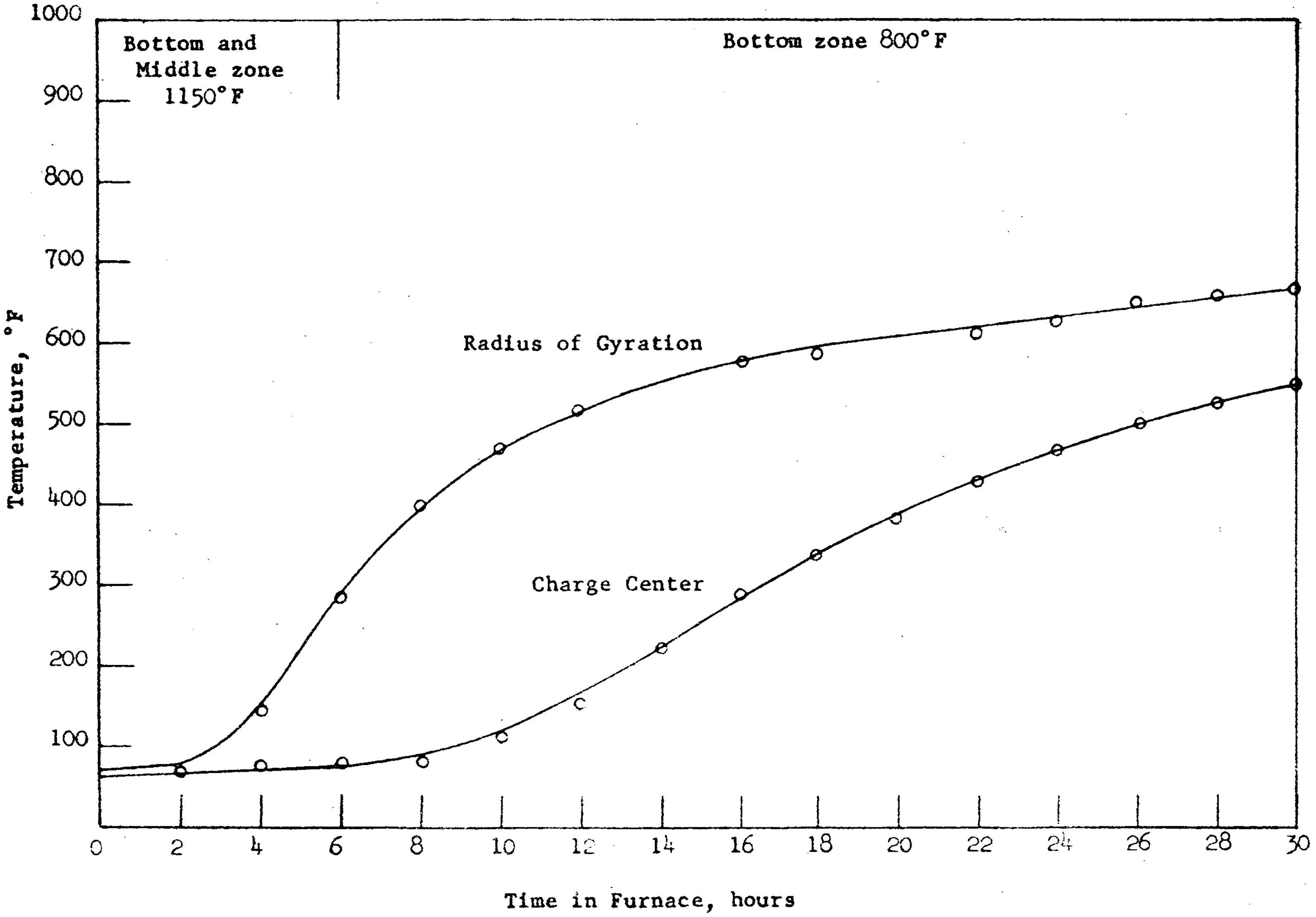
[b] One large circumferential fin.

[c] Seven per cent $UF_3$ in reaction slag.

All four dingots separated cleanly from the reaction slag on breakout; however, three of them had very rough surfaces, and the fourth had a large circumferential fin in the center.

Figure 1

DINGOT HEATING CURVES FOR CANADIAN GREEN SALT, RUN NOS. 1813, 1836, AND 1838



Two of the dingots had low crude yields, and one of these had a dark reaction slag, which, upon analysis, was found to contain about 7% $UF_3$. This indicates the possibility of a magnesium deficiency in the charge. Crude and machined yields for the dingots are shown in Table III.

Dingots 1836 and 1838, produced by the long-soak technique, were press-scalped, slow-cooled, and shipped to Fernald for rolling as part of the additive and grain size program. However, the evaluation of the rolled slugs is incomplete. The remaining two dingots were treated as normal production.

The hydrogen contents of dingots 1836 and 1838 were 3.9 and 3.4 ppm, respectively, which is higher than normally found in metal produced by the long-soak technique. Other analytical data for the two dingots are given in Table IV. The analyses indicate that the level of impurities is similar to that found in Weldon Spring material.

## Table IV

## Chemical Analysis of Dingot Metal Produced from Canadian Green Salt

(Results in parts per million)

| Element | Dingot 1836[a] | | | Dingot 1838[b] | |
|---|---|---|---|---|---|
| | 1 | 2 | 3 | 1 | 2 |
| Ag | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| Al | < 10 | 18 | 11 | 18 | 24 |
| As | < 10 | < 10 | < 10 | < 10 | 12 |
| B | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| Ba | < 10 | < 10 | < 10 | < 10 | < 10 |
| Be | < 0.1 | < 0.1 | < 0.1 | < 0.1 | < 0.1 |
| Bi | < 5 | < 5 | < 5 | < 5 | < 5 |
| C | 36 | 38 | 34 | 32 | 26 |
| Cd | < 0.10 | < 0.1 | < 0.1 | < 0.1 | 0.13 |
| Co | < 5 | < 5 | < 5 | < 5 | < 5 |
| Cr | 10 | 14 | 10 | 12 | 14 |
| Cu | 2 | 2 | 2 | 4 | 4 |
| Fe | 27 | 35 | 28 | 32 | 40 |
| $H_2$ | 4.1 | 3.6 | 3.9 | 3.1 | 3.6 |
| In | < 1 | < 1 | < 1 | < 1 | < 1 |
| Li | < 1 | < 1 | < 1 | < 1 | < 1 |
| Mg | < 10 | 14 | 10 | 12 | 14 |
| Mn | < 10 | < 10 | < 10 | < 10 | < 10 |
| Mo | < 5 | < 5 | < 5 | < 5 | < 5 |
| Na | < 10 | < 10 | < 10 | < 10 | < 10 |
| Ni | 35 | 40 | 35 | 42 | 40 |
| P | < 50 | < 50 | < 50 | < 50 | < 50 |
| Pb | < 5 | < 5 | < 5 | < 5 | < 5 |
| Si | 17 | 20 | 21 | 23 | 24 |
| Sn | < 5 | < 5 | < 5 | < 5 | < 5 |
| V | < 20 | < 20 | < 20 | < 20 | < 20 |
| Zn | < 20 | 21 | < 20 | 27 | 28 |

[a] Triplicate analyses.

[b] Duplicate analyses.

## Conclusions

Green salt produced at the Port Hope Refinery appears to be similar to Weldon Spring material except in hydrogen content and density. The former is higher and the latter is somewhat lower than is normally found in Weldon Spring green salt.

Dingot metal produced from the Canadian green salt by the long-soak technique contained more hydrogen than is normally found in metal produced by this method. The level of other impurities in the metal was comparable to that of Weldon Spring metal.

## Glossary of Specialized Terms

| | |
|---|---|
| AOI | - ammonium oxalate insoluble (oxides of uranium) |
| 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 |
| $E^o_A$ | - distribution coefficient (organic to aqueous) |
| ESU | - easily soluble uranium |
| E-Z Hollow slug | - a hollow fuel element with approximately ¼-inch wall thickness, 8-inch nominal length, and nominal ODs of 2 and 3 inches. |
| green salt | - $UF_4$ containing small amounts of $UO_2F_2$ and uranium oxides |
| I & E slug | - (hollow) internally and externally cooled slug |
| ingot | - recast uranium metal |
| MFL | - magnesium-fluoride liner |
| NOK | - a uranyl nitrate solution obtained by stripping uranyl nitrate from tributyl phosphate-hexane solvent with water |
| 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 |

(continued on next page)

## Glossary (continued)

| | |
|---|---|
| preignition time | - time interval between placing bomb in hot furnace and initiation of reduction reaction |
| raffinate | - the aqueous residue remaining after tributyl phosphate extraction of a uranium concentrate previously digested with $HNO_3$ |
| RMF | - reject magnesium fluoride |
| rod | - cylindrical length of uranium produced by rolling or extruding uranium billets and ingots |
| slag | - magnesium fluoride formed in the thermite bomb reaction; it contains small quantities of uranium and magnesium |
| 6-4 $UF_4$ | - $UF_4$ produced by reduction of $UF_6$ |
| 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 |
| water soluble (or W.S.) | - $UO_2F_2$, the water-soluble component of green salt |