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CONTINUOUS DISSOLUTION OF URANIUM-ALUMINUM FUELS

J. C. Bresee
D. L. Foster
E. O. Nurmi

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Chemical Technology Division

Unit Operations Section

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CONTENTS

		Page
0.0	ABSTRACT	1
1.0	SUMMARY	1
2.0	INTRODUCTION	2
3.0	DISSOLVER TYPES	4
	3.1 General Dissolver Types	4
	3.2 Dissolver Types for Enriched Fuel	5
	3.3 Details of the Continuous Column Dissolver	6
4.0	EXPERIMENTAL PROCEDURE	10
5.0	STABILITY OF DISSOLVER OPERATION	12
	5.1 Entrainment Effects	13
	5.2 Channeling	14
	5.3 Variations in Packing Distribution	15
6.0	EFFECT OF FEED ACID ON DISSOLVER PRODUCT	19
	6.1 Cast Slugs	20
	6.2 Extruded Slugs	24
	6.3 Summary of Performance Equations	26
7.0	VARIATION OF ACID CONSUMPTION AND CONDENSATE RECYCLE WITH DISSOLVER PERFORMANCE	28
	7.1 Acid Consumption	28
	7.2 Acid Recycle	33
8.0	APPLICATIONS TO DESIGN CALCULATIONS	38
	8.1 Product Concentration	38
	8.2 Range of Dissolver Capacity	40
	8.3 Sample Design Calculation	40
9.0	REFERENCES	42
	Appendix 1	
10.0	DETAILS OF EQUIPMENT AND PROCEDURE	43
	Appendix 2	
11.0	FEED MATERIALS SPECIFICATIONS	52
	Appendix 3	
12.0	ANALYTICAL PROCEDURES	54
	Appendix 4	
13.0	SUMMARY OF DATA AND CALCULATED VALUES	55
	Appendix 5	
14.0	NOMENCLATURE	61

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0.0 ABSTRACT

The results of a full-scale continuous trickle-type column dissolver for enriched uranium-aluminum alloy fuels are presented. Both cast and extruded unirradiated slugs were dissolved, and correlations are given relating dissolving rate and product concentration to feed acid rate and concentration for both types of slugs. The application of the correlations to column design and operation is discussed.

1.0 SUMMARY

Dissolution rates of unirradiated uranium-aluminum fuels in a trickle-type column dissolver were, based on aluminum, from 6 to 230 kg/day for cast slugs (7.5 wt % uranium) and 40 to 400 kg/day for extruded slugs (5.4 wt % uranium). These rates were equivalent to 0.5-18.5 and 2.3-22.8 kg of uranium per day, respectively. The dissolvent was 4-8 M HNO_3 containing 0.005 M $Hg(NO_3)_2$ catalyst. Acid feed rates were varied from 0.1 to 7.0 liters/min.

During any one run, the dissolver operation was stable. The average deviation of the aluminum concentration and dissolution rate was about 4%, while the average deviation in the acid consumption rate was about 2%. However, between runs, probably because of changes in dissolvent flow patterns, the reproducibility of the product aluminum concentration, when the slug bed height was held constant, was only ±20%.

The aluminum (and uranium) dissolution rates increased as the acid feed rates increased, approximately as the 0.8 power of the acid feed rate in the case of the cast slugs and linearly with acid feed rate in the case of extruded slugs. All cast data were correlated by one equation, while extruded data were correlated by a series of equations with feed acid molarity as a parameter. The product aluminum concentration decreased as the 0.2 power of the acid feed rate in the case of cast slugs and was relatively independent of the acid feed rate with extruded slugs.

When dissolver acid consumption rates were compared to aluminum dissolution rates, the consumption rate was found to vary nearly linearly with the dissolution rate. Over the range of aluminum dissolution rates from 5 to 400 kg/day, the ratio of consumption to dissolving rates changed from 3.95 to 3.78 moles/mole.

Comparison of recycle rates to dissolution rates revealed that, as had been the case with the aluminum dissolving rate vs. acid feed rate,

[redacted]

all cast data could be correlated regardless of the feed acid concentration. Again, separate correlations were found for various acid concentrations during runs with extruded slugs. A much higher recycle ratio (moles of acid returned per mole of aluminum dissolved) was obtained with cast slugs, showing that the gaseous products were at higher oxidation state in the off-gas stream during cast slug dissolution than during extruded slug dissolution. This final conclusion is consistent with the finding that, everything else being equal, extruded slugs dissolve faster than cast slugs, since the quantity of reduced mercury is an important factor determining the aluminum dissolution rate in nitric acid, and a higher oxidation state in the dissolvent means a lower concentration of reduced mercury on the slug surface.

The use of the correlations obtained by this investigation in dissolver design and operation is discussed and a sample design calculation is presented.

2.0 INTRODUCTION

The continuous dissolution of cast and extruded unirradiated uranium-aluminum alloy slugs was studied in a trickle-type column dissolver. The purpose of the study was (1) to investigate the performance of a full-scale continuous dissolver with suitable dimensions for enriched fuel dissolution, and (2) to determine the capacity of this scale equipment at a specified product concentration. The target product concentrations for the latter stages of this investigation were approximately 1.8 M aluminum and 0.2 M acid deficiency. (For a definition of acid deficiency, see Sec. 7.1.3.)

The batch dissolution of enriched fuel elements must be carried out with critically safe charges of metal to the dissolver. Also, to prevent the buildup of an undissolved heel, the dissolving necessarily is carried to completion for each batch. As the area for chemical reaction becomes zero, the dissolution rate becomes quite small. Consequently, the capacity of a single batch dissolver for enriched fuel elements is quite low.

A continuous column dissolver may be operated with critically safe dimensions; hence, this type of dissolver may have an unlimited charge of metal per unit. There is no theoretical upper limit to the capacity of such a dissolver. With the added advantage that a continuous dissolver may better serve a continuous solvent extraction process than a batch dissolver, the continuous column dissolver is potentially the most satisfactory type for short fuel elements or sections of elements.

The two operational types of continuous column dissolvers which combine the best features of feed distribution and overall reaction rate are the cocurrent (gas, liquid) trickle and the cocurrent flooded

dissolver. The performance of the latter type has been studied thoroughly and reported recently.[1] The results of studies of the trickle type dissolver (with initial runs countercurrent and the bulk of the runs cocurrent) reported here may be compared directly with the results from the flooded dissolver.

Dissolution tests were made with unirradiated, nonenriched uranium-aluminum alloy slugs, cast and extruded. Nitric acid containing 0.005 M $Hg(NO_3)_2$ as a catalyst was used as dissolvent, the HNO_3 concentration being varied from 4 to 8 M and the flow rate from 0.1 to 6.8 liters/min. Owing to the large amount of heat released by the dissolution reaction, all tests were made at the boiling point of the dissolvent, essentially 100°C.

Various equipment modifications were made during the runs, the most important of which was the change of off-gas withdrawal position from the dissolver top to bottom. Other changes included increasing the off-gas pipe inside diameter from 2 in. to 4 in. and lagging and steam-tracing the line to prevent premature condensation.

The dissolver was operated fully packed to a height of 10.25-10.66 ft during all but two runs; during these two runs a constant slug feed rate was used, and the packed level decreased accordingly.

Included are a comparison of dissolver types, to indicate the reasons for the selection of the trickle type column dissolver and to compare its features with those of other possible dissolver types, an outline of the experimental procedure, and a discussion of the stability of the trickle type dissolver.

The experimental results are analyzed from two points of view, the "external" and "internal" effects. The external effects are the effects of dissolvent conditions on product rates and concentrations, while the internal effects are the relations between the acid and gas reactions (as they affect acid consumption and condensate recycle) and the dissolution rates.

The ranges of experimental work and predicted dissolver performance are summarized in the form of shaded-area plots, and the application of these graphs and performance equations to design calculations is indicated by a sample calculation.

3.0 DISSOLVER TYPES

3.1 General Dissolver Types

When no restrictions are placed on dissolver design by criticality requirements, there are three basic types of dissolvers which may be operated, with no theoretical upper limit to the capacity of any one unit. The three types are batch, continuous pot, and continuous column dissolvers.

3.1.1 Batch Dissolver

Batch dissolvers operate with one charge of dissolvent and metal per cycle. The dissolving rate decreases continuously throughout a cycle, but all auxiliary gas handling equipment (reflux condensers and absorbers) must be designed to handle the vapor rate at the initial maximum value. To operate batch dissolvers in conjunction with a continuous process such as solvent extraction, additional storage capacity must be provided for continuous feed to succeeding steps in the process.

3.1.2 Continuous Pot Dissolver

A continuous pot dissolver has a continuous dissolvent feed, a steady product stream, and semicontinuous metal charges. The distinctive feature of a continuous pot dissolver is a large diameter/length ratio. In such a dissolver, the linear velocity of the liquid through the dissolver due to the feed stream and product withdrawal is small compared to the mixing velocity due to gas evolution. The liquid contents of the pot are well mixed, and the concentration of the liquid is essentially that of the product. Since the dissolving rate in general is a minimum at the end of a batch run, the average rate per unit metal surface area in a continuous pot dissolver is quite low compared to a batch dissolver producing the same product.

3.1.3 Comparison of Batch and Continuous Pot Dissolver

The continuous pot dissolver is maintained effectively charged with metal at all times. Thus the area for dissolving is maintained high, actually higher than the area of the initial charge to the batch dissolver. Throughout a batch dissolver cycle, the area decreases steadily as the dissolvent concentration, and consequently the rate per unit area, decreases.

In addition to rate and area changes, the capacity of a batch dissolver is limited by the initial surge of gas as high concentration dissolvent contacts metal. Sufficient dissolvent must be charged to a batch dissolver to reduce the metal heel to a predetermined value. In order for the charge not to be removed from the container as entrainment in the vapor, additional freeboard must be provided to allow for the expansion of the gas-liquid mixture.

As a result of a balance of the higher average dissolving rate per unit metal surface of a batch dissolver with the larger surface area and total charge per unit dissolver volume of a continuous pot dissolver, the capacities of the two dissolver types are comparable on a dissolver volume basis. However, this comparison applies to operating time only. When the additional downtime of batch dissolvers for draining, cleaning, and recharging is considered, continuous pot dissolvers generally have higher capacities than batch dissolvers.

3.1.4 Continuous Column Dissolver

The capacity of a continuous pot dissolver may be increased further by a technique which increases the average reaction rate per unit surface area. As was mentioned earlier, the rather complete mixing of the dissolvent in a pot dissolver is the result of a high diameter/length ratio. If this ratio is decreased, the superficial axial velocity of the dissolvent is increased. When the axis of the pot is oriented vertically, the mixing of dissolvent from top to bottom is decreased and portions of the dissolver operate with higher concentrations of dissolvent than the product. In this way, the overall reaction rate is increased. Such a dissolver is designated as a "continuous column" dissolver.

The continuous column dissolver has potentially a very high capacity. In addition, its applicability to systems with criticality requirements increases its importance to the atomic energy program. A detailed discussion of the various types of continuous column dissolvers will be included later in the report. (Sec. 3.3)

3.2 Dissolver Types for Enriched Fuel

Enriched fuel dissolvers may be divided into two types, depending on the method of handling the criticality problem: types with critically safe charges and those with critically safe geometries. A dissolver with a critically safe charge must be operated as a batch dissolver. In order to prevent the buildup of a heel of undissolved fuel, the dissolving must be carried out to zero heel. As the concentration of the chemically active ion in the dissolvent decreases and the metal area goes to zero, the amount of metal dissolved per unit time becomes very small. Consequently, the capacity of a batch dissolver operating with a critically safe charge is quite low.

On the other hand, dissolvers with critically safe geometry may be operated with an unlimited charge per unit. Therefore, such types may be fed with enriched fuel elements continuously, and the dissolving area may be held relatively constant and large compared with batch types.

3.2.1 The Slab Dissolver

Critically safe geometry may be achieved by reducing only one dimension to a critically safe value. A dissolver that is critically safe in one dimension only is called a "slab" dissolver. For

certain types of fuel elements, such as very long cylinders which cannot be conveniently reduced in size, the slab dissolver may be the only possible design for continuous operation. However, with smaller elements, such as Hanford J slugs, the problem of obtaining even distribution of metal along a dimension perpendicular to the safe dimension makes the slab dissolver less attractive than a dissolver safe in two dimensions.

3.2.2 The Critically Safe Continuous Pot Dissolver

A continuous dissolver with three safe dimensions could be constructed; it would be comparable to the continuous pot dissolver discussed previously. By the same argument used earlier, it may be seen that the capacity of such a dissolver could be increased by increasing the length/diameter ratio while the dissolver is maintained critically safe in two dimensions. The continuous column dissolver is sufficiently important for enriched fuel dissolving that a detailed analysis of the various types of continuous column dissolvers will now be given.

3.3 Details of the Continuous Column Dissolver

Basically, there are three phases which flow through a continuous column dissolver. The solid phase is made up of the metal fuel elements which enter at one end of the column and dissolve completely in the process of moving to the other end. The liquid dissolvent passes through the column in contact with the solid and leaves as product. The gas formed by the reaction of the dissolvent and metal appears throughout the column at various rates and may be removed from either end of the column. It is the interaction of these phase flows that distinguishes the various continuous column dissolver types.

3.3.1 Classification by Phase Flow

In theory, at least, there are eight different combinations of phase flows and potentially eight different dissolver designs based on these combinations. However, half the combinations (those involving upflow of the solid phase) may be eliminated because of the very difficult problem of feeding irradiated fuel elements into the bottom of a packed column. In addition, all types with upflow liquid plus downflow gas may be eliminated as being impossible. The remaining types are:

Dissolver Type	Phase Flows		
	Solid	Liquid	Gas
1	Downflow	Downflow	Downflow
2	Downflow	Downflow	Upflow
3	Downflow	Upflow	Upflow

Before further discussion of these types, the concepts of (a) relative volumetric flow rates, (b) velocities of the various phases, and (c) phase continuity, must be introduced.

3.3.2 Relative Volumetric Flow Rates

In a typical column dissolver, if the solids volumetric feed rate is taken as unity, a representative liquid feed rate would be 100. The gaseous products of the dissolving reaction (largely steam, oxides of nitrogen, and hydrogen when nitric acid is the dissolvent) would leave the dissolver at a volumetric flow rate as high as 80,000. The actual liquid flow rate in the column would be larger than the feed rate, since the steam in the off-gases would probably be condensed and returned to the dissolver. Thus the average liquid rate through the column might be as high as 130.

3.3.3 Phase Velocities and Continuity

The relative velocities of the three phases would depend on their flow rates, directions of flow, and the fraction of the column cross section occupied by the phases. Approximately half a cross section is occupied by solids. With a very low relative volumetric flow rate, the solids may be considered to be stationary. If, at the end of the dissolver at which the gas is removed the liquid and gas are moving with comparable velocities, the gas necessarily occupies more than 99% of the remaining column cross section. Therefore the gas phase may be considered the continuous fluid phase, with the liquid present as a film on the metal, a froth, or entrained droplets.

3.3.4 Trickle-Type Column Dissolver

From the above discussion it will be seen that in the continuous dissolver type 1 the gas phase must be the continuous phase at the bottom of the column. Some gas must be formed at the top of the column, and, in order for it to flow down the column, the gas phase must be continuous throughout. Such a dissolver is called a "trickle" dissolver. As the name implies, dissolvent is fed to the top of a dissolver and trickles down over the metal "packing". The gas phase is continuous in the same way as in a packed absorption column operating at low liquid rates.

3.3.5 The Flooded Column Dissolver

In type 3 the gas phase may also be considered continuous at the gas exit point, the top of the column in this case. Liquid will have to be pumped through the column, but the flow of liquid will be aided by the "gas-lift" due to gas produced by the dissolving reaction. Immediately at the bottom of the column the liquid phase is continuous, but at higher points the mass flow rate of the gas phase past any cross section increases until at the top the gas again is the continuous phase. (Note: If the liquid at the top is present as a froth,

the liquid phase may actually be continuous even though the density of the mixed fluid is essentially that of the gas phase.)

A continuous column dissolver of type 3 is called a "flooded" dissolver. It is well to keep in mind that such a dissolver is flooded only near the bottom. There is essentially no difference in liquid hold-up near the vapor takeoff point between a flooded and a trickle-type dissolver.

3.3.6 Dual Dissolver Types

There are two possible variations of dissolver type 2: the trickle and the flooded. Since, in a trickle dissolver, the gas phase is continuous over the length of the dissolver, gas upflow is as easily achieved as downflow. By analogy to a packed absorption column, liquid may flow down the column in a like manner, countercurrently to the gas flow.

However, in contradistinction to an absorption column, no gas enters the bottom of a trickle dissolver with upflow gas. Thus at the bottom of the column the liquid phase may be made continuous. A jackleg liquid takeoff device may be used to increase the average density of the fluid in the column, limited only by severe entrainment and flooding at the top of the column. A flooded as well as a trickle dissolver might be operated in this way.

3.3.7 General Operational Types

The four operational types of continuous column dissolvers are:

Dissolver Type	Phase Flows			Operational Types
	Solid	Liquid	Gas	
1	Downflow	Downflow	Downflow	Trickle
2	Downflow	Downflow	Upflow	Trickle, flooded
3	Downflow	Upflow	Upflow	Flooded

All four operational types have been studied experimentally. The flooded dissolver has been investigated at the Idaho Chemical Processing Plant and the trickle at Oak Ridge National Laboratory.

3.3.8 Theoretical Comparison of Operational Types

It is highly desirable to maintain as large a concentration gradient in the liquid phase of a continuous column dissolver as possible. At a fixed feed and product concentration, the greater the liquid

mixing along the length of the column, the more closely the column resembles a continuous pot dissolver. As was mentioned earlier, the continuous pot dissolver has a low dissolving rate per unit area and therefore requires more area and correspondingly more volume for a given production rate than a column dissolver.

In a continuous column dissolver most of the agitation of the liquid results from gas formation. It is obvious that countercurrent flow of gas and liquid would result in much more backmixing of product strength dissolvent with feed than would cocurrent flow. Consequently, dissolver types 1 and 3 would maintain a higher overall reaction rate per unit wetted surface area than would type 2.

Types 1 and 3 also offer better feed distribution than type 2. In both of the type 2 operational types, the liquid feed enters the column at the point of highest gas rate. To avoid severe entrainment problems, the liquid must flow onto the top of the packed bed at points of low local gas velocity, such as down the wall of dissolver or down the outside of a slug addition tube. By contrast, the feed to a trickle dissolver of type 1 may be sprayed onto the surface and the feed to a type 3 flooded dissolver enters the reaction zone uniformly over the entire cross section from a liquid pocket.

Finally, entrainment, which results in more backmixing in the dissolver types with countercurrent than with cocurrent gas and liquid flow, also imposes lower flooding rates on these types. Thus, the cocurrent types have a potentially higher ultimate capacity per unit column volume.

Comparison of types 1 and 3 indicates the possible advantages of each. Type 3, the upflow flooded dissolver, operates with a higher density in the fluid phase (i.e., the liquid holdup during column operation is larger in the flooded than in the trickle dissolver). Therefore at any instant the total area of the column "packing" that is wet by dissolvent in a flooded dissolver of type 3 is probably larger than that in a type 1 dissolver.

The distribution of total solids area and dissolvent strength within the two cocurrent types is also important in the determination of dissolver capacity. As packed solid fuel elements dissolve (assuming a uniform surface attack), the packed density increases, with a corresponding decrease in void fraction. Since the movement of fuel elements is from top to bottom, the total area per unit column volume should increase steadily down the column and become very large at the bottom of the dissolver.

At first glance it might appear that there would be an advantage to operation of a column with a countercurrent flow of area and dissolvent concentration. That is, the strongest dissolvent would enter the dissolver at the point of minimum area per unit column volume, and, as the dissolvent strength decreased, the reaction rate per

unit volume would be maintained by an increase in reaction area. Thus the gas evolution rate per unit volume would not change as much in a type 1 trickle dissolver as in a type 3 flooded dissolver.

However, the overall reaction rate in dissolver types 1 and 3 depends on the product of the wetted area and dissolvent strength as a function of position in the column integrated over the column length. Owing to the complicated hydrodynamics of the continuous column dissolver, the distribution of wetted area and dissolver strength can only be determined experimentally in a full-scale model and then only indirectly.

4.0 EXPERIMENTAL PROCEDURE

The trickle dissolver used in carrying out the experimental work was a vertically mounted 5.5-in.-i.d. column, 10 ft 8 in. high (see Appendix I for complete description of all items of equipment and procedure). Uranium-aluminum alloy slugs were loaded into the column as needed from the top so as to maintain a full dissolver during all but the final two tests (see stream A of equipment flowsheet, Fig. 4.1). During the final two tests, slugs were added at a pre-set rate, and the packed height was allowed to seek its own level.

The dissolvent, 4-8 M HNO_3 containing 0.005 M $Hg(NO_3)_2$, was fed to the dissolver at the top of the column of slugs (stream B). This acid was heated to 90-95°C before it entered the dissolver. No attempt was made to contain a definite quantity of dissolvent in the column by liquid-level control. The acid trickled over the slugs in much the same manner as the absorbent in a packed absorption tower trickles over the packing, i.e., gas phase continuous. The acid feed rate was maintained constant during any one test but was varied over the range 0.1-7 liters/min during the program. As the acid passed down the tower, it reacted with the uranium-aluminum alloy slugs, transferring these elements into solution. The acid, containing aluminum and uranyl nitrates, emerged from the bottom of the column as the dissolver product stream (stream D).

As the reaction proceeded, gases were formed by the decomposition of nitric acid, giving from 0.3 to 3.0 moles of nitrogen-bearing gases per mole of aluminum dissolved plus a small amount of hydrogen. The reaction was exothermic to the extent of approximately 200 kcal/mole of aluminum dissolved. This heat for the most part was removed from the dissolver as steam. The combined gas stream, steam plus nitrogen oxides, left the dissolver at one of three points---the top, center, or bottom of the reaction zone---and was transferred to the top of a downdraft condenser (stream E).

The location of the dissolver off-gas removal point determined the maximum dissolution rates that could be produced in the dissolver due to the variation in flooding rates with the position of the off-gas removal point. With the removal point at the top, the gas stream

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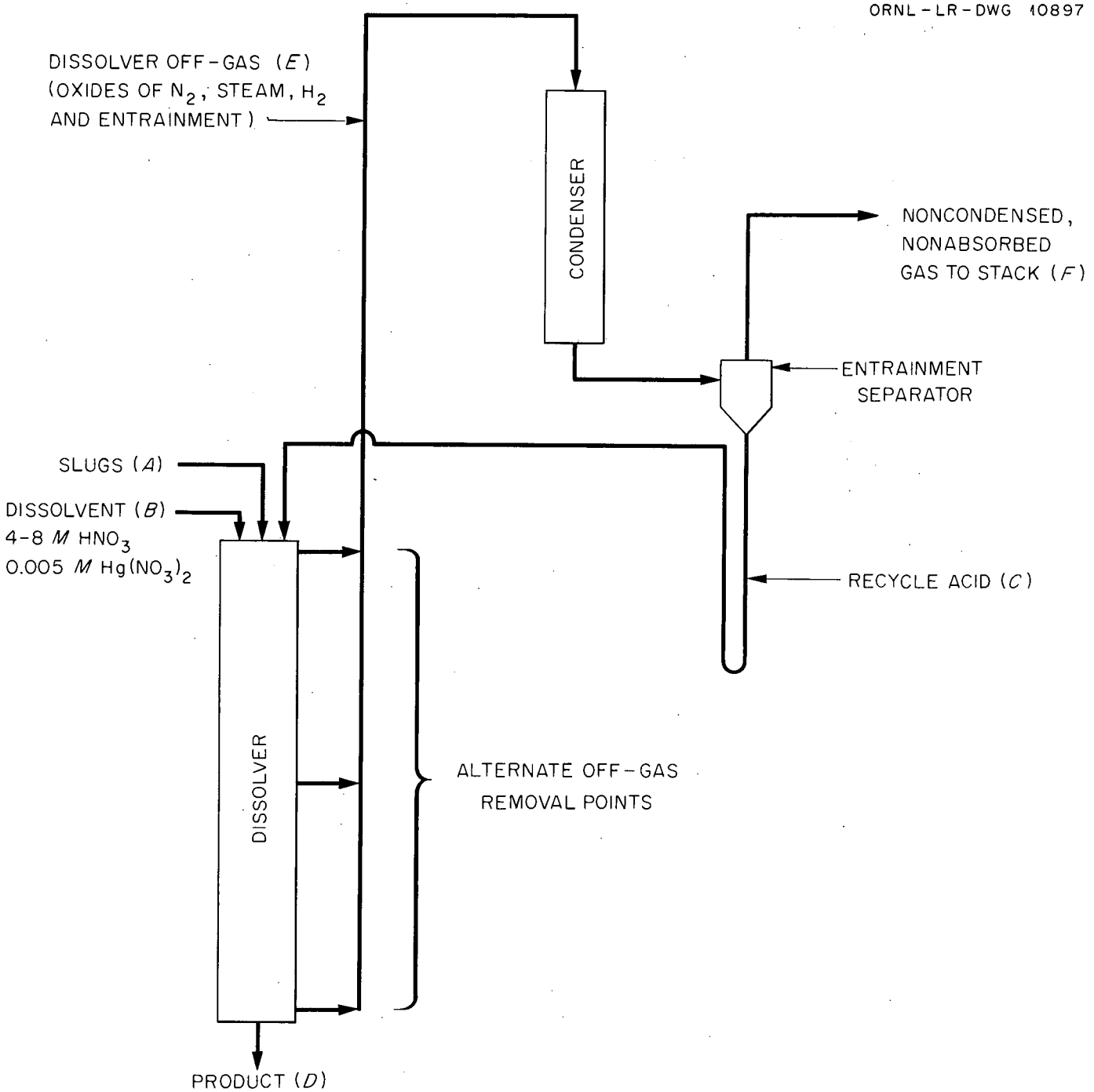

Fig. 4.1. Schematic Equipment Flowsheet of Experimental Trickle Type Dissolver.

flow was entirely countercurrent to the liquid stream, and consequently the flooding rate was very low. With the removal point at the midpoint, most of the gas flowed cocurrent to the liquid, and therefore a higher dissolution rate could be attained before flooding occurred (approximately a factor of 4 greater than with a top removal point). Flooding was never experienced with a bottom gas removal point. Approximately three-quarters of the runs were made with bottom gas removal (type 1 trickle dissolver).

As dissolution and gas rates became higher, entrainment of dissolver product in the gas stream became a problem. Intermixing of the product stream with the feed acid, which would result under these conditions, is not intolerable but is undesirable, since a definite concentration gradient from the top of the column to the bottom is needed for a good overall reaction rate. Change-of-direction entrainment separators were installed in the off-gas line, which allowed greater throughputs before entrainment became excessive. Even with these separators, however, entrainment was the factor limiting the dissolution rate. With more efficient separators, possibly of the cyclone type, higher dissolution rates could probably be obtained.

The gas stream from the dissolver was cooled in a downdraft condenser, with the condensed water vapor acting as an absorbent for the absorbable nitrogen oxides and the condensing surface as a falling film--wetted wall absorber. The combined streams of noncondensible gases and condensed-absorbed acid were separated by a small cyclone separator. The acid was recycled to the top of the dissolver without preheating (stream C), and the gases were vented from the system through the cell radioactive off-gas ducts (stream F).

During a run, hourly samples were taken of the dissolver product and occasional samples were taken of the recycle acid. The flow rate of the feed was measured by a rotameter, and the product rate was determined periodically by level changes in a collection tank.

Gas samples were taken from the dissolver off-gas line, but, since the dissolver was operated under a slight vacuum, air inleakage prevented the obtaining of representative samples.

A continuous measure of the dissolving rate was possible during most runs (with no additional steam heating) by measuring the flow rate and temperature change of the condenser cooling water. This method of control is discussed in detail in Sec. 10.6.5.

5.0 STABILITY OF DISSOLVER OPERATION

The stability of operation of a continuous column dissolver is affected by three factors: (1) entrainment, (2) channeling, and (3) variations of packing distribution. The first two factors are encountered in the operation of all types of packed columns with gas-

liquid contact; the third factor is peculiar to a packed column dissolver. Before quantitative interpretation of the trickle dissolver performance is possible, a qualitative discussion of the effect of dissolver stability on the reproducibility of operating data is desirable.

Instability in operation of a continuous dissolver is reflected by variations in the product concentration with time during a single run and by differences in average product concentrations between runs. During any one run, variation with time may not only be short-term random fluctuations about a mean value but also a gradual change in the position of the mean. Entrainment and channeling may result in short-term variations, while packing distribution changes may cause long-term changes. A combination of packing changes and channeling probably results in product concentration changes between runs.

5.1 Entrainment Effects

For the purposes of the following discussion, it will be assumed that the concentration of the liquid leaving a column dissolver as an entrained phase in a gas stream is the same as the concentration of the liquid in the dissolver at the point of exit. In 57 of the 78 runs made with the trickle-type dissolver, the off-gas was withdrawn at the bottom of the column. It will be assumed therefore that the entrainment concentration was that of the product during these 57 runs.

There are several opposing effects of entrainment in the acid condensate recycle. Fundamentally, the recycle of acid with a lower concentration than the feed to the top of a trickle dissolver would result in an overall decrease in the dissolution rate, by diluting the dissolvent and destroying the acid concentration gradient from the dissolver top to bottom. During runs with little or no entrainment in the recycle acid, the acid concentration in the recycle rarely exceeded 50% of the feed acid concentration and was often less than 10%. At the same time, the recycle acid flow rate averaged more than 50% of the feed flow rate and in one case actually exceeded it. The effect of dilution on the dissolvent is obvious.

Batch experiments have shown that a decrease in acidity and an increase in aluminum concentration in the dissolvent both decrease the dissolution rate of uranium-aluminum alloy.[2] Thus, entrainment may have two parallel effects: the dilution of recycle acid (with only four exceptions, product acidity was lower than recycle acidity) and the poisoning effect of aluminum recycle.

It might appear that recycle of entrainment-free acid would mean recycle of catalyst-free acid also. A very large decrease in dissolution rate might be expected due to the dilution of the mercuric nitrate catalyst concentration in the dissolvent at the top of the column if no entrainment occurred.

Actually, experiments with nitric acid dissolution of extruded

aluminum slugs in a trickle dissolver have shown* that the mercuric concentration in the recycle acid in the absence of entrainment exceeds the feed concentration (0.0069 compared with 0.005 M). Apparently, reduced mercury was recycled along with nitric acid as a result of steam distillation, and the increased catalyst concentration in the dissolvent compensated in part for the decreased acidity.

In addition to mercury recycle, one other effect tends to increase the dissolution rate as the result of acid recycle and entrainment. Liquid return to the column top increases the liquid throughput per unit volume of feed. There is, therefore, an increase in the wetted and reacting surface area in the column.

The result of the balance of the several effects of entrainment and condensate recycle (acid dilution, aluminum poisoning, mercury recycle, and flow increase) depends in part on the difference in concentration between the acid feed and product. The probable overall effect of entrainment alone is a decrease in the dissolving rate in a column with a bottom off-gas withdrawal. For runs made with a top off-gas withdrawal (11 runs), neither dissolvent dilution nor increased column throughput would result from entrainment. For center withdrawal (10 runs) the reaction in the top half of the column would be affected by both phenomena.

If the product concentration were to decrease for some reason, the effect of entrainment would be to return the concentration to a higher value. The decrease in product concentration would reduce the poisoning effect of the entrainment recycle and therefore increase the concentration. However, the system reaction would be delayed by the holdup time in the recycle loop, so a cycling operation might be induced. Under certain conditions the cycling might be so poorly damped that one perturbation would result in short-term variations over many multiples of the holdup time.

The effect of entrainment on dissolver stability may be minimized by suitable vapor-liquid disengaging at the point of off-gas removal.

5.2 Channeling

As in all packed-column operation with a continuous vapor phase, the slug packing in a trickle dissolver is more or less incompletely wetted, depending on the liquid volumetric throughput (feed plus recycle). As the dissolvent trickles over the packing, the flow paths change from time to time, but, on the average, at any cross section, certain regions will be more completely wetted than others.

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*The results of these experiments were reported in a weekly status report for Aug. 20, 1954, published as an internal memorandum, CF-54-8-164.

The effect of channeling on a trickle dissolver was graphically illustrated when, after 1375 slugs had been charged to the dissolver (during the first 43 runs), the remaining slugs were taken from the column. They were arranged according to the level at which they were found, and photographed (see Fig. 5.1). As would be expected, there was a general trend of a decrease in slug size from top to bottom, but at any level there was a large variation in slug size and shape. This size distribution was particularly noticeable at the lower end of the dissolver column (see Fig. 5.2). Some slugs apparently moved from the top of the column to quite near the bottom with little chemical attack.

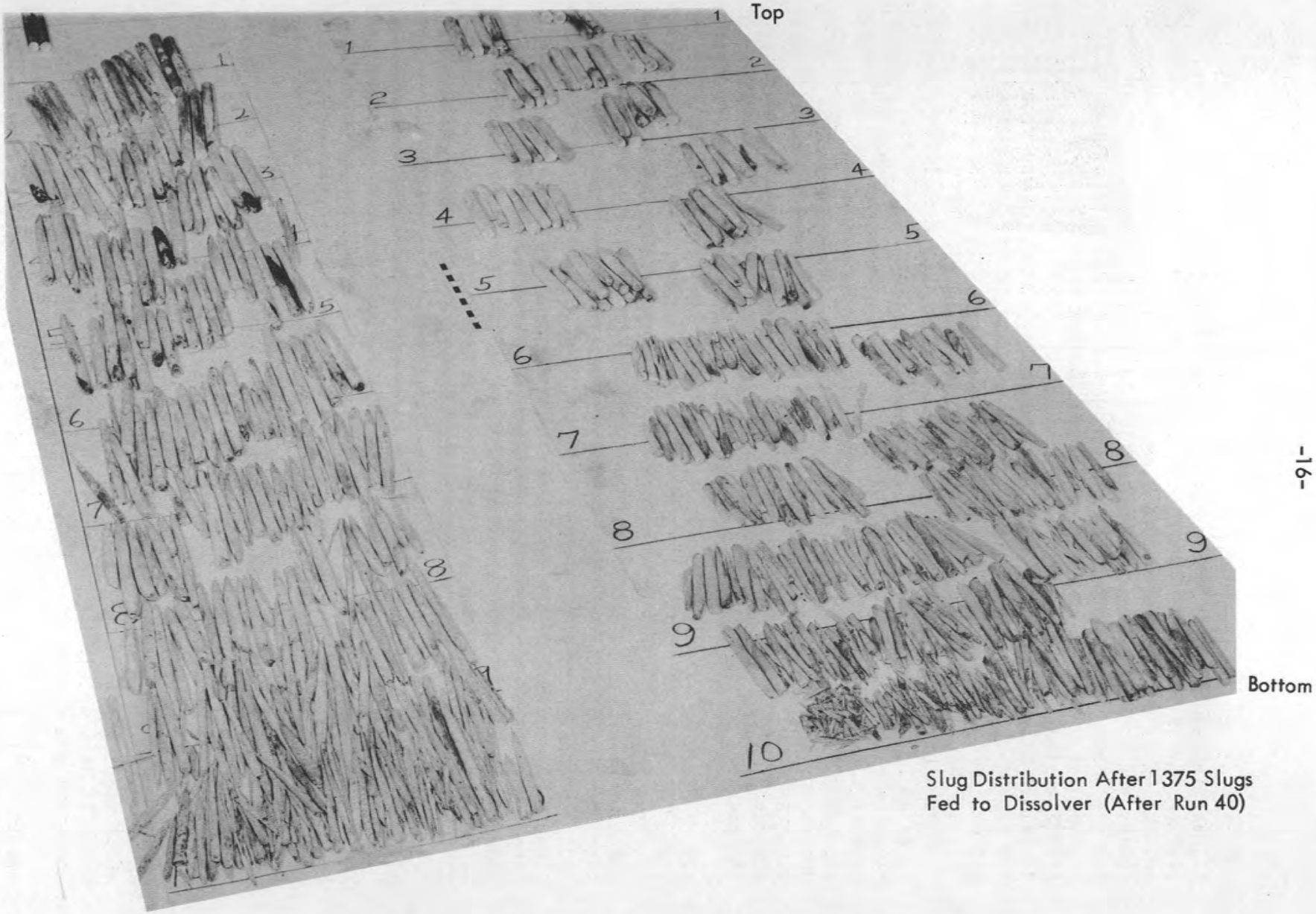
If a stream of dissolvent were to pass over more such large slugs at any time while flowing through the dissolver, the total reaction area would be lower than for flow over smaller slugs. The product aluminum concentration would decrease correspondingly. On the assumption that such random fluctuations in flow paths occur during any one run in the trickle dissolver, random concentration variations would be expected. If the average flow paths for two supposedly identical runs are different, product concentration differences would be expected for the same reason.

5.3 Variations in Packing Distribution

The slugs pictured in Figs. 5.1 and 5.2 were weighed and measured, and the approximate surface area per unit packing weight was calculated for ten regions at 1-ft intervals (see Table 5.1). The results indicated that, after 1375 slugs had been fed to the dissolver and after a 38-hr run had just been completed (run CA-40), the total surface area in the column was approximately twice that for the initial charge. It is interesting to note that there had been very little change in the total weight of slug metal present. It appears likely that the total percentage voids in the column (approximately 60%) did not change appreciably during the runs.

It is obvious that the same acid fed to a newly packed column would produce a different product from that with the distribution shown in Table 5.1. Depending on the time required to reach a steady-state packing distribution, the product might change during the first few runs after initial charging. In addition, if the steady-state packing distribution changed with the dissolving rate or acid molarity, product changes at the beginning of each new run might be expected.

Most runs after run 37 were made for 2 hr or less, before conditions were changed (see Table 13.1, Appendix 4). Only if the steady-state packing distribution for all runs was approximately the same would it be possible to achieve the steady operating conditions of a long-term run during short runs. Run CA-40 was made after eight such short runs had been completed. As was mentioned earlier, this run lasted 38 hr. As an indication that the operating data from



Slug Distribution After 1375 Slugs
Fed to Dissolver (After Run 40)

Fig. 5.1. Dissolver Slug Packing at Various Positions in Column.

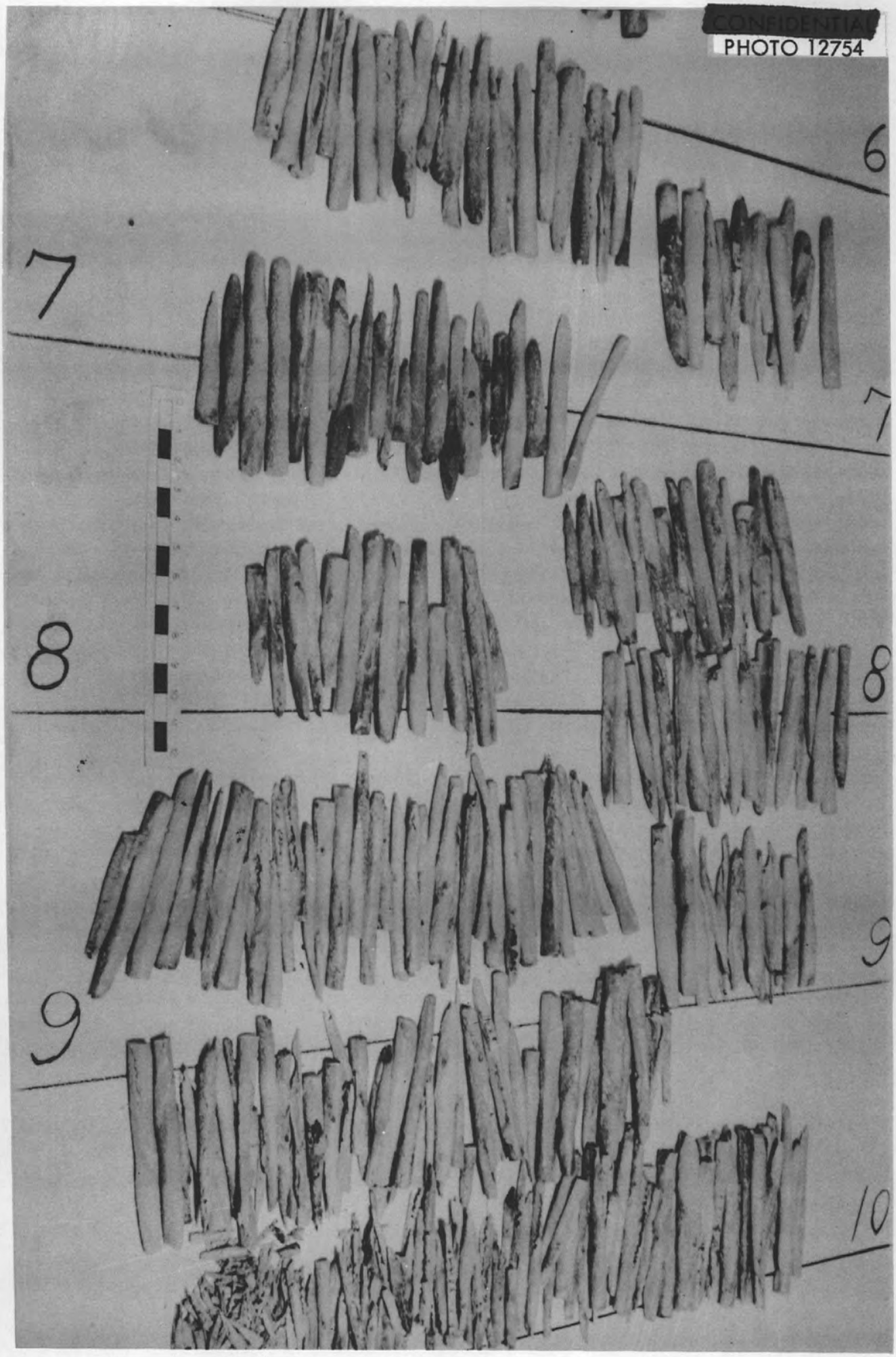


Fig. 5.2. Dissolver Slug Packing in Lower End of Column.

Table 5.1. Approximate Slug Distribution in Dissolver after 1375 Slugs Had Been Charged

Depth from Dissolver Top (ft)	No. of Slug Pieces	Avg. Dimensions Length (in.)	Avg. Dimensions Diameter (in.)	Surface Area (in^2)	Weight (kg)	Area/Wt Ratio ($in.^2/kg$)
Original charge	80	8.00	1.50	3300	51.2	64.7
1	9	7.88	1.28	271	3.1	87.5
2	7	7.83	1.19	431	4.9	87.9
3	12	7.74	1.18	364	4.4	82.7
4	11	7.70	1.10	337	3.8	88.7
5	20	7.41	1.03	480	5.0	96.0
6	36	6.74	0.88	361	3.7	97.5
7	37	6.65	0.81	875	4.9	179
8	53	5.87	0.71	715	4.7	152
9	58	6.65	0.60	896	5.4	166
10	154	----	----	~ 1300	6.5	~ 200
Total	405	----	----	~ 6000	46.4	~130 (avg.)

short runs probably did represent long-term average dissolver performance, the following results are presented:

Feed acid concentration (M)	6.0
Average product aluminum concentration (M)	1.64
Maximum deviation of aluminum concentrations from mean (samples taken hourly) (M)	0.20
Average deviation of aluminum concentration from mean (M)	0.06
Average product free acid concentration (M)	0.28
Maximum deviation of free acid concentration from mean (samples taken hourly)(M)	0.40
Average deviation of free acid concentration from mean (M)	0.08

Note that from the point of view of concentration changes during the run, the maximum variation in product concentration and dissolution rate was 12%, while the maximum variation in acid consumption rate was approximately 7%. The average deviations were much lower, 3.7% and 1.5%, respectively.

In spite of the stability of dissolver operation during any single run, differences in channeling flow paths and packing variations were present from run to run. The result was that the reproducibility of the product concentration between runs was lower than within each run. An average concentration scatter of 20% was found between runs (see Sec. 6.0 for graphical product concentration correlations).

The original data for all runs showing hour-by-hour variations of the product concentrations as well as all other operating data are presented in ORNL Central Files memoranda 54-6-51 and 55-11-99.[3,4]

6.0 EFFECT OF ACID FEED ON DISSOLVER PRODUCT

A total of 78 runs were made in the trickle-type dissolver, 40 with cast slugs and 38 with extruded slugs. Aluminum dissolving rates from 6 to 230 kg/day were obtained for cast slugs and from 40 to 400 kg/day for extruded slugs.

The aluminum (and uranium) dissolution rates increased as the dissolvent flow rates increased, approximately as the 0.8 power of the acid rate in the case of the cast slugs and approximately linearly in the case of extruded slugs. The product aluminum (and uranium) concentration decreased as the 0.2 power of the acid rate in the case of cast slugs and was relatively independent of acid rate for

extruded slug dissolutions. The nitric acid dissolvent had a mercuric nitrate catalyst concentration of 0.005 M.

Specifications for the product of the dissolution of aluminum-enriched uranium alloy slugs, with Al/U atom ratios greater than 100, are usually written in terms of the aluminum concentrations. Similarly, the capacity of a dissolving operation for such enriched slugs is based on the rate of dissolution of aluminum, usually in kilograms of aluminum per day. Although the aluminum basis results in numerically convenient concentrations and dissolving rates, the most important reason for its selection is that the aluminum is the limiting dissolution reactant. Not only is the quantity of dissolvent (nitric acid) determined by the aluminum charge, but also the maximum product concentration is dictated solely by the solubility of the various aluminum hydroxy nitrates in the product.

It may be assumed that there is no selectivity in the nitric acid dissolution of uranium-aluminum alloys; that is, the relative dissolution rates are determined solely by the atom ratios. Therefore, throughout the following discussion, values reported for aluminum may be converted to the appropriate values for uranium by the atom ratio in the specific fuel element. For cast slugs the Al/U ratio was 108.5/1 and for extruded, 155/1.

6.1 Cast Slugs

6.1.1 Dissolution Rate

The aluminum dissolution rate increase with increasing acid feed rate was linear when the results were plotted on log-log paper, and a single straight line fit all the data from 40 runs with dissolvent acid concentrations ranging from 4 to 7 M (Fig. 6.1). The straight line represents the following equation:

$$D = 14.0\ a^{0.78} \qquad (1)$$

where D = aluminum dissolution rate, kg/day

a = acid feed rate, g-moles/min

Thus the dissolving rate increased approximately as the 0.8 power of the acid feed rate.

6.1.2 Product Concentration

The product aluminum concentration decreased as the acid feed rate increased (Fig. 6.2). The equation for calculation of the product aluminum concentration is derived from Eq. 1 and the product/feed volume ratio. For the 78 runs, with both cast and extruded slugs, the average ratio was 0.92; i.e., 100 liters of dissolvent resulted in 92 liters of product, the volume decrease being due to loss of gases from the dissolver condenser-absorber system. The

[redacted]

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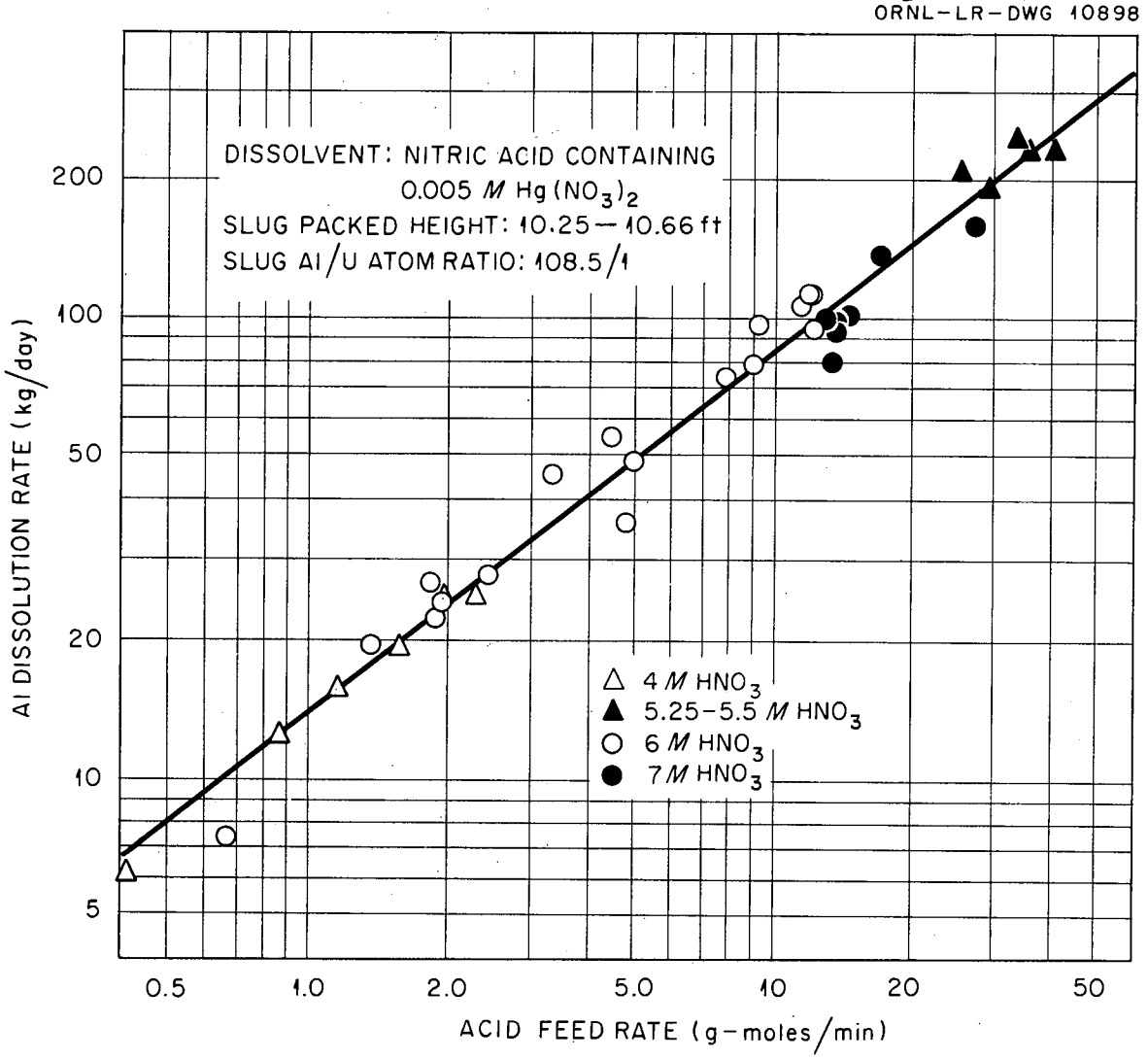

Fig. 6.1. Effect of Acid Feed Rate on Dissolution Rate of Aluminum in Cast Uranium—Aluminum Alloy Slugs.

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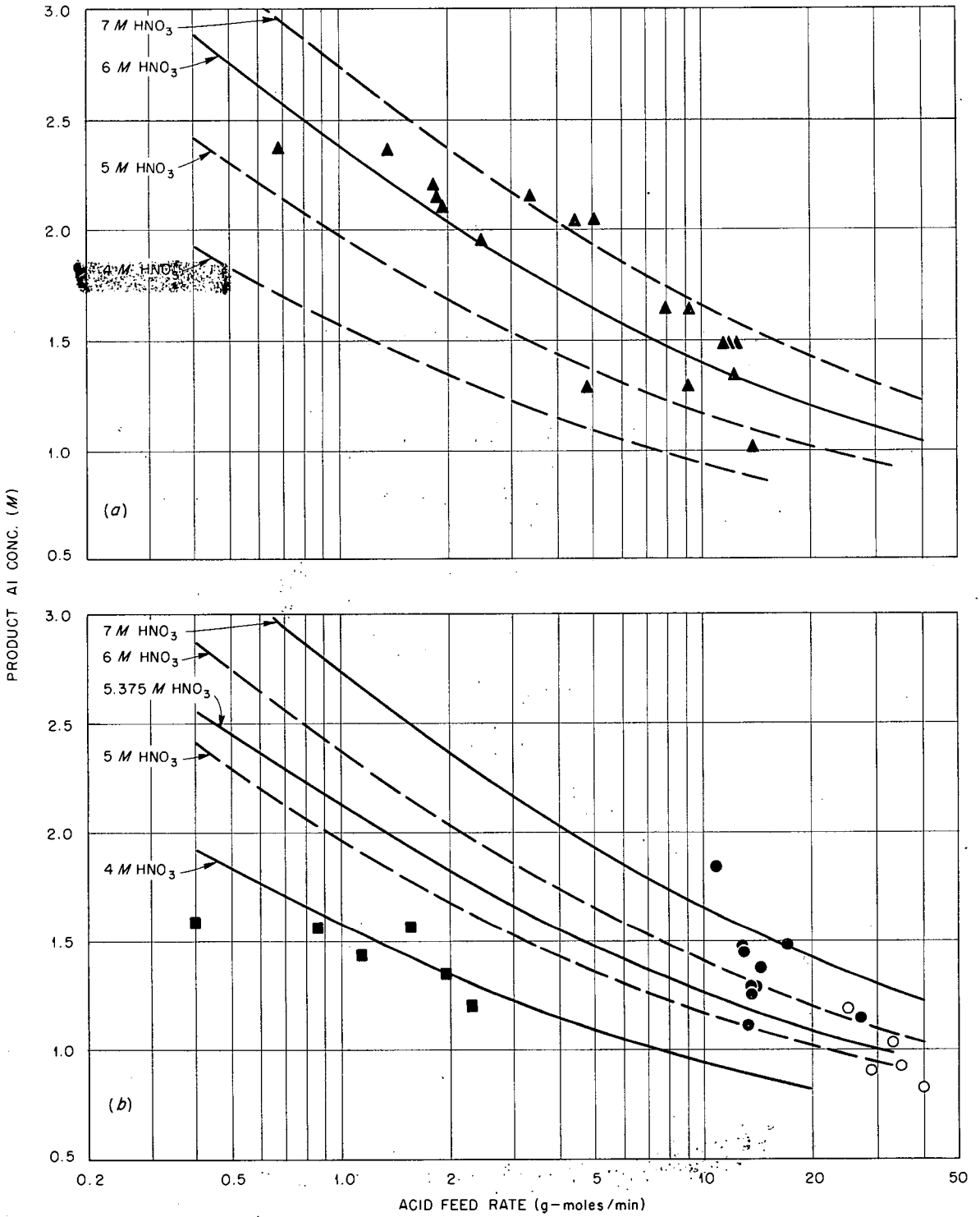

DISSOLVENT: HNO_3 CONTAINING 0.005 *M* $Hg(NO_3)_2$
SLUG PACKED HEIGHT: 10.25 – 10.66 ft
SLUG Al/U ATOM RATIO: 108.5/1

● 7 *M* HNO_3 ○ 5.25, 5.5 *M* HNO_3
▲ 6 *M* HNO_3 ■ 4 *M* HNO_3

NOTE: LINES CALCULATED FROM EQ. 5; SOLID LINES ARE FOR POINTS PLOTTED; DOTTED LINES INCLUDED FOR COMPARISON.

Fig. 6.2. Effect of Acid Feed Rate on Aluminum Concentration in Product from Dissolution of Cast Uranium — Aluminum Alloy Slugs.

equation is derived as follows:

$$a = FM \tag{2}$$

$$D = PA \times \frac{27 \text{ g/g mole} \times 1440 \text{ min/day}}{100 \text{ g/kg}} = 38.9 \text{ PA} \tag{3}$$

where F = dissolvent feed rate, liters/min

M = dissolvent acid concentration, M

P = product rate, liters/min

A = product aluminum concentration, M

Substitution of the above value for D in Eq. 1 gives

$$38.9 \text{ PA} = 14.0 \text{ a}^{0.78} \tag{4}$$

Since P = 0.92 F,

$$38.9 \text{ (0.92 a/M) A} = 14.0 \text{ a}^{0.78}$$

$$A = 0.391 \text{ M/a}^{0.22} \tag{5}$$

From the data in Fig. 6.1, it may be seen that only the runs made with 6 M HNO_3 feed covered essentially the entire range of acid feed rates studied, and, for the sake of clarity, the data for these runs are presented separately in Fig. 6.2 a. The data scatter along a band roughly bounded by the 5 M and 7 M lines, with an average variation in product concentrations of approximately 20%. The data for 21 of the 22 runs made with dissolvent acidities other than 6 M also lie within 20% of the predicted values of product concentrations (Fig. 6.2 b). Thus it should be possible to predict within 20% the product concentration for cast slug dissolution at a constant packed bed height over the range of acid feed concentrations studied.

The line for a feed of 5.375 M HNO_3 is also shown to allow a comparison of the predicted product concentration as a function of acid feed rate for 5.25 and 5.5 M HNO_3 dissolvent. The runs at 5.25, 5.5, and 7 M acid feed were made over narrow ranges of acid feed rates (25-40 and 10-27 g-moles/min, respectively). Numerically, the range was very much narrower for the 4 M runs (0.4-2.3 g-moles/min) but on a per cent variation basis, of course, the range actually is larger than in the runs with higher concentration acid.

It should be pointed out that the fact that the product concentration data follow the predicted curve fairly well in Fig. 6.2 is in no way a triumph of a theoretical analysis of the dissolver operation but rather a necessary result of an empirical analysis. Equation 3 was used to calculate the dissolving rate data presented in Fig. 6.1. Conversion of the data to the form shown in Fig. 6.2, by Eq. 5, required only the simplifying assumption inherent in Eq. 4, i.e., P/F = 0.92. The only purpose of the presentation in Fig. 6.2

is to show the scatter of concentration data due to variations between runs in the operation of the trickle-type dissolver.

6.2 Extruded Slugs

6.2.1 Dissolution Rate

The effect of acid feed rate on the aluminum dissolution rate was greater with extruded than with cast slugs. In addition, the data for 31 runs with dissolvent nitric acid concentrations of 4, 6, 6.5, and 7 M were correlated by three parallel straight lines on log-log graph paper (Fig. 6.3 a) rather than by a single line as in cast slug dissolution. Results of seven runs with 8 M HNO_3 were sufficiently dissimilar that no conclusions could be drawn (Fig. 6.3 b).

The equations are of the general form

$$D = Ka^n \tag{6}$$

For 4 M HNO_3 $\quad D = 17.6\ a^{0.98}$

For 6 M HNO_3 $\quad D = 14.2\ a^{0.98}$

For 6.5-7 M HNO_3 $\quad D = 10.2\ a^{1.0}$

During run series 46, three runs were made at a feed acid concentration of 8 M HNO_3. The run conditions were duplicated in run series 49, during which four runs were made. The effect of acid feed rate on dissolving rate was different for the two series. In each case, a straight-line correlation was obtained on log-log graph paper, but the equations representing the two series differed markedly. The two equations are

For 8 M HNO_3 $\quad D = 13.4\ a^{1.0}$ (Run series 46)

$\quad D = 17.2\ a^{0.83}$ (Run series 49)

6.2.2 Product Concentration

Following the procedure outlined in Sec. 6.1, equations of the type

$$A = K'N/a^{(1-n)} \tag{7}$$

(where K' is a constant) may be derived which predict the effect of acid feed rate on product aluminum concentration at various feed acidities. It is obvious from the form of Eq. 7 that A must be quite insensitive to changes in a for values of n near unity.

For 4 M HNO_3 $\quad A = 1.97/a^{0.02}$

For 6 M HNO_3 $\quad A = 2.27/a^{0.02}$

[redacted]

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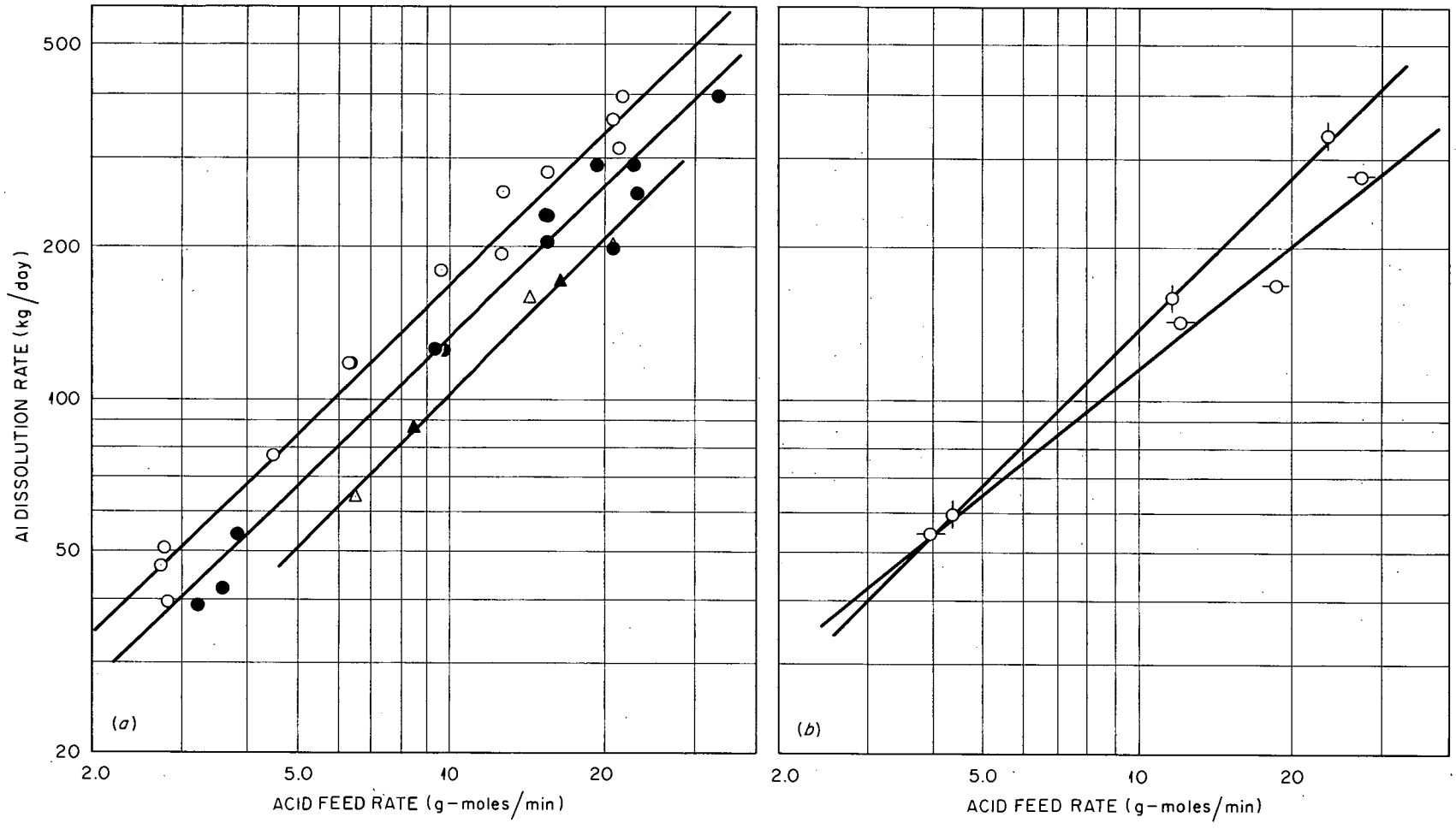

○ 4 *M* HNO_3 DISSOLVENT
● 6 *M* HNO_3 DISSOLVENT
▲ 6.5 *M* HNO_3 DISSOLVENT
△ 7 *M* HNO_3 DISSOLVENT
8 *M* ACID FEED, RUN SERIES 46
8 *M* ACID FEED, RUN SERIES 49

DISSOLVENT: NITRIC ACID CONTAINING 0.005 *M* $Hg(NO_3)_2$
SLUG PACKED HEIGHT: 6.5 *M* ACID — 5.3, 7.5 ft
ALL OTHER CONCENTRATIONS, 10.25 — 10.66 ft
SLUG ATOM RATIO Al/U = 155/1

Fig. 6.3. Effect of Acid Feed Rate on Dissolution Rate of Aluminum in Extruded Uranium — Aluminum Alloy Slugs. (*a*) 4–7 *M* HNO_3 Dissolvent; (*b*) 8 *M* HNO_3 Dissolvent.

For 6.75 M HNO_3 $\quad A = 1.95$

Plots of these equations were compared with the experimental data and the range of scatter around the predicted lines was again approximately 20% for 4-7 M HNO_3 (Fig. 6.4 a-c).

Prediction of the product concentrations changes with acid feed rate for the runs with 8 M HNO_3 resulted in the equations

For 8 M HNO_3 $\quad A = 3.05$ (Run series 46)

$$A = 3.84/a^{0.17} \text{ (Run series 49)}$$

The experimental data for the two series with 8 M HNO_3 check the predicted lines within 10%. No explanation is offered for the differences noted (Fig. 6.4 d).

The two runs made at 6.5 M HNO_3 differed from all others in that the packed heights in the dissolver were less than the 10.25-10.66 ft used in the remaining runs (76 of 78 runs —both with cast and extruded slugs —were made with approximately 10.5 ft of packed bed). The run with an acid feed rate of 16.5 g-moles/min was made with a packed height of 7.5 ft, while the run at 8.5 g-moles/min was with a height of 5.3 ft. It is interesting to note that the data taken at these lower packed heights correlate quite well with those at 7 M dissolvent acidity and a greater packed height.

6.3 Summary of Performance Equations

For convenience the equations relating dissolution rates and product concentrations to acid feed rates for the entire range of acid feed concentrations studies are listed below:

Cast Slugs: Equation No.

Dissolution Rate

$$D = 14.0\, a^{0.78} \qquad (1)$$

Product Aluminum Concentration

$$A = \frac{0.391\, N}{a^{0.22}} \qquad (5)$$

Extruded Slugs

Dissolution Rate (6)

$$4 \text{ M } HNO_3 \text{ dissolvent} = 17.6\, a^{0.98}$$

$$6 \text{ M } HNO_3 \text{ dissolvent} = 14.2\, a^{0.98}$$

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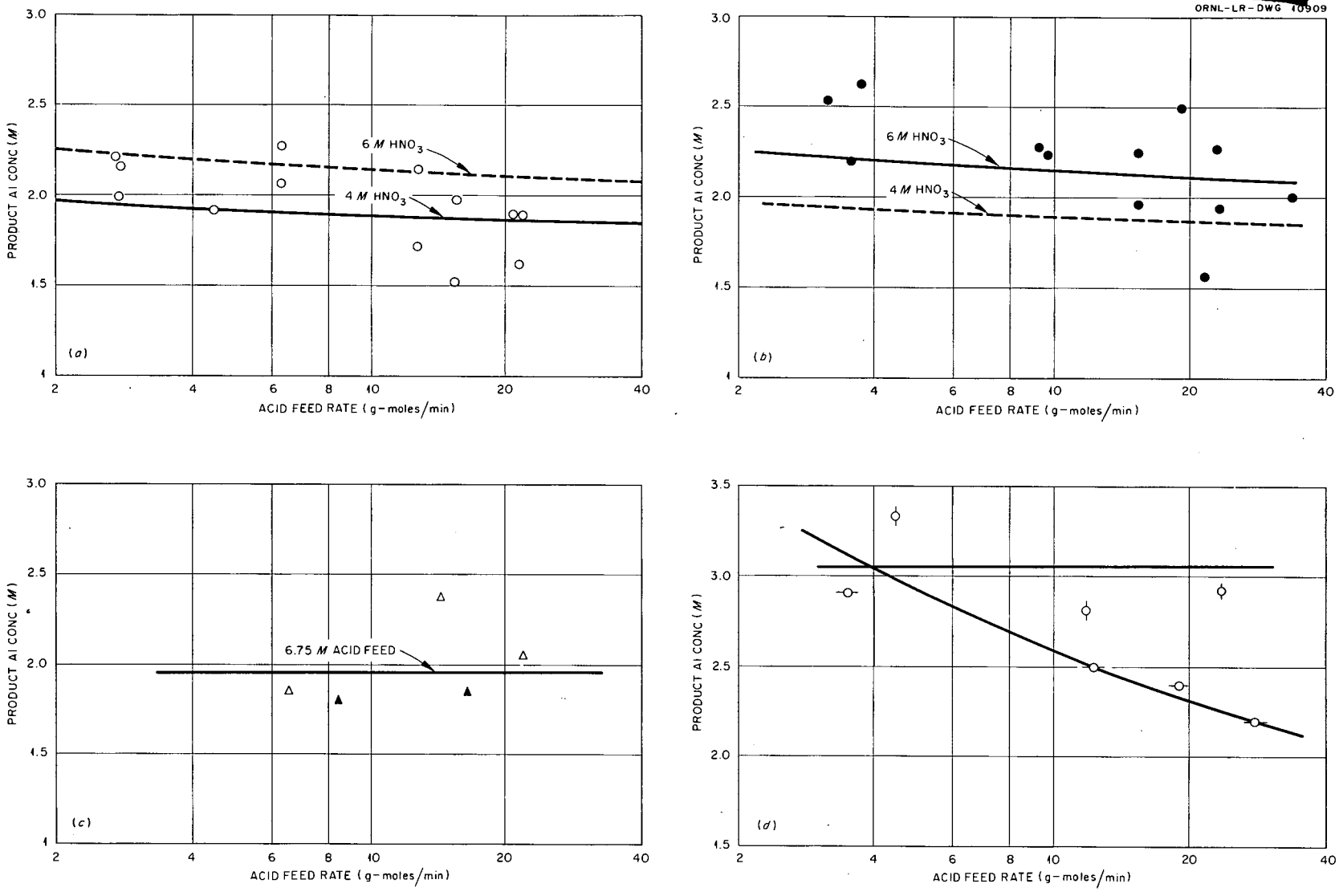

○ 4 M HNO_3 DISSOLVENT
● 6 M HNO_3 DISSOLVENT
▲ 6.5 M HNO_3 DISSOLVENT
△ 7.0 M HNO_3 DISSOLVENT
ϕ 8 M ACID FEED, RUN SERIES 46
-O- 8 M ACID FEED, RUN SERIES 49

DISSOLVENT: NITRIC ACID CONTAINING 0.005 M $Hg(NO_3)_2$
SLUG PACKED HEIGHT:
4, 6, 7, 8 M HNO_3 – 10.25 – 10.66 ft
6.5 M HNO_3 – 5.3, 7.5 ft
SLUG Al/U ATOM RATIO: 155/1

Fig. 6.4. Effect of Dissolvent Feed Rate on Aluminum Concentration in Product from Dissolution of Extruded Uranium-Aluminum Alloy Slugs. Lines calculated from appropriate equations. Solid lines for points plotted, broken lines for comparison.

6.5-7 M dissolvent $= 10.2\ a^{1.0}$

8 M dissolvent $= 13.4\ a^{1.0}$

$= 17.2\ a^{0.83}$

Product Aluminum Concentration (7)

4 M $A = 1.97/a^{0.02}$

6 M $A = 2.27/a^{0.02}$

6.75 M $A = 1.95$

8 M $A = 3.05$

$A = 3.84/a^{0.17}$

7.0 VARIATION OF ACID CONSUMPTION AND CONDENSATE RECYCLE WITH DISSOLVER PERFORMANCE

The acid consumption rate varied almost linearly with the aluminum dissolution rate. Over a range of aluminum dissolving rates from 5 to 400 kg/day, the acid consumption changed from 3.95 to 3.78 moles per mole of aluminum. For cast slugs, acid recycle rates correlated with dissolution rates regardless of dissolvent acid concentration, but with extruded slugs correlations were separate for the various acid concentrations. A much higher recycle ratio (moles of acid returned per mole of aluminum dissolved) was obtained for cast slug runs, showing that the average oxidation state of the off-gas was higher during cast than during extruded-slug dissolution.

This conclusion is consistent with the finding that, everything else being equal, extruded slugs dissolve faster than cast slugs[2] since a higher oxidation state in the dissolvent means a lower concentration of reduced mercury on the slug surface. The quantity of reduced mercury is an important factor determining the aluminum dissolution rate in nitric acid.

7.1 Acid Consumption

Two factors affect the moles of acid consumed per mole of aluminum dissolved: (1) the primary oxidation state of the product gases, and (2) the efficiency of recovery of fixed nitrogen from the product gas. In addition, the ratio of moles of acid fed per mole of aluminum dissolved is affected by the state of hydrolysis of the aluminum nitrate product. The distinction between the various factors and effects can best be shown by illustrations.

7.1.1 Primary Oxidation State Effects

Consider the various possible chemical reactions between aluminum and nitric acid in the presence of a mercury catalyst.[1] The reactions below are written in order of decreasing oxidation states of the gaseous products. The acid consumption ratios listed are based on the assumptions that there is no free acid in the product and no recovery of the fixed nitrogen in the off-gas.

	Equations	Mole Ratio of Acid Consumption to Metal Dissolved
(a)	$Al + 6HNO_3 \longrightarrow Al(NO_3)_3 + 3NO_2 + 3H_2O$	6/1
(b)	$Al + 4HNO_3 \longrightarrow Al(NO_3)_3 + NO + 2H_2O$	4/1
(c)	$8Al + 30HNO_3 \longrightarrow 8Al(NO_3)_3 + 3N_2O + 15H_2O$	3.75/1
(d)	$10Al + 36HNO_3 \longrightarrow 10Al(NO_3)_3 + 3N_2 + 18H_2O$	3.6/1
(e)	$2Al + 6HNO_3 \longrightarrow 2Al(NO_3) + 3H_2$	3/1

Note that for the production of the same liquid product (i.e., a product containing exactly 3 moles of nitrate per mole of aluminum) and with no acid recovery from the off-gas, the acid consumption per mole of aluminum decreases with a decrease in the oxidation state of the gaseous product. It should be pointed out here that all five of the gaseous products plus, of course, steam have been identified in the off-gas from the trickle-type dissolver during aluminum dissolutions.

7.1.2 Efficiency of Recovery

Consider now, as an example, Eq. a above. It will be rewritten taking into consideration the recovery of acid for return to the dissolver:

$$Al + 6HNO_3 \longrightarrow Al(NO_3)_3 + 3NO_2 + 3H_2O$$

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

$$\overline{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}$$

$$Al + 4HNO_3 \longrightarrow Al(NO_3)_3 + NO + 2H_2O$$

Obviously, the overall effect of recovery without nitric oxide oxidation is exactly the same in terms of acid consumption as if the primary gas products had been nitric oxide. If, on the other hand, air or oxygen is introduced into the off-gas line, then a sequence of oxidation and absorption reactions may take place:

$$Al + 4HNO_3 \longrightarrow Al(NO_3)_3 + NO + 2H_2O$$

$$NO + O_2 \longrightarrow NO_2$$

$$NO_2 + 1/3\ H_2O \longrightarrow 2/3\ HNO_3 + 1/3\ NO, \text{ etc.}$$

In the limit:

	Mole Ratio of Acid Consumption to Metal Dissolved
$4Al + 3O_2 + 12HNO_3 \longrightarrow 4Al(NO_3)_3 + 6H_2O$	3/1

Thus, the minimum ratio by complete absorption which can be achieved by reactions following Eqs. a and b is 3/1. The gaseous products from Eqs. c, d, and e are not recoverable by normal absorption techniques, so this same ratio represents the minimum consumption ratio for all conditions of operation.

7.1.3 State of Hydrolysis Effects

All the previous discussion has been based on the assumption that the dissolution product contains exactly 3 moles of nitrate per mole of dissolved aluminum. If more than 3 moles is present, there is necessarily free nitric acid present in the product, and a calculation of the acid consumption rate involves subtracting this quantity of free acid from the feed acid. But what of the situation when less than three nitrate ions per aluminum ion are present in the product?

Consider Eq. e. If the product is hydrolyzed, a series of reactions may occur in the dissolver which would seem to change the consumption ratio:

$$2Al + 6HNO_3 \longrightarrow 2Al(NO_3)_3 + 3H_2$$

$$2Al(NO_3)_3 + 2H_2O \longrightarrow 2AlOH(NO_3)_2 + 2HNO_3$$

$$2AlOH(NO_3)_2 + 2H_2O \longrightarrow 2Al(OH)_2NO_3 + 2HNO_3$$

$$\text{(f)} \qquad 2Al + 2HNO_3 + 4H_2O \longrightarrow 2Al(OH)_2NO_3 + 3H_2O$$

It might be presumed that the acid consumption ratio has been decreased from 3/1 to 1/1 by the hydrolysis of the product. The ratio of the feed acid rate to aluminum product rate has decreased by this amount. However, just as the case when positive free acid in the product must be allowed for in order to calculate the true consumption rate (note that feed rate exceeds consumption rate), the negative free acid must be taken into consideration. "Negative free acidity" is synonymous with "acid deficiency".

To place all calculations on a common basis, acid consumption is defined for an acid-deficient product as follows:

Acid consumption rate = acid feed rate - (free acidity in product x product rate)

where free acidity in product = nitrate molarity -3(aluminum molarity)

[if 3(Al molarity) > (NO_3^- molarity), free acidity ≡ acid deficiency]

and

acid consumption ratio = acid consumption rate/acid feed rate

The same definitions obviously apply equally to positive, negative, and zero free acid content in the product.

Applying the above definition of acid consumption ratio to Eq. f (Eq. e modified by aluminum hydrolysis);

$$\text{Acid consumption ratio} = \frac{2 - (2 - 6)}{2} = 3$$

In other words, the acid consumption rate is not affected by the possible hydrolysis of the aluminum product, nor is the acid consumption ratio.

The same calculations can be applied to all five equations listed earlier, modified by aluminum hydrolysis. In all cases, it can be shown that acid consumption rates are dependent only on off-gas oxidation states and acid recoveries.

It is interesting to note that, by the above definition of acid consumption rate, most of the runs with the trickle-type dissolver were made with acid consumption rates larger than acid feed rates.

7.1.4 Comparison of Acid Consumption of Cast and Extruded Slugs

No difference was found between runs made with cast slugs and extruded slugs in terms of acid consumption at various aluminum dissolution rates (see Fig. 7.1). A single straight line on log-log graph paper correlated the results from all runs. The equation for this line is

$$C = 3.87\, D_m^{0.99} \qquad (8)$$

where C = acid consumption rate, g-moles/min

D_m = aluminum dissolution rate, g-moles/min ($D_m = D/38.9$)

It may be seen from Eq. 8 that the ratio C/D_m (or acid consumption ratio) is only very slightly dependent on D_m over quite a wide range of dissolution rates. Values for the ratio as a function of D_m and D are shown in the tabulation on p. 33.

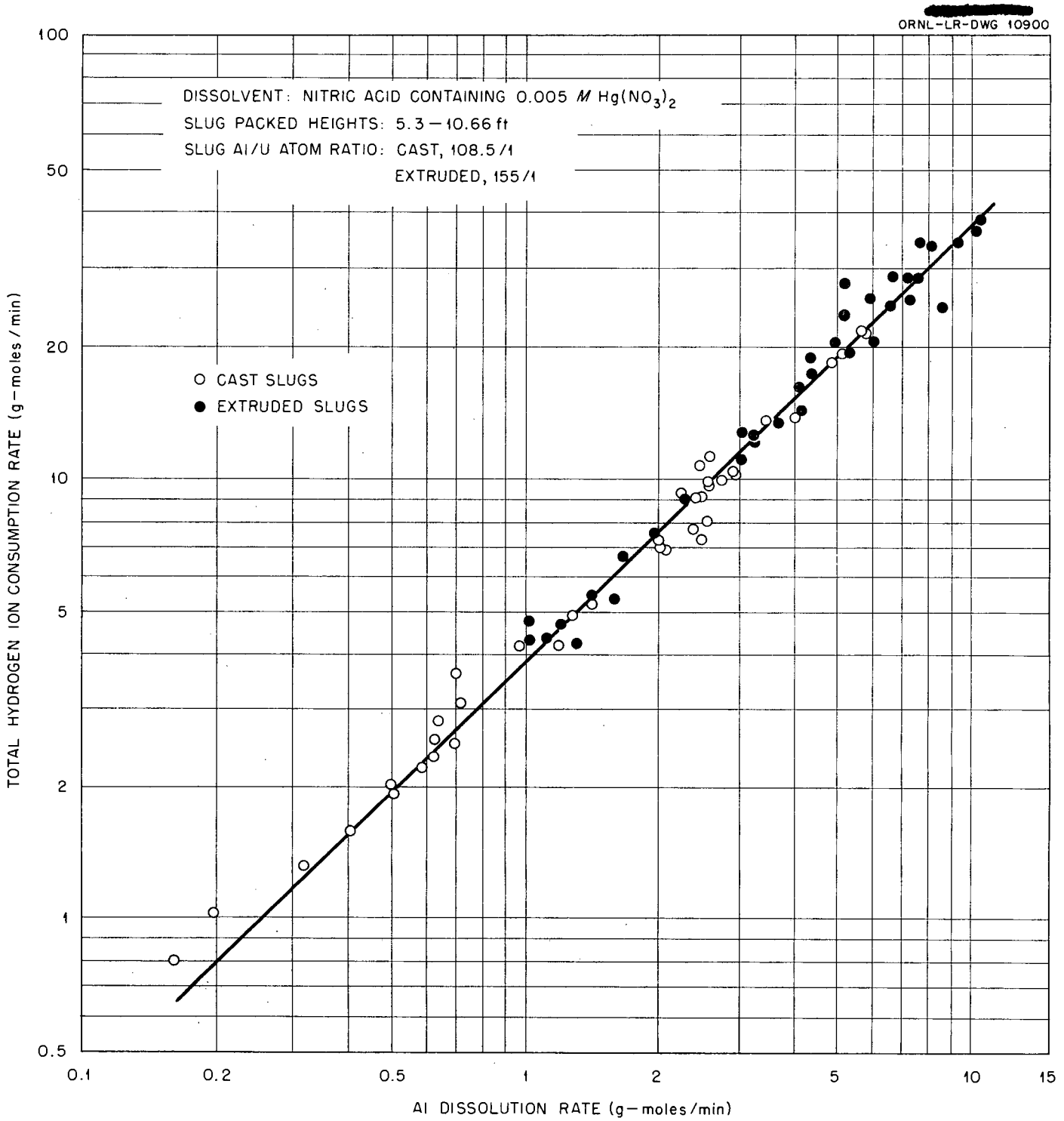

Fig. 7.1. Acid Consumption Rate as a Function of Aluminum Dissolution Rate.

D_m (g-moles/min)	D (kg/day)	C/D_m (moles/mole)
0.2	7.8	3.94
0.5	19.4	3.90
1.0	39	3.87
2.0	78	3.84
4.0	156	3.81
10	390	3.78
20	780	3.75

It is obvious that if primary oxidation states on the average were different in the off-gas from cast and extruded slug dissolutions, the absorption system was so efficient that no overall effect could be seen in the acid consumption ratios.

Although no representative off-gas samples were taken during the dissolver runs, and thus no experimental data are available to check the assumptions, it is interesting to speculate on the probable off-gas composition, based on the discussion in Sec. 7.1.1 and 7.1.2. It is probable that little hydrogen was produced during the dissolving runs, since the ratio would certainly be nearer 3 than it was found to be if appreciable quantities were in the off-gas. Further, if the off-gas consisted of mixtures of NO_2, NO, N_2O, and N_2 of any ratio, and if all the NO_2 were recovered by absorption without nitric oxide oxidation, then the acid consumption ratio necessarily would lie between 3.6 and 4.0.

7.2 Acid Recycle

Several times during each of the last 64 runs, samples were taken of the recycle acid returning to the dissolver from the downdraft condenser. There was sufficient instability in the off-gas system of the trickle-type dissolver operation that the condensate concentrations varied widely, sometimes as much as 1000%. It appeared that defining average operating conditions for the recycle system based on such data would be difficult.

The numerical averages of the operating conditions were used to calculate the rate of acid recycle in gram-moles of acid per minute due to off-gas absorption, taking into consideration the amount of entrainment which might be present. Comparison of the results with the corresponding aluminum dissolution rates gave a remarkably good correlation, considering the scatter of the original data.

It was again found, as had been the case with the effect of acid feed rates on dissolving rates, that the data for cast slugs correlated together, with no apparent effect of acid feed concentration. Again as before, the extruded slug data correlated as a series of curves, with the acid feed concentration as the parameter (see Figs. 7.2 and 7.3).

Best straight lines have been drawn through the data on log-log plots but it is not clear that the correlation should be linear (i.e., recycle rate proportional to dissolution rate raised to a power) in the case of the cast data and the data for extruded slugs with 4 and 6 M acid feed. On the other hand, the data for 7 and 8 M acid follow rather closely a straight line. Again, the operation of the dissolver with 6.5 M feed and a lower packed level was very similar to that with higher acidities and a normal (approximately 10.5 ft) packed level.

It was not felt that these correlations were sufficiently well defined to express as equations. However, if the correlations are nearly correct, it is possible to calculate the approximate effect of the dissolving rate on the acid recycle ratio (the ratio of acid return rate to aluminum dissolving rate)(see Fig. 7.4). Such a calculated effect can only be used to show the trends of the data. The most significant trend shown is the great difference in the recycle ratio between cast and extruded slug runs. The ratio is twice that for 7-8 M acid and more than four times that for 4 and 6 M acid.

The recycle ratio is indicative of the moles of absorbable off-gas produced per mole of aluminum dissolved. Referring again to the equations in Sec. 7.1.1, it is obvious that cast-slug dissolution produced an off-gas of a higher average oxidation state than did extruded slugs. Nitric oxide is only absorbable after oxidation, while 2/3 of all NO_2 molecules are immediately recoverable. The oxidation state of the off-gas is determined by the oxidation state of the liquid at the point of formation of the gas. It therefore appears that the average oxidation state of the dissolvent liquid during cast slug dissolution was higher than during extruded slug dissolution.

This conclusion is verified by the experimental fact that, at the same acid and catalyst concentrations, extruded slugs dissolve faster than cast slugs. Since the dissolution rate is proportional to the acid strength and the reduced mercury concentration on the surface, and since the reduced mercury concentration is a result of a balance between solution oxidation and surface reduction, the lower dissolution rate of cast slugs indicates a higher oxidation state of the dissolvent. It is interesting to note that even though the dissolution of aluminum and uranium involves the oxidation of these metals by the dissolvent, a high oxidation potential in the liquid phase is not a guarantee of a high dissolution rate.

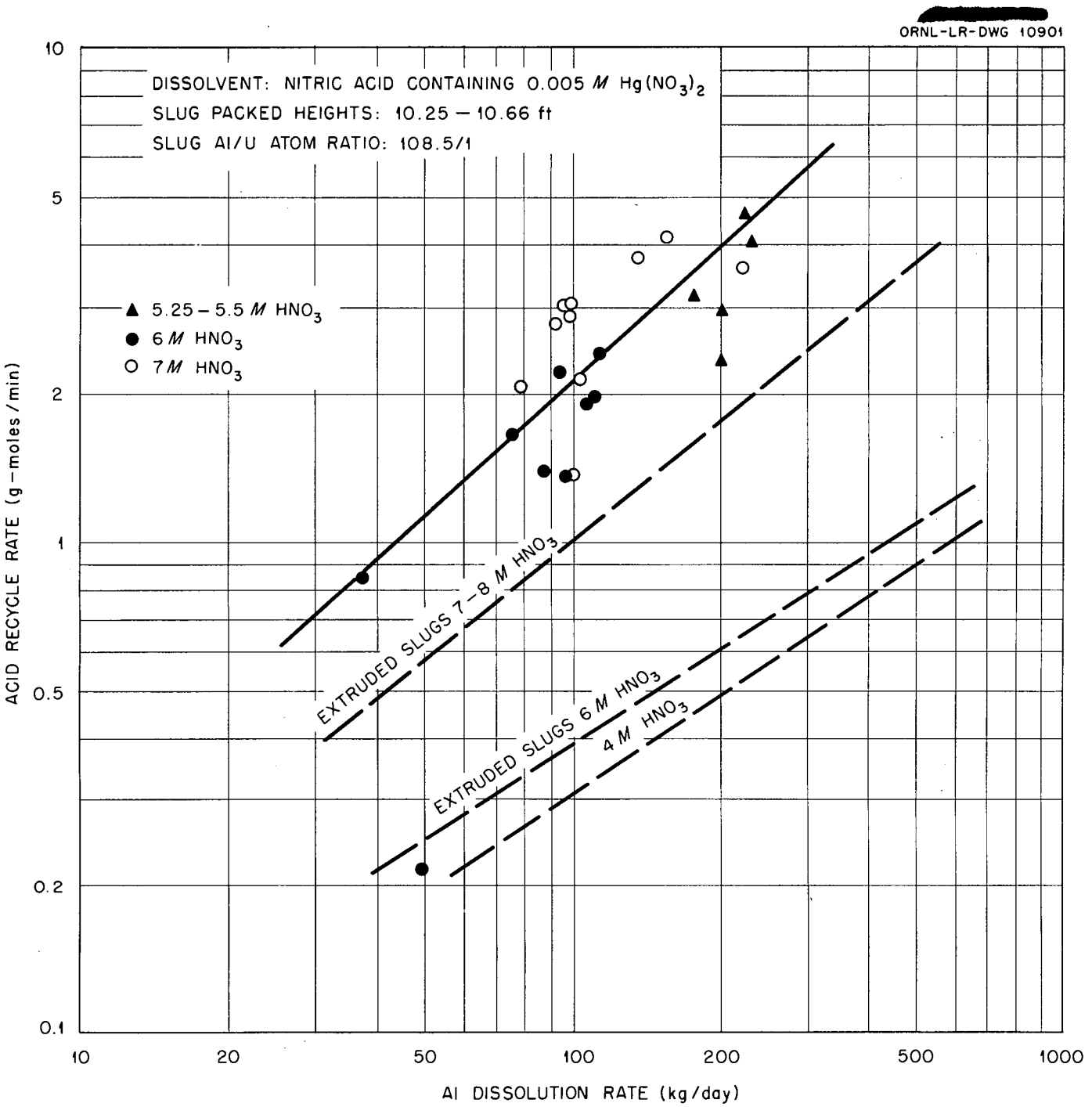

Fig. 7.2. Aluminum Dissolution Rate in Cast Slugs, as a Function of Acid Recycle Rate. Solid line drawn through data plotted, dashed lines for extruded slugs given for comparison.

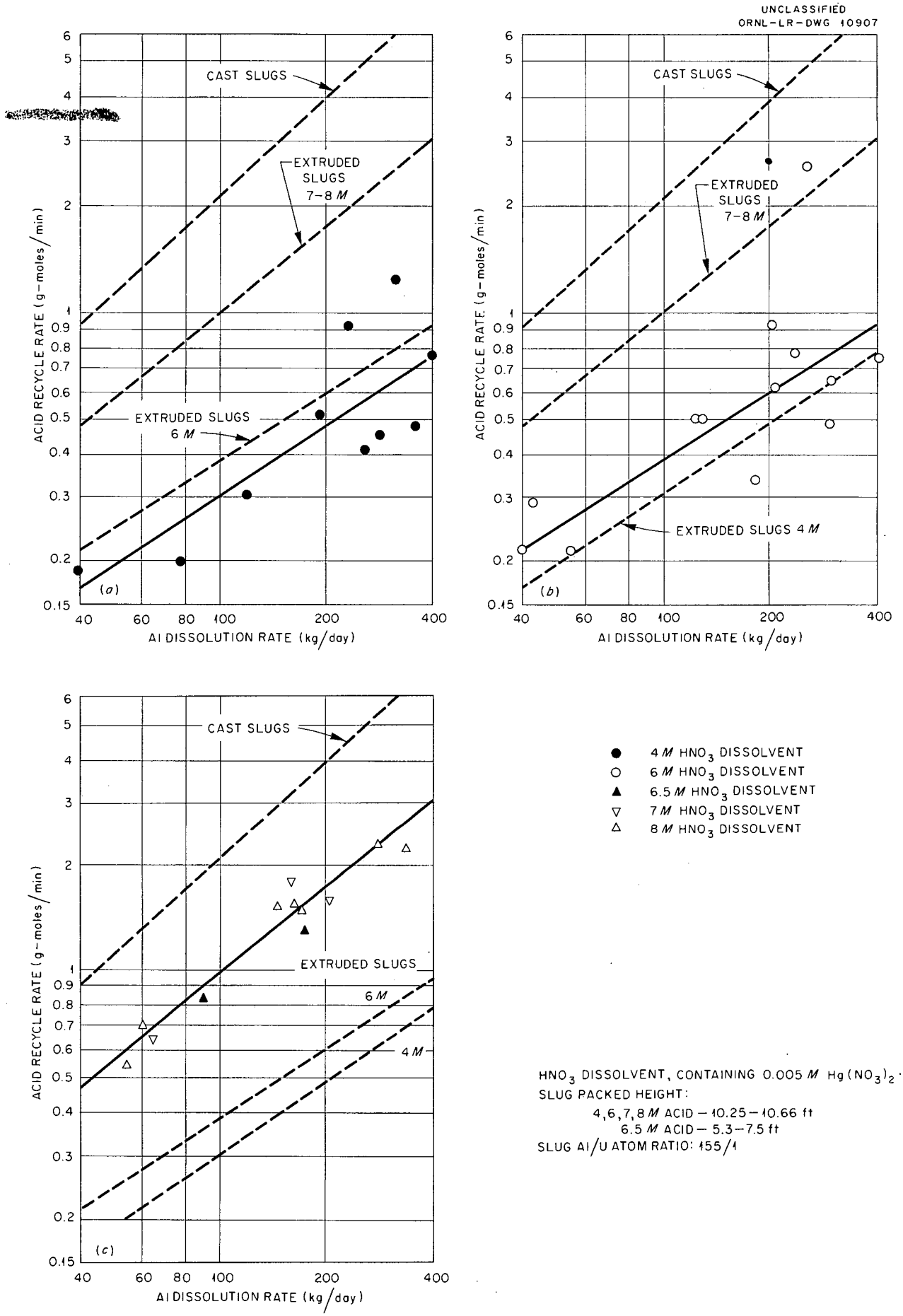

Fig. 7.3. Aluminum Dissolution Rate in Extruded Slugs as a Function of Acid Recycle Rate.

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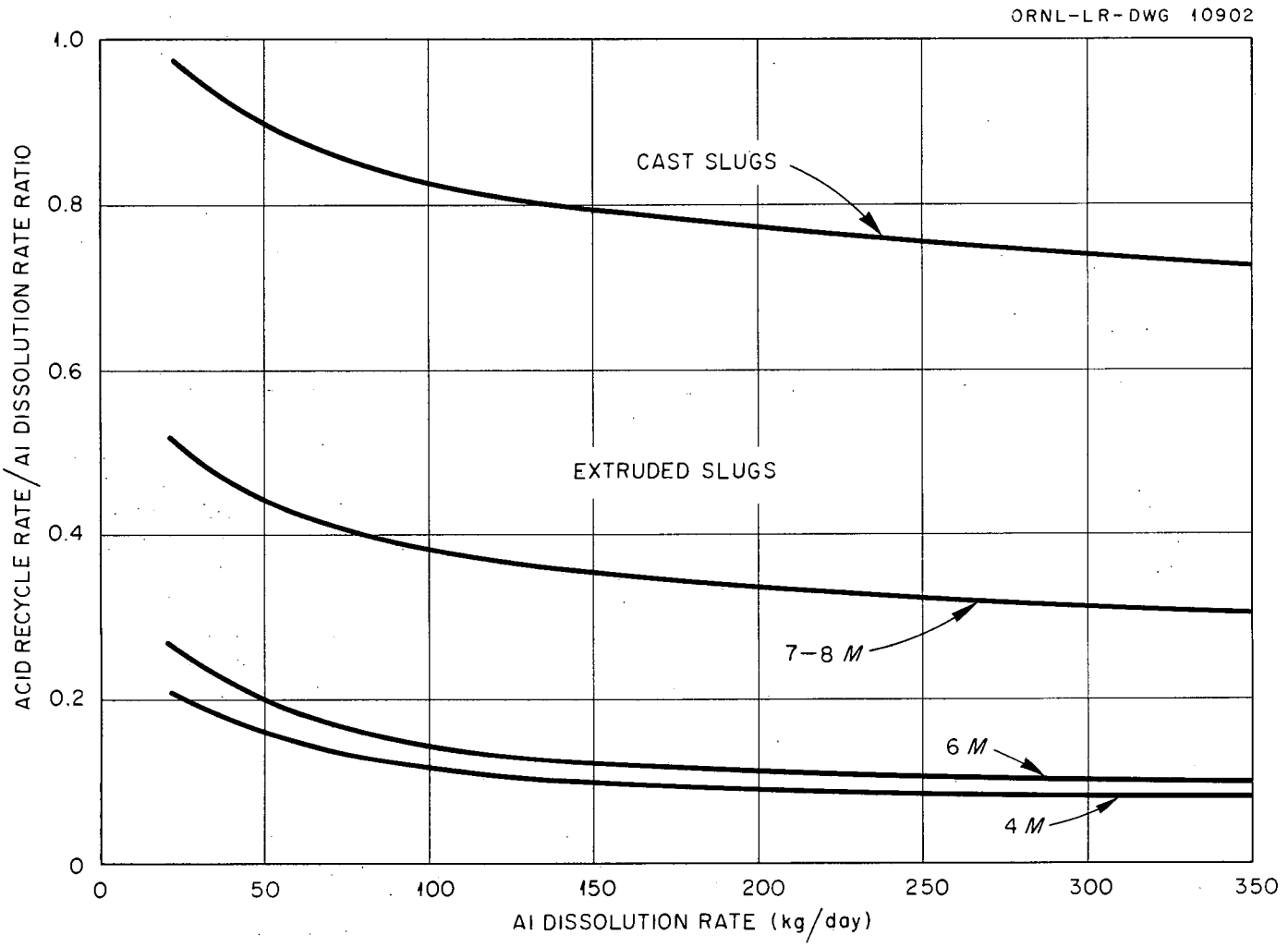

Fig. 7.4. Variation of Acid Recycle Ratio with Aluminum Dissolution Rate.

8.0 APPLICATIONS TO DESIGN CALCULATIONS

There are two important requirements that must be imposed on any dissolver: the product must be of the desired concentration and the dissolver capacity must be sufficient for the desired plant throughput.

8.1 Product Concentration

The product aluminum and acid concentrations necessarily are related by a simple mathematical formula (see Sec. 7.1.4). Assuming that C/D_m is constant and equal to 3.85, let

$$H = \text{free acidity in product, } \underline{M}$$

Then, using previously defined symbols, an acid balance may be written around the dissolver:

$$FM - PH = 3.85\ PA \tag{16}$$

But $P = 0.92\ F$; therefore

$$M/0.92 - H = 3.85\ A$$

$$H = 1.087\ M - 3.85\ A \tag{17}$$

An inconsistency is introduced by the use of the approximation $P = 0.92\ F$ since at zero dissolving rate ($A = 0$), the feed rate equals the product rate ($P = F$) and in Eq. 17, $H = M$, rather than $1.087\ M$. Therefore, in preparing the graphs, Eq. 17 was used with a correction at the limiting condition, $A = 0$. This defined the operating limits at $H = 0$, and H was set equal to M at $A = 0$. The result was a compromise between the approximation of $P = 0.92\ F$ and the boundary conditions. Graphs were prepared for both cast and extruded slug dissolution showing the relation between the product aluminum and the product free acidity concentrations (see Fig. 8.1, a and b). The graphs show the area covered by experimental work, using 4-7 $\underline{M}$ HNO_3 dissolvent. They are not intended to show the regions of operation predicted by concentration—dissolving rate correlations derived in Sec. 6.0.

The graphs also do not show the operating limits of the particular trickle-type dissolver studied. Consider the concentration range below 1 $\underline{M}$ aluminum in the product (a range not covered by the present experiments). For an example, assumed that 4 $\underline{M}$ HNO_3 is added to the dissolver at 4 liters/min. If at the same time cast uranium-aluminum alloy slugs are added at an average rate of 27 g/min, it is found that at steady state the product must be approximately 0.25 $\underline{M}$ in aluminum and 3 $\underline{M}$ in acid.

Notice that according to Fig. 6.1 the dissolving rate with a 10.25-10.67 ft packed height and 16 g-moles of acid per minute feed rate would be approximately 100 kg/day or 2.57 g-moles/min. Since the metal make-up rate is only 1 g-mole/min, the bed level would obviously decrease until the product of the average dissolving rate per

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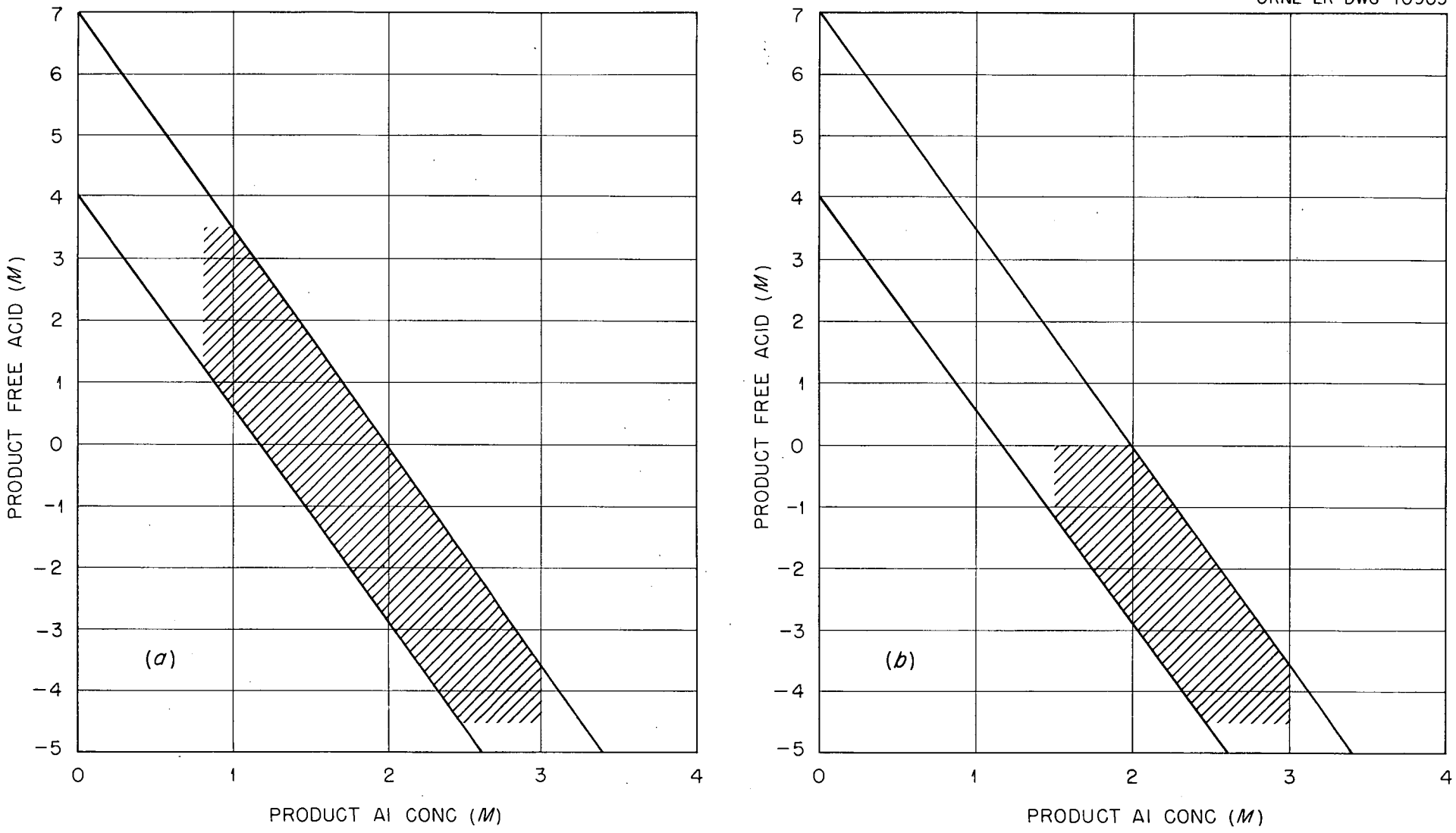

Fig. 8.1. Range of Product Concentration Variables Experimentally Determined. (*a*) Cast-slug dissolution; (*b*) extruded slug dissolution.

unit surface area and the total wetted area equaled 1 g-mole of aluminum per minute. The dissolver is obviously self-regulating, and measurements of dissolver performance with a completely packed bed define only upper limits to operating conditions. Aluminum concentrations (and dissolving rates) lower than those measured may be obtained at any feed rates and concentrations which were studied merely by decreasing the slug feed rates to the appropriate values.

During the final two runs, the dissolver was operated to demonstrate the principle of self-regulation of product concentration. The target product concentration was 1.8 M aluminum and -0.2 M free acid (0.2 M acid deficient). The assumption was made for the selection of feed conditions that the product/feed ratio was 1/1 and the acid consumption ratio was 4/1. Owing primarily to an error in the product/feed ratio, the final acid deficiency was somewhat larger than desired (0.4 M) but the product aluminum concentration was close to specifications (1.79 and 1.85 M). The runs, using 6.5 M acid feed, extended over 61 and 32 hr of continuous operation, respectively.

8.2 Range of Dissolver Capacity

Mathematical manipulation of the correlations of the dissolving rate and the product concentration with the acid feed rate will lead to a relation between the product rate and the product aluminum concentration at various values of the acid feed molarity. However, the final equations relating P and A are awkward. For this reason, the correlations have been plotted to show the predicted range of dissolver capacity over the dissolvent acid range of 4-7 M (see Fig. 8.2). These figures apply only for a fully packed dissolver (packed height approximately 10.5 ft). Also, the A vs. FM correlations resulted from data with approximately a 20% scatter. Consequently, some experimental data fall outside the shaded areas of the figures, to an extent shown by the product concentration ranges in Fig. 8.1.

The graphs show the wide range of aluminum product concentrations which can be achieved with cast- compared with extruded-slug dissolutions. Note also that only at very low product rates can product aluminum concentrations above 2 M be achieved with cast slugs. The narrow range of product concentration predicted for extruded-slug dissolving is a limiting condition for dissolver operation. As was discussed earlier, lower concentrations and dissolving rates can be obtained by allowing the packed level to decrease in the dissolver. Also, higher concentrations very likely would result from much lower acid feed rates than were employed during the extruded-slug runs.

8.3 Sample Design Calculation

Suppose it is necessary to use the continuous trickle dissolver to produce a product which is 1.5 M in aluminum and 0.5 M in free acid from cast slugs. Suppose, further, that the dissolver capacity is to be 100 kg of aluminum per day. Can the dissolver be operated

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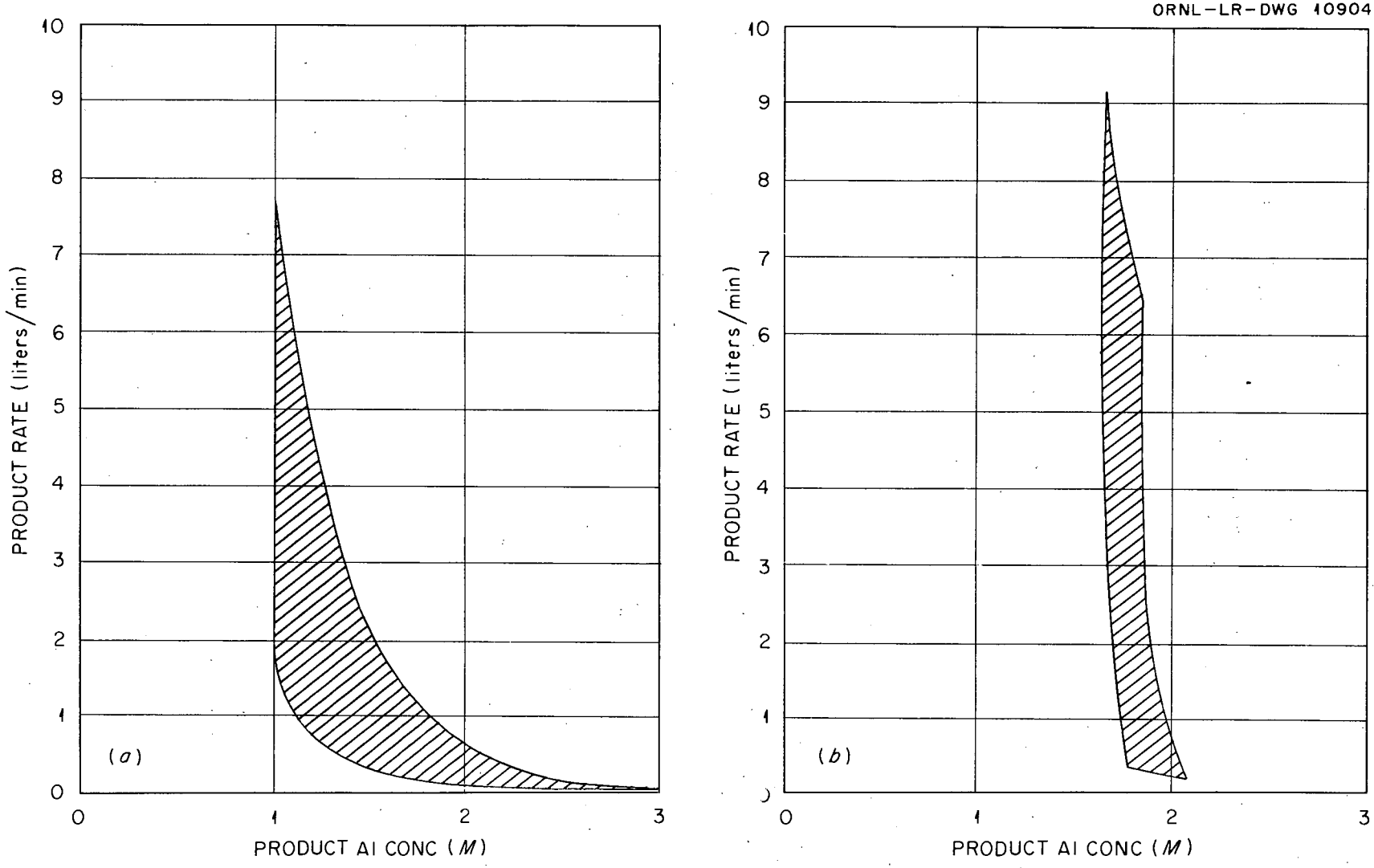

Fig. 8.2. Predicted Range of Dissolver Capacity. Packed Height: 10.25 - 10.67 ft. (*a*) Cast-slug dissolution; (*b*) extruded-slug dissolution.

under such conditions? And do the data and correlations from the present work allow a prediction of the dissolver performance?

From Fig. 8.1 it may be seen that the product concentrations specified lie in the range studied. At A = 1.5 M, a product acidity from approximately -1.0 to +1.75 M would be possible by varying the feed acidity from 4 to 7 M. The required feed acid concentration is calculated from Eq. 17:

$$0.5 = 1.087\ M - 3.85\ (1.5)$$

$$M = 6.1\ M$$

The dissolution rate of 100 kg of aluminum per day may be converted to gram-moles per minute by the relation

$$D_m = D/38.9 \text{ or } D_m = 2.58 \text{ g-moles/min}$$

If the product is to be 1.5 M in aluminum, the product flow rate, P, must be

$$P = 2.58/1.5 = 1.72 \text{ liters/min}$$

From Fig. 8.2 (a) it may be seen that at A = 1.5 M, P may vary from approximately 0.25 to 2.0 liters/min. Thus the dissolver has the required capacity when fully loaded.

Assume that P/F = 0.92, F = 1.87 liters/min, and the acid feed rate, FM = 1.87 x 6.1 = 11.4 g-moles/min. From the correlation in Fig. 6.2, it appears that 1.5 M aluminum product would be produced with the dissolver packed to 10.5 ft at an acid feed rate of 11 g-moles/min and a HNO_3 concentration of 6.1 M.

The recommended operating procedure would be to feed cast uranium-aluminum alloy slugs to the dissolver at an average rate of 2.6 g-moles of aluminum per minute. The acid feed rate would be 1870 ml/min with a HNO_3 concentration of 6.1 M and 0.005 M $Hg(NO_3)_2$. The column should operate with a packed level varying between 10 and 11 ft, based on the experience from the final two dissolution runs.

9.0 REFERENCES

1 A. F. Boeglin et al., "The Nitric Acid Dissolution of Uranium-Aluminum Alloy in a Flooded Continuous Dissolver", IDO-14321 (Dec. 3, 1954).

2 D. L. Foster and E. O. Nurmi, "Dissolution of Uranium-Aluminum Alloy Slugs", ORNL-1195 (July 7, 1952).

3 D. L. Foster and E. O. Nurmi, "Continuous Dissolution of Uranium-Aluminum Alloy Slugs", ORNL internal memo CF-54-6-51 (June 9, 1954).

4 J. C. Bresee, "Record of Original Data for ORNL-1672", ORNL internal memo CF-55-11-99 (Nov. 18, 1955).

5 D. E. Hamby, "Fabrication of Uranium-Aluminum Alloys", ORNL-911 (Jan. 8, 1951).

APPENDIX 1

10.0 DETAILS OF EQUIPMENT AND PROCEDURE

The equipment used in performing the trickle-type dissolution studies was installed in Cell 1A of Building 4505 (see final equipment flowsheet, Fig. 10.1). The operating panel board was located on the second floor at the east end of the cell bank. At various times during the test program, modifications were made in the equipment. These modifications divide the test program into 6 definite periods, henceforth called periods 1, 2, 3, 4, 5, and 6. With reference to the run numbers in the tabulated data section, period 1 covers the time interval during which Tests CAD-1 through CAD-16 were made; period 2, CA-1 through CA-8; period 3, CA-9 through CA-11; period 4, CA-12 through CA-28; period 5, CA-29 through CA-30; and period 6, CA-31 through CA-53. If under the discussion of a particular item of equipment a definite period is not mentioned, it can be assumed that this equipment went through the entire program unchanged.

10.1 Dissolver

The dissolving vessel had an available reaction zone 10 ft 8-3/4 in. long and was constructed of a 10-ft section of 6-in.-o.d. type 347 stainless steel tubing of 1/4-in. wall thickness. It was enlarged to an 8-in. IPS pipe on the top end. Slugs were stacked in this section, which was mounted with the longitudinal axis vertical, and were supported at the bottom by a 1/2-in.-thick support plate containing ninety-six 1/8-in. holes on 3/8-in. centers. The dissolver was provided with two jackets, each 4 ft long, with facilities for the application of either cooling water or steam to each jacket individually (refer to tabulated data as to when or where steam or water was applied).

The dissolver was fitted with thermocouple wells and pressure taps at top, center, and bottom.

10.1.1 Slug Loading

Slugs were charged to the dissolver by hand through a twin gate-valve arrangement. The two-valve system was used to prevent exposure of operating personnel to dissolver fumes and to minimize in-leakage of air. The operating technique used for slug loading passed through 5 distinct phases during the course of the program.

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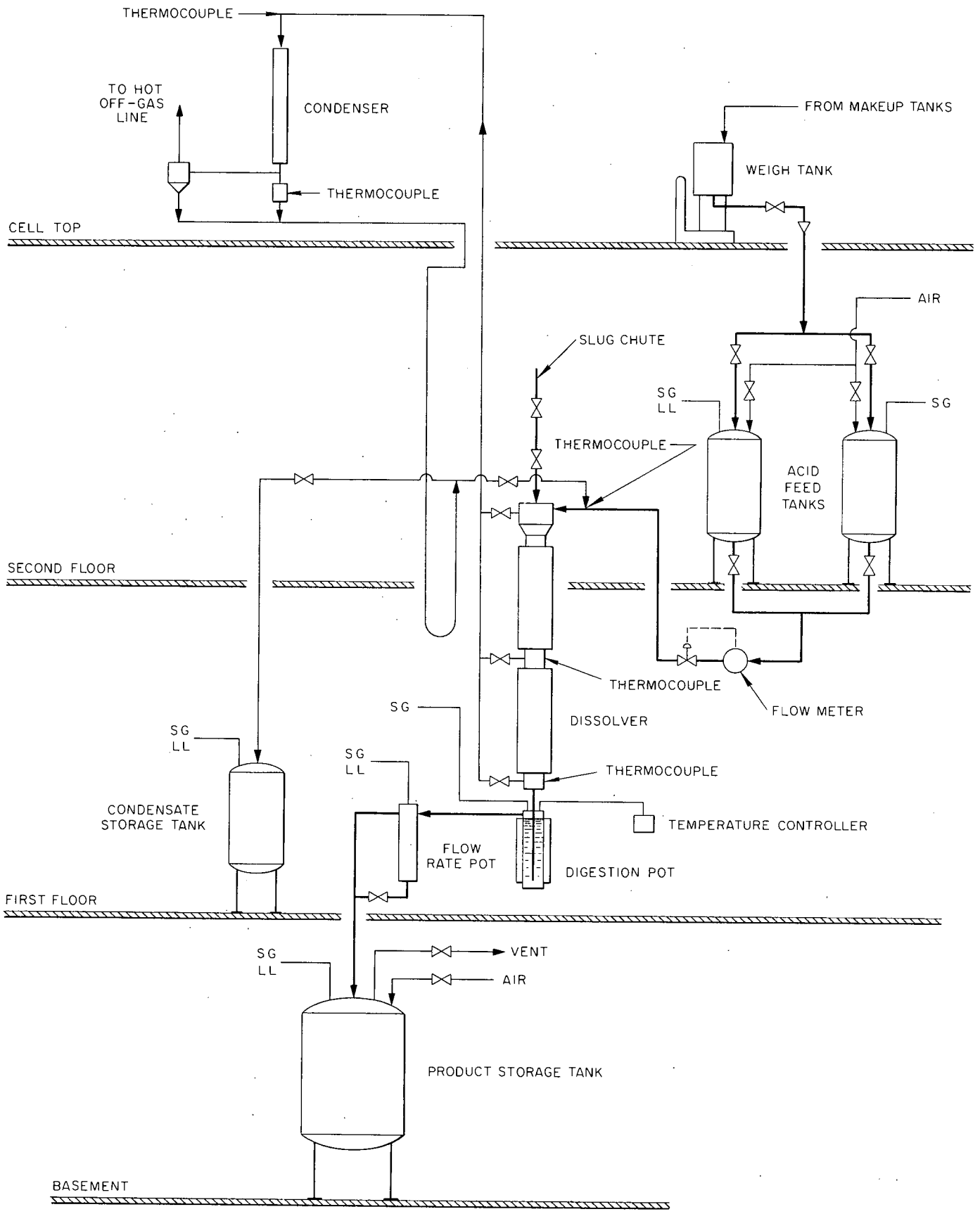

Fig. 10.1 Final Equipment Flowsheet of Experimental Trickle-Type Dissolver

During period 1, slugs were added so as to maintain the reaction zone full at all times, and an effort was made to develop a reliable indicator for determining when the dissolver would permit the addition of another slug. The dissolver at this time was fitted with a head assembly equipped with such an indicator (see Fig. 10.2). The slug chute extended down into the dissolver head. Inside the slug chute was a lever (6) that was connected through the wall of the dissolver to a bellows(4). This bellows made contact with a microswitch (3), which in turn actuated a light on the instrument panel. When a slug passed through the chute, the lever depressed, compressing the bellows and releasing the microswitch so that the light flickered. If the dissolver was full, the lever remained depressed since the slug could not clear the lever and the light remained off. When the slugs below this slug had dissolver, it dropped down, releasing the lever so that the light came on, thus indicating that it was time for the operator to add another slug.

The basis of operation of the slug height indicator was sound, but a more rigid fastening of the microswitch in its related position to the bellows would have been required for foolproof operation. As long as this switch maintained the correct position, the indicator worked satisfactorily, but vibrations present caused a loosening of the set screws (1), allowing a shifting of the switch so that contact was no longer made. If a modification of such a device should be used in an actual plant it would be anticipated that the signal transmitted could automatically release a slug to the dissolver.

It was considered that a more feasible method of loading would be to supply a reservoir atop the dissolver so that as the metal dissolved and collapsing took place, the new slugs would drop by gravity out of the reservoir into the reaction zone. The reservoir, which would never be allowed to become empty, could then be replenished by some simple arrangement such as a dumping bucket rather than requiring an elaborate charging mechanism.

During periods 2, 3, 4, and 5, a reservoir, which amounted to an additional 10-ft section of 6-in.-dia. tubing, was mounted atop the dissolver. Slugs were added in groups of 50 or 60, whenever the reservoir would take this many. This method did not prove to be reliable in that very tight jamming of the slugs in the reservoir resulted. These jams were such that very severe vibrations were necessary to break them. Jamming in the dissolver reaction zone proper sometimes occurred, but these were of a minor nature and persisted for only short intervals. The difference between the jamming phenomenon in the two sections undoubtedly lies in the fact that reaction is occurring in one zone but not in the other. A key slug creating a bridge in the reaction zone would soon dissolve and allow the bed to collapse, whereas this would not happen in the reservoir zone.

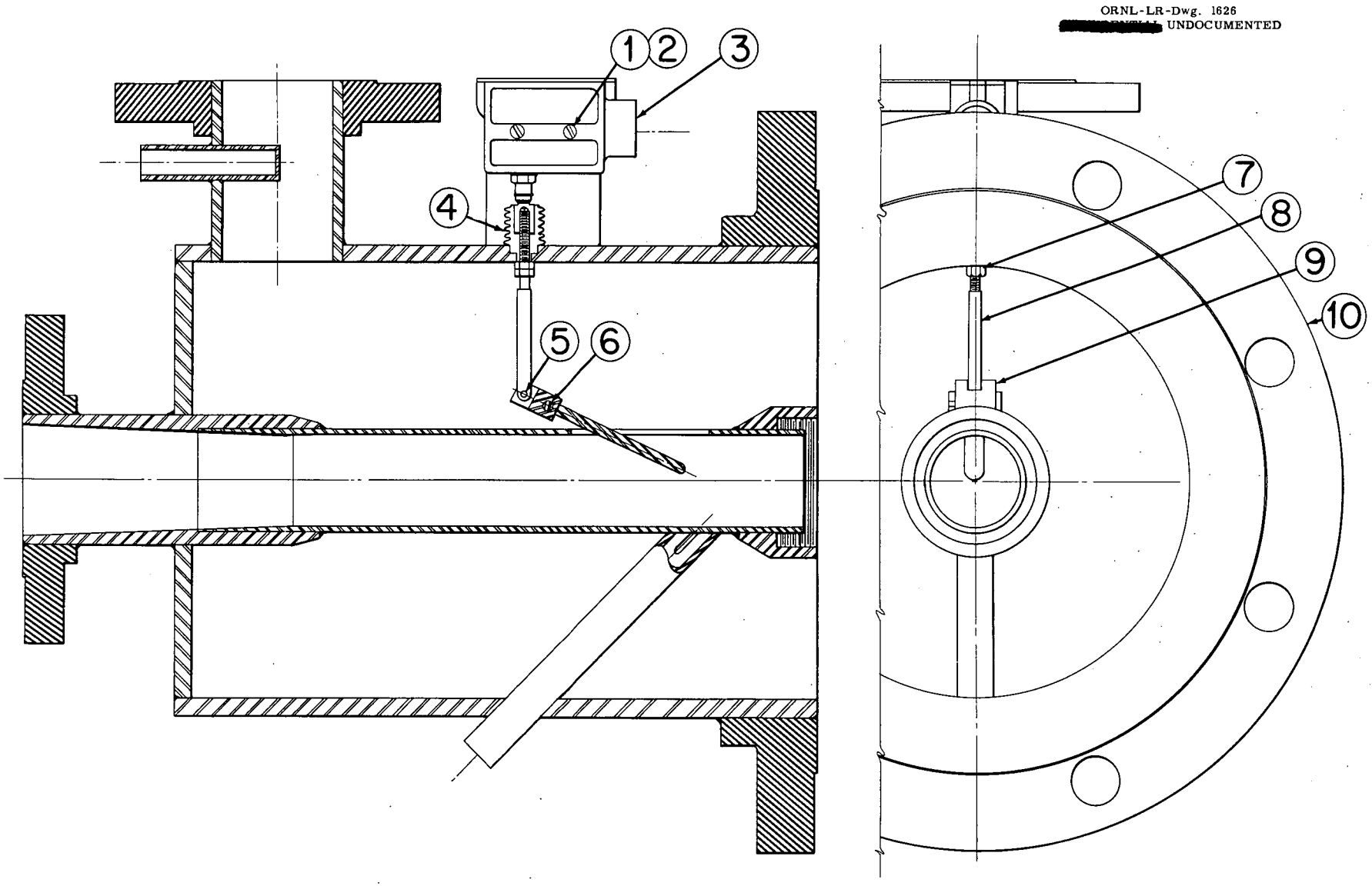

Fig. 10.2. Continuous Dissolver Head Assembly.

During period 6, the dissolver head assembly used in period 1 was reinstalled, replacing the slug reservoir, but the indicating mechanism was not used. In the last two tests during this period, the slugs were charged at a uniform rate (a rate equivalent to the desired dissolving rate), and the bed was allowed to seek its own level. If the desired dissolving rate is not larger than the size of the dissolver will allow, the bed will level off at some given distance from the top. This method of loading appeared to be the best method used but would require a charging mechanism that would feed slugs at a relatively uniform rate.

10.1.2 Dissolver Acid Feed Distributor

The nitric acid feed entered the dissolver during periods 1 and 6 through the dissolver head assembly and was introduced so that it would flow out of the acid feed line through slots and down the outer wall of the slug chute. It was thereby fed to the top center of the reaction zone with no effort being made to distribute the acid over the entire cross section of the bed. During this type of operation the recycled acid from the condenser was mixed in the line with the feed acid and entered the dissolver as one stream.

When the slug reservoir was installed on the dissolver (periods 2 through 5), the feed acid and recycle acid were admitted to the dissolver as separate streams. The feed acid was sprayed into the dissolver through three full-cone, wall-mounted spray nozzles mounted 120° apart around the periphery of the dissolver, 6 in. below the junction of the reaction zone and the slug reservoir. The recycle acid was admitted to the dissolver in an identical manner to the feed acid at a point 3 in. lower in the reaction zone.

No effect was detectable in the operation of the dissolver due to the manner by which the feed and recycle acid were admitted to the dissolver.

10.2 Off-Gas and Recycle Stream

The gaseous reaction products, a mixture of 90 to 95% steam, 5 to 10% oxides of nitrogen, were removed from the dissolver from one of three points: top, center, or bottom of the reaction zone (see tabulated data section for applicable position in each test). This gaseous mixture was carried to the top of a downdraft condenser which served as a condenser for the steam and as a wetted-wall absorber for the absorbable nitrogen oxide components. Upon leaving the condenser, the liquid and noncondensed, nonabsorbed gases were separated by a small cyclone separator, with the acid being recycled to the dissolver and the gases vented to the building radioactive off-gas system.

10.2.1 Dissolver to Condenser Transfer Line

It was found by pressure-drop measurement that the connecting line between dissolver and condenser for a dissolver of this size should be at least a 4-in. IPS line and should be jacketed or steam-traced to prevent uncontrolled condensation.

During the first portion (CAD-1 through -12) of period 1, the only dissolver off-gas outlet was at the top of the reaction zone. The line connecting this outlet with the condenser was a 2-in. IPS steam-jacketed line. A center off-gas outlet with a 2-in. IPS connecting line was added for the later runs of period 1. During period 2, a 2-in. off-gas line was provided to top, center, and bottom outlets on the dissolver (refer to Sec. 13.0 for which outlet was used during a particular test).

Pressure drop was such, as higher dissolution rates were obtained, that the 2-in. line was insufficient to carry the off-gas load. A 4-in. IPS line was installed with dissolver connections at the center and bottom of the reaction zone and used throughout periods 3, 4, 5, and 6.

If condensation was allowed to take place in the off-gas line, a considerable quantity of condensation-absorption produced acid would flow down this line, entering the dissolver at the gas take-off point in use. If the bottom off-gas outlet was in use, this acid would flow out of the dissolver without being allowed to come in contact with metal to be dissolved. The effect was essentially a by-pass of a portion of the dissolver feed around the dissolver. Steam tracing and lagging or jacketing the off-gas line prevented condensation. During period 1, the off-gas line was steam-jacketed and during period 6 the line was steam-traced and lagged. During periods 2, 3, 4, and 5, the off-gas line was bare.

10.2.2 Condenser

Two condensers were used during the program. The smaller condenser was replaced by a larger unit to lower the pressure drop through the system. Both condensers were mounted with the longitudinal axis in a vertical position. They were connected for downdraft flow with the gases entering the top and leaving the bottom of the condenser. The condenser therefore operated as a countercurrent condenser-cooler and a cocurrent wetted-wall nitric oxide absorber. The gases passed through the tube side of the condenser with cooling water on the shell side.

During periods 1, 2, 3, and 4, the condenser consisted of a 6-in. IPS schedule 40 stainless steel shell containing a bundle of nineteen 3/8-in. stainless steel tubes on 1-in. centers. The tubes were 6 ft long, which gave a heat transfer area of approximately 10 ft^2.

During periods 5 and 6, the condenser consisted of a 6-ft-long 8-in. IPS shell containing thirty-seven 3/4-in. tubes. The total heat transfer surface was approximately 44 ft^2.

10.2.3 Recycle Acid Return

Motive power for returning the condenser-produced recycle acid to the dissolver was supplied by either pump or gravity. During period 1, the recycled acid was returned to the dissolver by gravity. At this time, the condenser was mounted so as to provide a head differential of approximately 3 ft, which was sufficient for the low-rate tests. Pumps were used in periods 2, 3, 4, and 5. Centrifugal pumps did not prove satisfactory in that agitation brought about degassing and vapor locking of the pump. A positive displacement pump of the Eco type performed much better but still was not adequate.

In period 6, the condenser was elevated to provide approximately 13 ft of head differential and the recycle was returned by gravity. This system operated without difficulty.

10.3 Feed Makeup and Metering System

The feed acid in period 1 was made up in two 75-gal acid makeup and metering tanks. The usual procedure used in making up this acid was:

1. A weighed amount of demineralized water containing a weighed quantity of mercuric nitrate was transferred by gravity to the feed tank.

2. Enough 13 M HNO_3 to produce the desired concentration was transferred by gravity from a carboy to the feed tanks (total volume determined by liquid level—specific gravity manometers).

3. The resulting mixture was mixed by air sparging and then titrated and adjusted.

The two acid feed makeup tanks were equipped with pneumatic liquid level and specific gravity manometers and an air pressurization system for transferring acid to the dissolver.

Upon leaving the feed tanks, the acid passed through a stainless steel Cuno filter, a flow control system (see Sec.10.6), a heat exchanger where the acid was heated to 90-100°C, and finally into the dissolver.

During periods 2, 3, 4, 5, and 6, the acid-metering system was identical to that in period 1. Two 500-gal storage tanks for containing concentrated nitric acid were provided during these periods.

The feed acid was made up in a 500-gal stainless steel makeup tank. This tank, equipped with an agitator, was mounted on a strain gage which permitted making up the acid by weight. The feed acid was transferred by a centrifugal pump from the makeup tank to the 75-gal metering tanks.

10.4 Dissolver Product System

The dissolver product passed through a digestor for the dissolution of undissolved product and into product collection tanks. These tanks were emptied periodically, and the product was trucked to the shale chemical waste pits.

10.4.1 Digestion System

The product produced by the trickle-type dissolver was extremely murky as it issued from the dissolver. This condition resulted from tiny particles of undissolved slugs that passed through the slug-retaining plate with the solution. Where the product solution was kept at a temperature of 95°C or higher for a minimum of 15 min after leaving the dissolver, the bulk of this material dissolved. Steam-traced or -jacketed sections of 4- to 6-in. IPS pipe of sufficient length to provide a 15-min holdup were placed in the product transfer line to digest the sediment and produce a clarified product.

10.4.2 Metallic Mercury Elimination

During tests in which an acid-deficient product was produced, metallic mercury precipitated from the system. This mercury collected in low points of transfer lines and was drained periodically by valves. There was no evidence of metallic mercury formation in tests where product containing free acid was produced.

10.4.3 Product Collection Tanks

The dissolver product was collected in seven stainless steel tanks providing 2300 gal of storage capacity. Periodically, the solution in these tanks was pumped to a 1500-gal stainless steel tank mounted on a trailer bed, and was hauled to and dumped into shale chemical waste pits. A cost analysis had previously shown that the cost of processing this material would be greater than the value of the depleted or natural uranium involved.

10.5 Sampling

Two streams (the product stream and recycle acid stream) were periodically sampled for the determination of operating characteristics of the dissolver. These samples were instantaneous stream samples rather than a composite of an integrated interval. They were obtained through sampling valves heading directly into the respective lines.

10.6 Instrumentation and Controls

Two instrument panels were provided for the dissolver equipment, the control panel where operating characteristics were indicated, recorded, and controlled, and the product storage panel which contained liquid level and specific gravity manometers for all product storage tanks. At the control panel, temperatures, pressures, liquid levels, specific gravities, and flow rates were measured.

10.6.1 Temperatures

Temperatures of the top, center, and bottom of the dissolver reaction zone, the condenser gas inlet and outlet, condenser water inlet and outlet, acid feed, and dissolver product were measured by means of thermocouples and recorded by a 12-point Brown strip chart recorder.

The temperature of the feed acid was also recorded on a Brown circular-chart recorder-controller, which controlled the degree of throttling of the steam applied to the acid feed exchanger. This steam was controlled by an air-actuated Mason-Neilan valve.

10.6.2 Pressures

Pressure taps located in the top, center, and bottom of the dissolver reaction zone and connected to U-tube manometers indicated pressures at these points. Other pressures measured by means of gages were jacket and preheater steam pressures.

10.6.3 Liquid Level—Specific Gravity

All feed tanks and product collection tanks in the system were equipped with pneumatic liquid-level and specific-gravity probes connected to well-type manometers. The volumes in these tanks at any time could therefore be determined by these readings.

10.6.4 Flow Rate Measurements

Flow rate measurements were made on the acid feed stream and condenser cooling water. Attempts to obtain instantaneous readings of the flow rates of the dissolver off-gas and dissolver product were not successful. Rapid fluctuations in these streams made reliable readings impossible.

The acid feed rate was measured with a Fischer-Porter remote-recording rotameter and recorded on a Fischer-Porter circular chart recorder-controller. This controller pneumatically actuated a Hammel-Dahl spline valve that controlled the acid flow rate at the desired setting.

The condenser water rate was measured by means of a Fischer-Porter rotameter (100% range = 17.2 gpm) and manually controlled at some desired set point.

10.6.5 Condenser Duty as a Means of Indicating Dissolution Rate

The heat acquired by the condenser water was measured in all tests, and, as would be expected, was found to be a fairly accurate measure of the dissolution rate. A previous calculation of heat of reaction for aluminum in nitric acid gave an expected value of 190 kcal/g-mole of aluminum dissolved. A plot of all data obtained when an external source of heat on the dissolver was not used scattered around this value (see Fig. 10.3). It would be expected that under conditions of operation which minimize heat losses, the degree of scattering would be markedly decreased. From these results the condenser duty appears to be a likely measurement for controlling dissolver performance.

APPENDIX 2

11.0 FEED MATERIALS SPECIFICATIONS

11.1 Slugs

The unirradiated slugs used during these experiments were of two types, a cast uranium-aluminum alloy slug approximating the Hanford J slug, and an extruded uranium-aluminum alloy slug approximating the Savannah River alloy slug. These slugs were fabricated by the Oak Ridge National Laboratory, Metallurgy Division.[5]

The composition of the cast slugs was 7.5 wt % uranium — 92.5 wt % aluminum, a mole ratio of aluminum to uranium of 108.5 to 1. They were produced by melting 99.9% pure aluminum in a graphite crucible in a high-frequency induction furnace. When the aluminum was completely melted, the uranium was added to the molten bath. The temperature was raised to 850°C, and the bath was then agitated by stirring with a graphite rod and by induced currents. The well-mixed bath was cooled to 725°C and poured into vertical graphite molds, 1.5 in. dia and 9 in. long. When the slugs had solidified, the bell end was cut off, leaving an 8-in.-long slug.

In most cases, these slugs were fed to the dissolver without further treatment. Each slug weighed approximately 660 g. They differed from the conventional Hanford J slug in that the uranium content was normal uranium or depleted, not enriched, and, after being cut, the slugs were not machined to 1.36 in. in diameter, bonded with aluminum silica bonding material, or canned in aluminum cans as are the J slugs.

The simulated extruded Savannah River slugs contained 5.37% uranium—94.63% aluminum, an aluminum-to-uranium mole ratio of 155 to 1. They were made up in much the same manner as the cast slugs except that the melt was poured into a vertical graphite mold, to form a billet 4 in. dia by 12 in. long, instead of into slug molds.

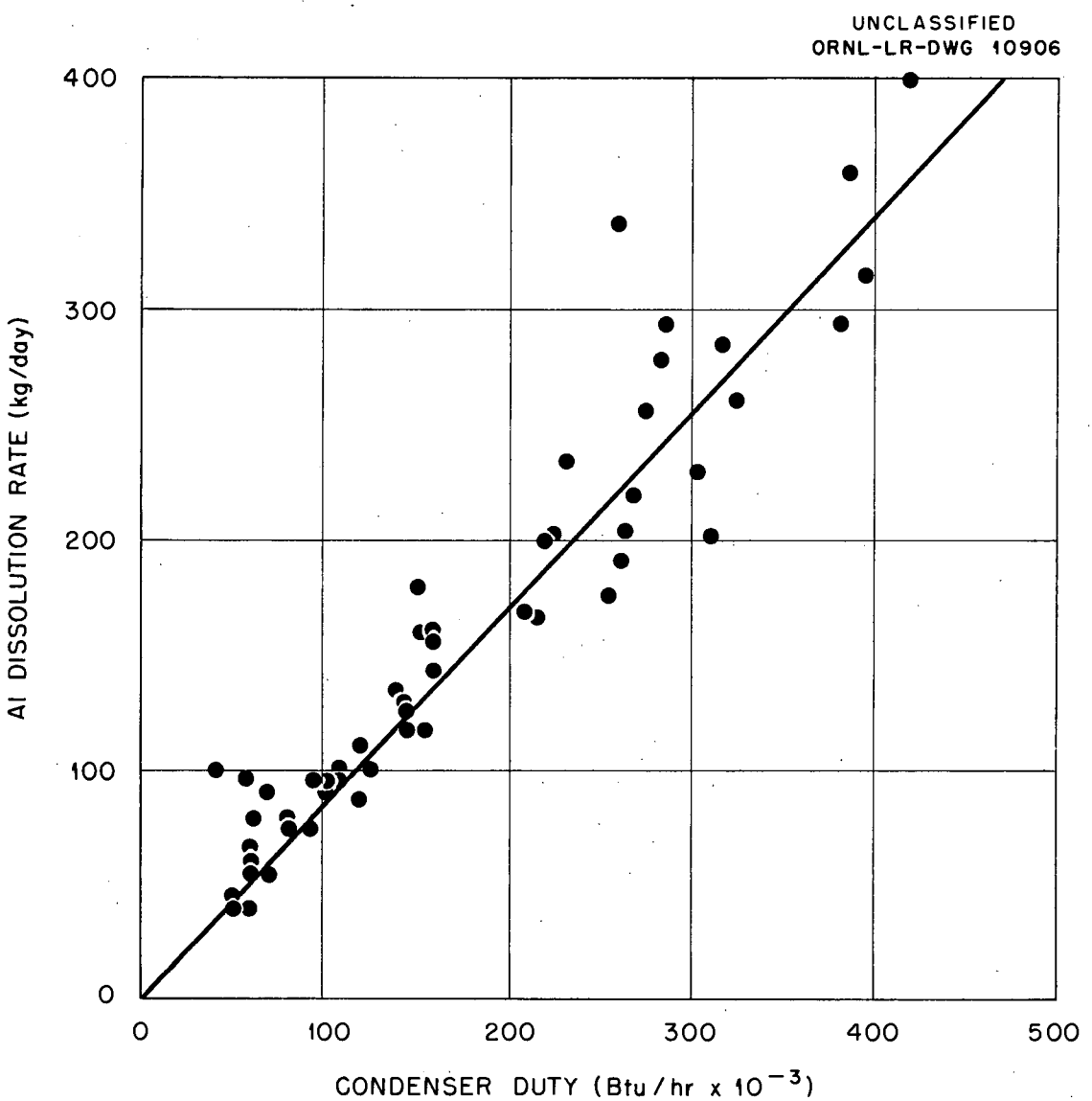

Fig. 10.3. Dissolving Rate of Aluminum in Nitric Acid as Indicated by Condenser Duty. Based on $\Delta H = -190$ kcal/g-mole.

This billet was extruded at a temperature of 300-400°C into a rod approximately 1-1/8 in. in diameter. The billet was extruded bottom end first under a ram pressure of 300 to 390 tons at a speed of 40 to 75 ft/min. The usual dissolver feed resulted from shearing this rod into 12-in. lengths. Each slug weighed approximately 548 g. These extruded slugs differed from Savannah River alloy slugs in enrichment, bonding, and canning, in the same way as the cast slugs did from Hanford J Slugs.

11.2 Nitric Acid

The nitric acid used in these tests was technical grade, 60% (13 M) nitric acid received at the Y-12 plant in tank car lots and hauled to Oak Ridge National Laboratory in stainless steel tanks mounted on a truck. It was diluted to the desired feed concentration by the addition of demineralized water (not less than 10^5 ohms specific resistance).

11.3 Mercuric Nitrate

The mercuric nitrate used as a catalyst for the nitric acid dissolution of aluminum was procured from three sources:

1. As crystalline $Hg(NO_3)_2 \cdot H_2O$, reagent grade, 1-lb lots, manufactured by Baker and Adamson.

2. As crystalline $Hg(NO_3)_2 \cdot H_2O$ reagent grade, 25-lb lots, manufactured by J. T. Baker Company.

3. By the dissolution of metallic mercury in boiling 70% reagent grade nitric acid. Solutions 3-4 M in mercury were made in this manner. The reaction proceeded according to the equation

$$Hg + 4HNO_3 \longrightarrow Hg(NO_3)_2 + 2NO_2 + 2H_2O$$

A 100% excess, or 8 moles, of nitric acid was used per mole of mercury to be dissolved. No difference could be detected in tests otherwise identical except for the source of mercury used.

APPENDIX 3

12.0 ANALYTICAL PROCEDURES

Three analyses were required to determine the dissolver product composition: uranium, aluminum, and acidity. In addition, the acidity of the condensate was determined to obtain some idea as to the efficiency of recovery of the oxides of nitrogen by the condenser.

12.1 Uranium in Product

A colorimetric method was used for this analysis. Hydrochloric acid was added to the dissolver solution for acidity and to break any possible polymers. Stannous chloride was then added to reduce any iron present, the color of which would interfere. A small quantity of ammonium thiocyanate was then added to develop the indicating color, and the resulting solution was compared with a standard by means of a spectrophotometer. The estimated accuracy for this analysis is $\pm 3\%$.

12.2 Aluminum in Product

The analytical method used for aluminum depends on the reaction of aluminum hydroxide with potassium fluoride to form $AlF_3 \cdot 3KF$ and to liberate 3 moles of potassium hydroxide per mole of aluminum present. The original sample is first titrated with barium hydroxide to promote the reaction $Al^{+++} + 3OH^- \longrightarrow Al(OH)_3$. This solution is titrated with excess potassium fluoride, with the reaction $Al(OH)_3 + 6KF \longrightarrow AlF_3 \cdot 3KF + 3KOH$ taking place. The potassium hydroxide formed is then titrated with standard hydrochloric acid and back-titrated with standard sodium hydroxide. This method was adapted from one reported by Snyder and complete details are described in "ORNL Master Analytical Manual".* The estimated error for the analysis is 5%, with a relative deviation of a single measurement of 2%.

12.3 Free Acid in Product

The dissolver product contained positive free acid in some cases but was acid-deficient in others. Complete details for the method of analysis used are found in "ORNL Master Analytical Manual".* In this method, the aluminum in the product solution is complexed as a soluble oxalate with excess potassium oxalate to prevent interference. If the solution contains free acid, it is then titrated with a standard sodium hydroxide solution. If it is acid deficient, an acid spike is added and then titrated against standard sodium hydroxide, the difference between the equivalents of acid added and the titer being the degree of acid deficiency.

12.4 Acidity of Condensate

The standard method by titration with standard sodium hydroxide was used.

APPENDIX 4

13.0 SUMMARY OF DATA AND CALCULATED VALUES

In Table 13.1 is presented a summary of the data and calculated values for all runs presented in this report. Included are all primary independent variables that were investigated, all directly

*ORNL Internal Memorandum CF-53-1-235, Method Numbers (Al) 1-210270, 9-00710270; (H) 9-012205.

TABLE 13.1. SUMMARY OF DATA AND CALCULATED VALUES

Continuous Dissolution of Uranium Aluminum Alloy Slugs in a Trickle-Type Dissolver, Using Nitric Acid, 0.005 *M* Hg^{++} (All Runs Made at the Atmospheric Boiling Point of Dissolvent)

Run No.	Length (hr)	Slugs		Dissolver Jacket[b]	Off-Gas System		Feed			Reflux Return System										Product					
		Type[a]	Packed Height (ft)		Type[c]	Position[d]	Acidity (*M*)	Rate (liters/min)	Rate (g-moles/min)	Return Position[d]	Condenser Duty (Btu/hr × 10^{-3})	Condensate Rate (liters/min)	Concentration (*M*) H^+	Concentration (*M*) Al^{+++}	Entrainment Fraction	Total Reflux Rate (liters/min)	Total Reflux Acid Rate (g-moles/min)	Entrainment Rate (liters/min)	Entrained Acid Return Rate (g-moles/min)	Absorbed Acid Recycle Rate (g-moles/min)	Concentration (*M*) H^+	Concentration (*M*) Al^{+++}	Rate (liters/min)	Acid Consumption Mole Ratio	Product/Feed Vol Ratio	Aluminum Dissolution Rate (kg/day)
CAD-1	18.0	C	10.66	S(T,B)	H,2	T	6	0.320	1.92	T	73.1	0.504	0.40								−1.36	2.01	0.293	3.77	0.915	23.9
3	14.7	C	10.66	S(B)	H,2	T	6	0.311	1.87	T	24.2	0.167	0.83								−1.85	2.14	0.270	4.10	0.868	22.5
4	19.0	C	10.66	S(B)	H,2	T	6	0.408	2.45	T	53.3	0.367	0.46								−1.72	1.96	0.360	4.35	0.883	27.5
5	20.0	C	10.66	S(B)	H,2	T	6	0.228	1.37	T	22.7	0.156	1.01								−2.52	2.36	0.212	3.80	0.930	19.5
6	21.0	C	10.66	S(B)	H,2	T	6	0.111	0.666	T	15.2	0.105	0.84								−4.16	2.37	0.083	5.13	0.743	7.6
7	17.0	C	10.66	S(T,B)	H,2	T	4	0.392	1.57	T	64.1	0.441	1.18								−1.35	1.57	0.314	4.04	0.801	19.1
8	23.0	C	10.66	S(B)	H,2	T	4	0.216	0.864	T	30.3	0.208	1.07								−2.22	1.57	0.199	4.18	0.922	12.2
9	24.0	C	10.66	S(B)	H,2	T	4	0.486	1.94	T	49.5	0.390	0.39								−1.27	1.35	0.459	4.08	0.944	24.0
10	14.0	C	10.66	S(B)	H,2	T	4	0.571	2.28	T	63.8	0.439	0.20								−0.98	1.20	0.526	4.44	0.921	24.5
11	23.0	C	10.66	S(B)	H,2	T	4	0.101	0.404	T	24.0	0.165	0.15								−3.87	1.59	0.100	4.97	0.990	6.2
12	18.0	C	10.66	S(B)	H,2	T	4	0.284	1.14	T	48.3	0.332	0.20								−1.52	1.44	0.277	3.90	0.976	15.5
13	16.0	C	10.66	S(T,B)	U,2	C	6	0.302	1.81	T	57.7	0.397	0.35								−2.00	2.20	0.312	3.55	1.033	26.6
15	22.0	C	10.66	S(T,B)	U,2	C	6	0.560	2.80	T	73.2	0.504	0.70								−1.48	2.16	0.547	3.53	0.976	45.9
16	21.0	C	10.66	S(T,B)	U,2	C	6	0.745	3.36	T	74.9	0.515	0.79								−1.06	2.04	0.688	3.70	0.923	54.6
CA-5	12.0	C	10.25	E	U,2	B	6	1.52	4.47	T	53.0	0.365	2.86	(0.01)							1.35	1.29	1.58	3.43	1.039	79.2
6	9.3	C	10.25	E	U,2	B	6	2.30	9.12	T	65.7	0.452	2.51	0.59	0.578	1.071	2.688	0.619	1.287	1.401	2.08	1.02	2.19	4.14	0.952	86.8
7a	7.3	C	10.25	S(T,B)	U,2	B	6	0.80	13.80	T	81.0	0.558	1.31	0.40	0.312	0.811	1.062	0.253	0.215	0.847	0.85	1.28	0.75	4.34	0.937	37.3
7b	3.5	C	10.25	S(T,B)	U,2	C	6	0.84	4.80	T	103.0	0.706	0.3	0.16	0.078	0.769	0.231	0.063	0.014	0.217	0.23	2.05	0.62	3.85	0.738	49.3
8	14.2	C	10.25	E	U,2	C	6	1.53	5.04	T	60.2	0.415	2.16	0.57	0.349	0.637	1.376	0.222	0.016	1.360	0.07	1.63	1.53	3.64	1.000	96.9
9	11.6	C	10.25	E	U,4	C	7	1.56	9.18	T	118.0	0.813	2.58	0.025	0.014	0.825	2.129	0.012	0.0026	2.132	−0.22	1.83	1.41	4.35	0.904	100.3
11	16.0	C	10.25	E	U,4	C	7	2.42	10.92	T	137.1	0.944	3.87	0.07	0.048	0.992	3.839	0.048	0.066	3.773	1.37	1.47	2.36	3.94	0.976	134.8
20	14.0	E	10.25	E	U,4	C	7	0.93	16.94	T	59.7	0.411	1.57	0.017	0.009	0.410	0.644	0.004	0.0006	0.645	−0.14	1.85	0.89	4.03	0.957	64.0
21	21.7	E	10.25	E	U,4	C	7	2.05	6.21	T	153.5	1.057	1.28	0.36	0.152	1.1246	1.595	0.189	0.219	1.814	−1.16	2.37	1.73	3.99	0.944	159.4
22	19.4	E	10.25	E	U,4	C	7	3.00	14.35	T	224	1.543	0.89	0.14	0.069	1.657	1.475	0.114	0.111	1.586	−0.98	2.04	2.54	4.53	0.847	202.0
29a	2.6	C	10.25	S(B)	U,4	B	5.5	7.2	21.0	T	340	2.342	2.0	0.03	0.037	2.432	4.864	0.090	0.23	4.634	2.60	0.82	7.0	3.73	0.972	223.0
29b	3.4	C	10.25	S(B)	U,4	B	5.5	6.0	39.6	T	338	2.328	1.83	0.18	0.175	2.821	5.162	0.494	1.097	4.083	2.22	1.03				232.0
29c	5.9	C	10.25	E	U,4	B	5.5	4.55	33.0	T	220	1.515	1.95	0.04	0.034	1.560	3.042	0.053	0.069	2.973	1.30	1.18	4.38	3.74	0.962	200.0
31a	9.0	C	10.25	E	U,4	B	5.25	5.53	25.0	T	254	1.749	1.82	0.026	0.030	1.803	3.281	0.054	0.089	3.192	1.64	0.86	5.25	3.83	0.950	175.4
31b	13.7	C	10.25	S(T,B)	U,4	B	5.25	5.42	28.6	T	270	1.859	1.34	0.078	0.084	2.029	2.719	0.170	0.359	2.360	2.11	0.93	5.45	3.83	1.005	197.7
32	13.0	C	10.25	E	U,4	B	5.25	6.58	34.5	T	271	1.866	1.95	0.11	0.12	2.12	4.070	0.254	0.518	3.552	2.04	0.92	6.21	3.83	0.943	222.0
33	11.0	C	10.25	E	U,4	B	7	1.89	13.2	T	79.0	0.544	4.74	0.026	0.023	0.557	2.119	0.013	0.043	2.076	3.33	1.11	1.82	3.55	0.963	78.5
34	5.5	C	10.25	E	U,4	B	7	3.68	27.0	T	162.0	1.116	3.70	0.017	0.015	1.133	4.192	0.017	0.057	4.135	3.33	1.13	3.53	3.51	0.960	155.0
35	16.0	C	10.25	E	H,4	B	7	1.93	13.51	T	96.3	0.663	4.52	0.057	0.046	0.695	3.141	0.0320	0.074		2.32	1.25	1.92	3.77	0.995	93.3
36	10.5	C	10.25	E	U,4	B	7	1.93	13.51	T	98.4		4.7								2.56		1.93		1.000	95.3
37	13.0	C	10.25	E	U,4	B	7	1.85	12.95	T	39.5	0.272	5.04	0.021	0.014	0.276	1.391	0.0039	0.007	1.387	1.75	1.46	1.75	3.87	0.946	99.3
38a	2.0	C	10.25	E	H,4	B	7	1.95	13.66	C	103.0	0.709	3.93	0.000	0.000	0.709	2.786	0.000	0.000	2.786	2.14	1.29	1.84	3.27	0.943	92.3
38b	1.5	C	10.25	E	H,4	B	7	1.93	13.52	0.5T-0.5C	110.0	0.758	4.00	0.013	0.010	0.765	3.060	0.0076	0.017	3.043	2.24	1.29	1.91	2.97	0.990	95.8
38c	2.5	C	10.25	E	H,4	B	7	1.85	12.95	0.78T-0.22C	113.0	0.778	3.70	0.015	0.010	0.786	2.908	0.0079	0.013	2.895	1.70	1.45	1.75	3.20	0.946	98.7
38d	1.5	C	10.25	E	H,4	B	7	2.04	14.30	T	126.0	0.868	3.38	0.013	0.009	0.876	2.961	0.0079	0.010	2.951	1.29	1.37	1.87	3.84	0.916	99.6
39a	1.5	C	10.25	E	H,4	B	6	2.01	12.06	0.48T-0.52C	109.0	0.751	2.88	0.047	0.035	0.778	2.241	0.0272	0.020	2.220	0.72	1.34	1.81	4.43	0.900	94.3
39b	2.5	C	10.25	E	H,4	B	6	1.98	11.88	T	122.0	0.840	2.81	0.033	0.022	0.859	2.414	0.0189	0.014	2.400	0.74	1.50	1.93	3.61	0.975	112.6
39c	1.7	C	10.25	S(T)	H,4	B	6	1.90	11.40	T	170.0	1.171	1.59	0.033	0.022	1.197	1.903	0.0263	0.021	1.882	0.78	1.48	1.86	3.62	0.978	107.0
39d	1.5	C	10.25	S(T,B)	H,4	B	6	2.01	12.06	T	220.0	1.515	1.29	0.02	0.014	1.531	1.975	0.0214	0.018	1.957	0.86	1.48	1.93	3.64	0.960	111.1

TABLE 13.1. (continued)

Run No.	Length (hr)	Slugs: Type[a]	Slugs: Packed Height (ft)	Dissolver Jacket[b]	Off-Gas System: Type[c]	Off-Gas System: Position[d]	Feed: Acidity (M)	Feed: Rate (liters/min)	Feed: Rate (g-moles/min)	Reflux Return System: Return Position[d]	Condenser Duty (Btu/hr × 10^{-3})	Condensate Rate (liters/min)	Concentration (M): H^+	Concentration (M): Al^{+++}	Entrainment Fraction	Total Reflux Rate (liters/min)	Total Reflux Acid Rate (g-moles/min)	Entrainment Rate (liters/min)	Entrained Acid Return Rate (g-moles/min)	Absorbed Acid Recycle Rate (g-moles/min)	Product: Concentration (M): H^+	Product: Concentration (M): Al^{+++}	Product: Rate (liters/min)	Acid Consumption Mole Ratio	Product/Feed Vol Ratio	Aluminum Dissolution Rate (kg/day)
CA-40	38.0	C	10.25	E	H,4	B	6	1.31	7.86	T	88.0	0.612	2.86	0.021	0.013	0.620	1.662	0.0081	0.002	1.660	0.28	1.64	1.18	3.89	0.900	75.2
44a	2.0	E	10.66	E	H,4	B	6	0.59	3.54	T	50.4	0.347	0.78	0.049	0.022	0.355	0.277	0.00781	0.01226	0.289	−1.57	2.20	0.50	3.93	0.847	42.8
44b	2.0	E	10.66	E	H,4	B	6	1.55	9.30	T	146.0	1.006	0.49	0.026	0.011	1.017	0.498	0.00112	0.00234	0.500	−2.09	2.28	1.44	3.75	0.929	127.6
44c	1.7	E	10.66	E	H,4	B	6	2.59	15.54	T	254.0	1.749	0.34	0.020	0.010	1.767	0.601	0.01767	0.00242	0.625	−1.37	1.97	2.69	3.63	1.038	206.0
44d	1.7	E	10.66	E	H,4	B	6	5.6	33.6	T	427.0	2.941	0.04	0.353	0.176	3.569	0.1428	0.628	0.603	0.746	−0.96	2.00	5.22	3.70	0.932	406.0
44e	1.7	E	10.66	E	H,4	B	6	3.88	23.3	T	326.0	2.245	0.71	0.313	0.161	2.676	1.900	0.431	0.698	2.598	−1.62	1.94	3.43	4.33	0.884	259.0
45a	2.0	E	10.66	E	H,4	B	4	0.68	2.72	T			0.31	0.031	0.016						−2.33	1.99	0.65	3.27	0.956	50.3
45b	2.0	E	10.66	E	H,4	B	4	1.11	4.44	T	76.2	0.536	0.32	0.038	0.020	0.536	1.715	0.0107	0.0292	0.201	−2.73	1.91	1.04	3.66	0.937	77.2
45c	2.0	E	10.66	E	H,4	B	4	3.17	12.68	T	263.0	1.846	0.23	0.032	0.019	1.846	0.425	0.0351	0.0940	0.519	−2.68	1.72	2.87	4.13	0.906	191.9
45d	2.0	E	10.66	E	H,4	B	4	5.45	21.8	T	400.0	2.808	0.22	0.035	0.019	2.808	0.618	0.0534	0.1463	0.764	−2.74	1.89	5.41	3.58	0.993	398.0
46a	2.0	E	10.66	E	H,4	B	8	0.55	4.40	T	60.8	0.429	1.59	0.075	0.023	0.429	0.674	0.00987	0.01974	0.694	−2.0	3.33	0.47	3.41	0.855	59.7
46b	2.0	E	10.66	E	H,4	B	8	1.48	11.84	T	161.7	1.136	1.32	0.053	0.019	1.136	1.500	0.0216	0.0380	1.538	−1.76	2.80	1.47	3.51	0.993	160.0
46c	2.0	E	10.66	E	H,4	B	8	2.96	23.7	T	258.0	1.800	1.22	0.053	0.018	1.810	2.208	0.0326	0.0114	2.219	−0.35	2.91	2.95	2.88	0.997	333.8
47a	2.0	E	10.66	E	H,4	B	4	0.67	2.68	T			0.49	0.015	0.007						−3.7	2.21	0.54	3.92	0.806	46.4
47b	2.0	E	10.66	E	H,4	B	4	1.56	6.24	T	154.0		0.62								−3.7	2.27	1.33	3.70	0.852	117.4
47c	2.0	E	10.66	E	H,4	B	4	3.17	12.68	T	258.0	1.786	0.21	<0.01	0.005	1.786	0.375	0.00893	0.0346	0.410	−3.88	2.13	3.09	3.75	0.975	256.0
47d	2.0	E	10.66	E	H,4	B	4	5.22	20.9	T	385.0	2.709	0.12	0.04	0.021	2.709	0.225	0.0569	0.1559	0.481	−2.74	1.88	4.91	3.72	0.941	359.0
47e	2.0	E	10.66	E	H,4	B	4	3.88	15.52	T	284.0	1.956	0.20	>0.02	0.010	1.976	0.395	0.01976	0.0545	0.449	−2.76	1.98	3.69	3.53	0.946	282.0
48a	2.0	E	10.66	E	H,4	B	6	0.53	3.18	T	58.0	0.399	0.30	>0.016	0.006	0.401	0.1203	0.00241	0.0933	0.213	−3.87	2.53	0.40	4.67	0.755	39.3
48b	2.0	E	10.66	E	H,4	B	6	1.59	9.54	T	151.0	1.040	0.24	0.01	0.003	1.043	0.355	0.00313	0.01067	0.366	−3.41	3.01				181.4
48c	2.0	E	10.66	E	H,4	B	6	3.22	19.32	T	286.0	1.969	0.23	<0.021	0.005	1.978	0.455	0.00989	0.0307	0.486	−3.1	2.5	3.03	3.79	0.941	294.0
48d	2.0	E	10.66	E	H,4	B	6	3.84	23.00	T	381	2.624	0.20	<0.03	0.013	2.659	0.532	0.0346	0.1176	0.650	−3.4	2.28	3.34	4.52	0.870	296
49a	2.0	E	10.66	E	H,4	B	8	0.50	4.00	T	60.8	0.419	1.27	0.031	0.011	0.424	0.538	0.00466	0.00932	0.547	−2.0	2.9				54.1
49b	2.0	E	10.66	E	H,4	B	8	1.53	12.24	T	161	1.109	1.35	0.018	0.007	1.117	1.508	0.00782	0.00704	1.515	−0.9	2.49	1.48	3.68	0.967	143.3
49c	2.0	E	10.66	E	H,4	B	8	2.35	18.80	T	214	1.474	0.97	0.057	0.024	1.510	1.465	0.0362	0.0036	1.469	−0.1	2.39	1.81	4.39	0.770	168.2
49d	2.0	E	10.66	E	H,4	B	8	3.45	27.6	T	314	2.163	1.03	<0.038	0.017	2.200	2.266	0.0374	0.01122	2.277	−0.3	2.19	3.27	3.99	0.948	278.4
50a	2.0	E	10.66	E	H,4	B	4	0.69	2.76	T	50.0	0.244	0.47	<0.04	0.019	0.351	0.165	0.00667	0.0220	0.187	−3.3	2.15	0.47	4.27	0.681	39.3
50b	2.0	E	10.66	E	H,4	B	4	1.58	6.23	T	144	0.992	0.22	<0.04	0.019	1.011	0.222	0.0192	0.0845	0.306	−4.4	2.06	1.47	4.22	0.930	117.7
50d	2.0	E	10.66	E	H,4	B	4	3.87	15.48	T	305	2.101	0.44	0.000	0.000	2.101	0.924	0.000	0.000	0.924	−2.7	1.54	3.85	4.36	0.995	230
50e	2.0	E	10.66	E	H,4	B	4	5.35	21.40	T	392	2.700	0.47	0.000	0.000	2.700	1.269	0.000	0.000	1.269	−2.5	1.62	4.98	4.20	0.931	314
51a	2.0	E	10.66	E	H,4	B	6	0.63	3.78	T	68.0	0.468	0.44	0.01	0.004	0.470	0.207	0.00188	0.00607	0.213	−3.23	2.63	0.53	3.94	0.841	54.2
51b	2.0	E	10.66	E	H,4	B	6	1.62	9.72	T	146	1.006	0.49	0.01	0.004	1.010	0.495	0.00404	0.00808	0.503	−2.0	2.24	1.45	3.88	0.895	126.2
51c	2.0	E	10.66	E	H,4	B	6	2.58	15.48	T	231	1.591	0.48	0.002	0.001	1.593	0.765	0.00159	0.00286	0.768	−1.8	2.25	2.67	3.38	1.038	234
51d	2.0	E	10.66	E	H,4	B	6	3.49	20.9	T	309	2.128	0.32	<0.07	0.045	2.228	0.713	0.1003	0.211	0.924	−2.1	1.56	3.33	5.38	0.954	202
52	61	E	7.5	E	H,4	B	6.5	2.54	16.51	T	211	1.453	0.88	0.01	0.005	1.460	1.285	0.0073	0.00314	1.288	−0.43	1.85	2.37	4.00	0.933	170.5
53	32	E	5.3	E	H,4	B	6.5	1.30	8.45	T	121	0.833	0.91	0.03	0.017	0.898	0.817	0.0153	0.00704	0.824	−0.46	1.79	1.27	3.98	0.977	88.4

For original data from which average operating conditions were calculated, see References 3 and 4.

[a] C = cast, E = extruded.

[b] E = empty, S = steam, T = top, B = bottom

[c] H = heater, U = unheated, figures represent line size in inches.

[d] T = top, C = center, B = bottom

measured dependent variables, certain indirectly measured quantities (those pertaining to the reflux return system), and calculated ratios used in various correlations.

13.1 Origin of Data and Calculated Values

After the first column identifying the run numbers, the next 10 columns contain the primary independent variables of the studies, with two exceptions. The packed heights for the last two runs were dependent variables, determined by the product concentration and rate imposed on the system (see Sec. 8.1).

Under the heading "Reflux Return System", values listed for condenser duty, condensate rates, and concentrations were directly measured. The first two values were obtained from the average condenser water rates and temperature changes, and the third values were obtained from average analytical results.

The last six columns of the same heading are indirectly calculated values based on the aluminum concentrations in the reflux return. Since the reflux samples were not analyzed for aluminum in the first 14 runs, no values are presented. The analysis of run CA-5 was obtained from only one sample taken during the 12 hr of dissolving. Consequently, no calculations were made with such a nonrepresentative datum. The calculation procedure used for all other runs is outlined in Sec. 13.2, "Sample Calculations".

The values listed under the heading "Product" for concentrations and rates were measured directly. The acid consumption ratio was calculated from the definitions and equations discussed in Sec. 7.1. The product/feed ratios (P/F) were calculated from the ratio of the two values mentioned previously, the product flow rate and the feed flow rate, both measured in liters per minute.

The final column of aluminum dissolution rates was obtained from the product of two values measured directly, the product volumetric flow rate and the product aluminum concentration.

13.2 Sample Calculations

A detailed description of the calculation procedure and sample calculations will be given for the indirectly obtained values of the reflux return system only. All other calculations are either obvious or have been discussed in previous sections.

An assumption which is basic to all the following calculations is the assumption that the concentration of the liquid in the dissolver at the point of off-gas removal is the product concentration. The assumption must be correct for runs 6, 7a, and later runs beginning with run 29a, since the gas removal point was at the bottom of the dissolver in all cases. For the previous seven runs (7b

through 22) a center off-gas position was used. Depending upon the amount of dissolution taking place in the bottom half of the dissolver, an error is introduced into the calculations by the assumption.

Let f = entrainment fraction (the fraction of the recycle stream which is entrainment)

A_R = reflux aluminum concentration, M

H_R = reflux hydrogen ion concentration, M

c = condensate rate, liters/min

R = total reflux rate, liters/min

E = entrainment rate, liters/min

By definition:

$$f = E/R = (R - c)/R$$

Assuming that the entrainment has the same concentrations as the product,

$$RA_R = EA$$

Therefore

$$f = A_R/A$$

The condensate rate, c, was obtained from the condenser duty (see Sec. 10.1.6), assuming that the heat of vaporization plus the sensible heat of the condensed liquid equaled 1100 Btu/lb.

By the appropriate conversion factors,

$$\frac{\text{Condenser duty, Btu/hr}}{1.452 \times 10^5} = c, \text{liters/min} \qquad (18)$$

If $(R-c)/R = f$, it follows that

$$R = c/(1-f) \qquad (19)$$

The total reflux acid rate then equals RH_R, and the entrainment rate equals fR or $R-c$. Also, the entrained acid return rate = EH. The final value, the absorbed acid recycle rate, by a simple acid balance, is equal to $RH_R - EH$.

For a specific example of the above calculations, consider run CA-6, a run with a 2-in. off-gas line and a high entrainment rate.

Condensate rate (Eq. 18), $c = \frac{65,700}{1.452 \times 10^5} = 0.452$ liters/min

Entrainment fraction (Eq. 17), $f = 0.59/1.02 = 0.578$

Total reflux rate (Eq. 19), $R = \frac{0.452}{0.422} = 1.071$ liters/min

Total reflux acid rate = 1.071 x 2.51 = 2.688 g-moles/min

Entrainment rate = 1.071 - 0.452 = 0.619 liters/min

Entrained acid return rate = 0.619 x 2.08 = 1.287 g-moles/min

Absorbed acid recycle rate = 2.688 - 1.287 = 1.401 g-moles/min

APPENDIX 5

14.0 NOMENCLATURE

Symbol	Definition	Units
a	Acid feed rate	g-moles/min
A	Product aluminum molarity	g-moles/liter
A_R	Recycle aluminum molarity	g-moles/liter
c	Condensate rate	liters/min
C	Acid consumption rate	g-moles/min
D	Aluminum dissolution rate	kg/day
D_m	Aluminum dissolution rate	g-moles/min
E	Entrainment rate	liters/min
f	Entrainment fraction	
F	Acid feed rate	liters/min
H	Free acidity in product	g-moles/liter
K,K',n	Constants	
M	Feed acid molarity	g-moles/liter
P	Product rate	liters/min
R	Total reflux rate	liters/min