RECOVERY OF ICPP FROM CRITICALITY EVENT
OF OCTOBER 17, 1978


PART II

Support and Safety Justification of the
Specific Approach to Emptying H-100


by

TECHNICAL DIVISION PERSONNEL


January 1979


**Allied Chemical**

IDAHO CHEMICAL PROGRAMS

## Tables

RECOVERY OF ICPP FROM CRITICALITY EVENT OF OCTOBER 17, 1978

PART II

Support and Safety Justification of the
Specific Approach to Emptying H-100

## I. INTRODUCTION

At about 8:40 p.m. on October 17, 1978 a criticality involving about $3 \times 10^{18}$ fissions occurred in a solvent extraction column at the Idaho Chemical Processing Plant (ICPP). The plant was being operated for the recovery of highly enriched uranium from in-plant created salvage solutions; the criticality was proven to have occurred in the first-cycle scrub column (1B). Immediately after the event, the plant was shut down and personnel evacuated until very short-lived activity had decayed. On the morning of October 18, extensive technical efforts were started to secure the vessel in which the criticality was thought to have occurred and to assure that other portions of the plant were suitable for recovery actions.

As a basis for the recovery operation, diagnostic, planning, experimental, modeling, and other technical activities were undertaken to serve as a basis for the recovery procedures to be used and to justify their safety. Another document, Part I - Basic Technical Data, contains information about the uranium inventory, history of the plant status, the criticality event, support for corrective actions, and the plan of action. This document contains information about the plan of action, the options considered, support activities for the option selected, and safety justifications for that plan of action. In addition, the appendix contains information about emergency contingency plans.

## II. OPTIONS FOR REMOVAL OF URANIUM FROM H-100

The options discussed (A-E) show the specific safety justification items associated with the several actions required to execute the removal of uranium from column H-100 by several different options. This analysis was prepared as we recognized that the safety justification statements were associated with specific actions rather than with the individual steps in a procedure.

A summary of the several Required Safety Justification Items is given in Table I to identify the generic statements required to justify the safety of the several options. These could be justified in advance of identifying the specific operating procedure; the experimental and calculational work to do so was underway or starting.

## TABLE I
## REMOVAL OF URANIUM FROM H-100
### (Required Safety Justification Items)

1. Jackleg control at full pressure.

2. Jackleg control with flowout of bottom.

3. Personnel exposure; organic phase in sample or transfer line.

4. Personnel exposure; aqueous phase in sample or transfer line.

5. Criticality calculations for aqueous layer of different thickness, with uranium and boron in top head.

6. Criticality calculations; organic layer at ∿6 g/L above aqueous layer in top head.

7. Modeling of B and U concentrations in effluents as a function of time or batch from either top or bottom of column.

8. Uranium analysis; boron analysis (w/cadmium).


## 1. Option A

| Actions | Required Safety Justification |
|---|---|
| 1. Add boric acid solution (B) at top of the column. | (1) Aqueous layer rising into head must be safe by geometry; (2) Jackleg must support column. |
| 2. Remove organic at top; down to lower DRA probe. | (1) Personnel exposure; (2) Jackleg must be stable; (3) Prove organic or aqueous; (4) Analyze for uranium. |
| 3. Repeat until organic depleted. | (1) Same as above. |
| 4. Add (B) at the bottom incrementally. | (1) Aqueous layer rising into the head must be safe; (2) Jackleg must hold. |
| 5. Remove aqueous from top; analyze for B and U; set limit on B/U or the absolute uranium concentration. | (1) B/U ratio in the effluent must be >(TBD). If value not exceeded, additional (B) added to top and operation resumed. |
| 6. Continue until B/U ratio and U concentration and material balances for liquid suggest that essentially all U has been removed. | Same as above. |

## 2. Option B (Procedure #2)

| Actions | Required Safety Justification |
|---|---|
| 1. Remove organic from top of H-100 to J-cell (J-135). | (1) Personnel exposure; (2) Jackleg must be stable; (3) Prove organic or aqueous; (4) Analyze for uranium. |
| 2. Add 10 L (B) to bottom of H-100. | (1) Aqueous (or potential aqueous layer) must be safe by geometry; (2) Model to predict when aqueous will start transferring; (3) Stable jackleg; (4) Allow time for mixing B in column base. |
| 3. Continue incrementally until aqueous sample is obtained. With each addition, empty head down to probe; Monitor B and U and note ratio. | (1) Aqueous (or potential aqueous layer) must be safe by geometry; (2) Jackleg must be stable; (3) Watch for bubbles and check manometer on DRCA H-100; (4) Model to predict anticipated U and B concentrations. |
| 4. Change to continuous mode of feed and bleed. | (1) Establish that U valve is <TBD or that B/U is greater than TBD g/g; Demonstrate model for elutriation and check that model is followed. |

## 3. Option C (Procedure #1)

| Actions | Required Safety Justification |
|---|---|
| 1. Add 10 L (B) solution to base of H-100. | (1) U in organic below critical conc. at saturation for solvent; (2) Jackleg must be stable; (3) Mixing; (4) U in aqueous must be safe by geometry in large head at low height. |
| 2. Remove 10 L of solution from base of H-100 via Jackleg to G-165. | (1) Stability of jackleg pressure; (2) Metering through jackleg; (3) Mixing. |
| 3. Transfer G-165 to G-108. | (1) Assure criticality safety in G-108; (2) Analyze G-108 for U and B. |
| 4. Repeat in 10 L increments. | Same as above. |

## 4. Option D (Trivial)

| Actions | Required Safety Justification |
|---|---|
| 1. Add B solution to base of H-100 until aqueous reaches the high pressure DRA probe. (see Option A) | (1) Top head safe with aqueous and organic; (2) Jackleg must be stable. |

## 5. Option E

| Actions | Required Safety Justification |
|---|---|
| 1. Remove organic from top. | (1) Jackleg must be stable; (2) Personnel exposure. |
| 2. Add boron solution to top. | (1) Jackleg must be stable; (2) Aqueous layer rising into top head must be safe by geometry. |
| 3. Remove organic from top. | (1) Jackleg must be stable; (2) Personnel exposure. |
| 4. Repeat 2 and 3 until organic depleted. | Same as above. |
| 5. Add boron solution to bottom incrementally. | (1) Jackleg must be stable; (2) Aqueous layer rising into top head must be safe by geometry. |
| 6. Pump aqueous from top through high-pressure DCA probe. | (1) Personnel exposure; (2) B/U ratio must be >(TBD) as modeled. |

## 6. Plan of Action

After due consideration of the five options and safety justification items identified in Table I, it was decided that Option E represented the most appropriate course of action. Consequently, the following plan of action was developed:

(1) Remove organic from top of H-100 to J-cell down to lower DRCA probe level.

(2) Add boron solution to top with Tracer #1.

(3) Remove organic via top to J-cell. Sample to verify organic and not aqueous.

(4) Repeat 2 and 3 until aqueous shows up in sample prior to withdrawal of organic.

(5) Add boron solution to bottom with Tracer #2.

(6) Check top for organic or aqueous by sampling. Withdraw organic.

(7) Continue to add boron solution at bottom with Tracer #2.

(8) When sample shows aqueous at top and essentially all organic is removed, sample bottom.

4

(9) Establish contents of column with analyses of samples of uranium, boron, and tracers, and continue addition to bottom until criteria for removal are met.

(10) Empty the column.

## III.  SUPPORT ACTIVITIES

Before implementing the prescribed plan of action, certain support activities had to be conducted.  Four principal assignments were: (1) the determination of the maximum height of the lower DRCA H-100 probe; (2) the evaluation of the jackleg pressure control; (3) boron stability; and (4) the determination of the concentration of uranium in the H-100 column.

### 1.  Maximum Height of Lower DRCA H-100 Probe

It was necessary to establish the maximum height of this probe since this placed a physical limit on the height of the liquid layer in the column head.

In determining the maximum height of the lower DRCA probe in the upper head of H-100, it is assumed that numbered dimensions on the vessel drawing (Figure 1) are more certain than obtaining dimensions from the drawing and scaling up.

(1) From the drawing, the distance from the lower head bottom tangent to the liquid overflow is 177 inches.

(2) Distance from lower head bottom tangent to lower head upper tangent is 36 inches.

(3) Distance from lower head upper tangent to lowest column plate is 6 inches.

(4) Distance from lowest column plate to highest column plate is 116 inches.

(5) Distance from highest column plate to bottom of column head is 2 inches.

(6) From the above dimensions, the distance from the liquid overflow in the column head to the bottom of the upper head is 17 inches.

(7) From the drawing, the upper DRCA probe level can be no higher than 1/2 inch above the liquid overflow.  Actually, the upper DRCA probe is most likely at or below the liquid overflow since it should be immersed in liquid during normal operation.

(8) The DRCA probe spacing is 14 inches.

5

H-100
(1B Column)
Scale 1" = 2'0"

4"

Liquid
Overflow

14"

DRCA

3.5" max.

Highest
Column
Plate

2"

116"

121"

181"

177"

162.5" max.

Lowest
Column
Plate

3"

6"

36"

LRA
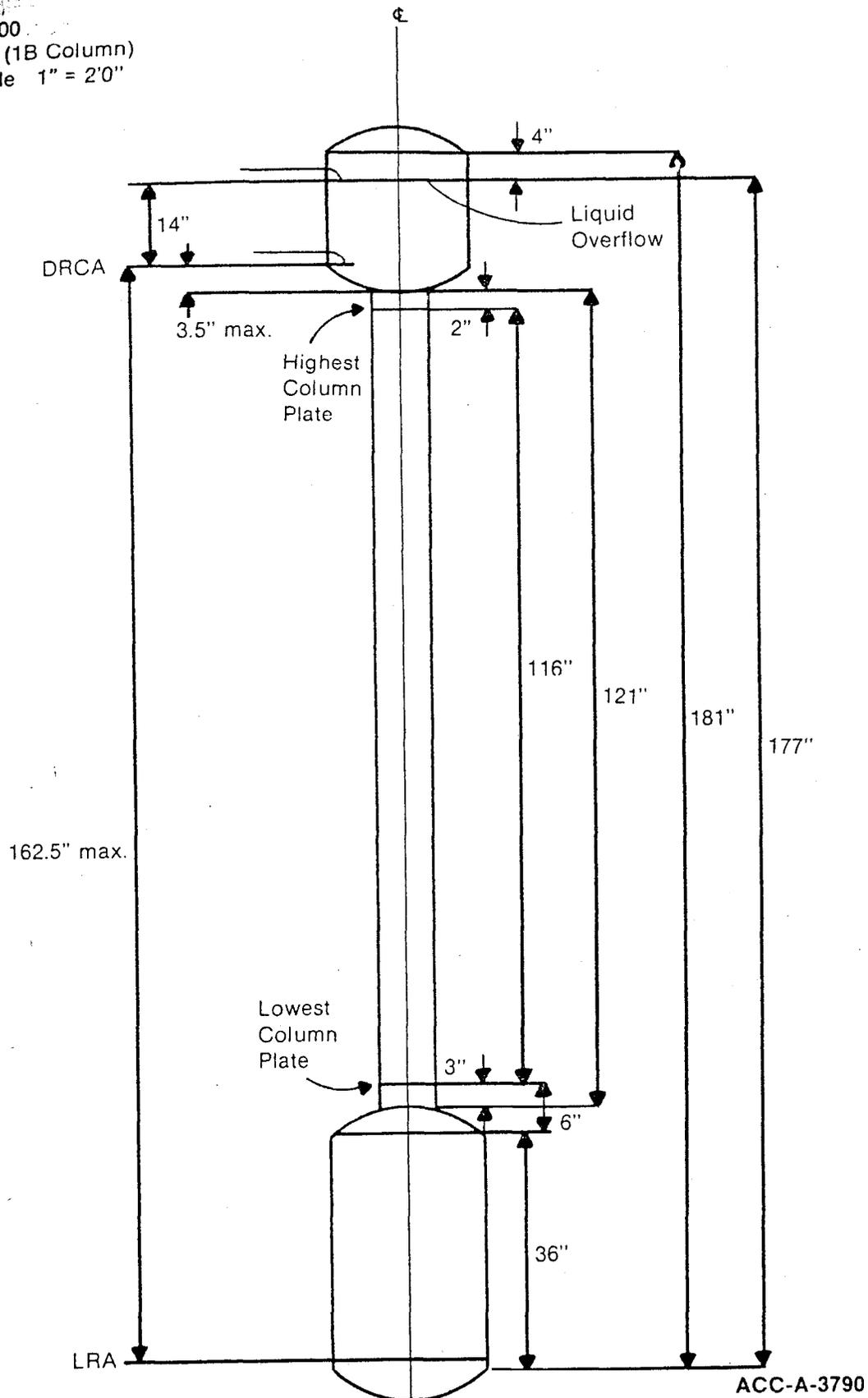
ACC-A-3790

**Figure 1. DRCA Probe Height Determination**

24"

24"

18"

3 1/2"

Tangent

2"

1/2"

3"

0.9"

9"

8"
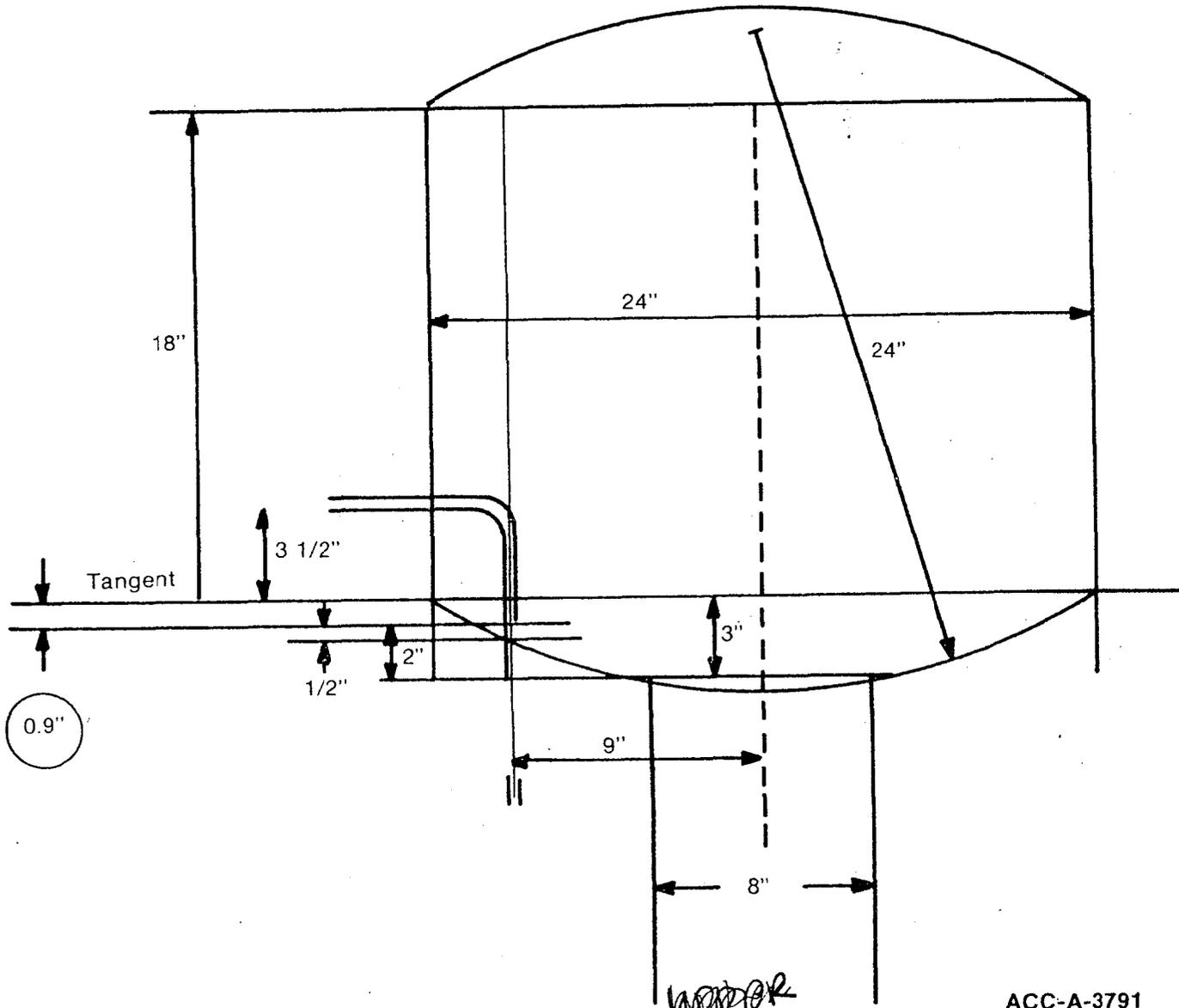
upper

ACC-A-3791

Figure 2.   H-100 Column Head

(9) Assuming the upper DRCA probe is 1/2-inch above the liquid overflow, the maximum height of the lower DRCA probe above the bottom of the upper head is 3-1/2 inches.

(10) A detailed drawing (Figure 2) on the vessel print shows the bottom of the lower DRCA probe is 1/2-inch from the inside surface of the vessel, and the probe tip center is 9 inches from the vessel center-line. From these dimensions and from a drawing of a standard 24-inch ASME dished vessel head, the height of the DRCA lower probe could be as low as 2 inches above the bottom of the vessel head.

## 2. Jackleg Pressure Control

### 2.1 Description

The controller, DRCA H-100, receiving a signal from pressure probes inside the upper head of the H-100 column, controls the pressure applied to the control pot H-101. As more pressure is applied to the H-101 control pot, the air dis-places liquid in the pipe between H-100 lower head and H-101, raising the liquid level in H-100. As pressure is relieved, the liquid in the line flows toward the H-101 control pot, and if the pressure is reduced sufficiently, the liquid will spill over the weir in the H-101 pot and drain into the jackleg between H-101 and H-102 (Figures 3 and 4). The control pressure will also be applied on the jackleg pipe between H-101 and H-102, causing the liquid level to drop in the side from H-101 and rise in the side to H-102. The pressure must be controlled to prevent the liquid from being pushed down to the level at which air can pass from H-101 to H-102 in the jackleg. An air lift would result and the H-100 column would drain to the level of the H-101 control pot weir. The corrective measure is to reduce control pot pressure to zero, allow the jackleg to refill, and reapply control pressure below that which caused the jackleg to blow.

The control air for the H-101 control pot is supplied by the DRCA H-100 control-ler. The air is relieved to the VOG system when the control pressure is reduced through a flow restrictor orifice (Figure 5). The control air continuously bleeds through the orifice and is maintained at the control pressure by continuous supply.

### 2.2 Jackleg Pressure Control Test

To verify the control capability for discharging aqueous solution from the bottom of the H-100 and G-111 column, a test was conducted using similar equipment in the second-cycle extraction system. A Foxboro controller identical to the one installed on the H-100 column was connected to the density-recorder-controller (DRCA-P-102) for the second-cycle column, P-102. A mercury manometer was connected into the instrument line for PR-102 to give a more accurate jack-leg pressure reading. A water manometer was connected across the DRCA-P-102 probes for an accurate measurement of the level in P-102 column.

4"

6'-4" = 2.75 psig
@ SG 1.0

6' 8"

H-100

H-101

H-102

12'-5" = 5.39 psig
@ SG 1.0
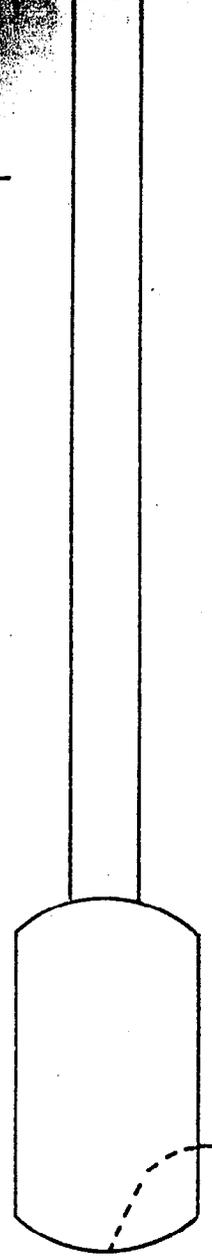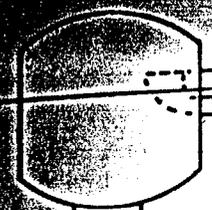
**Figure 3.**

Geometry of the H-100 Jackleg System

9

ACC-A-3792

| FITTING | | | SCHEDULE |
|---|---|---|---|
| MARK | NO REQ'D | DESCRIPTION | REMARKS |
| A | I | 1/4" PIPE STUB | AIR INLET |
| B | I | 3/4" PIPE STUB | LIQUID INLET |
| C | I | 3/4" PIPE STUB | LIQUID OUTLET |

6" SCHEDULE 40 PIPE CAP

OVERFLOW WEIR

3 1/2"

3 1/2"

2"

1/4"
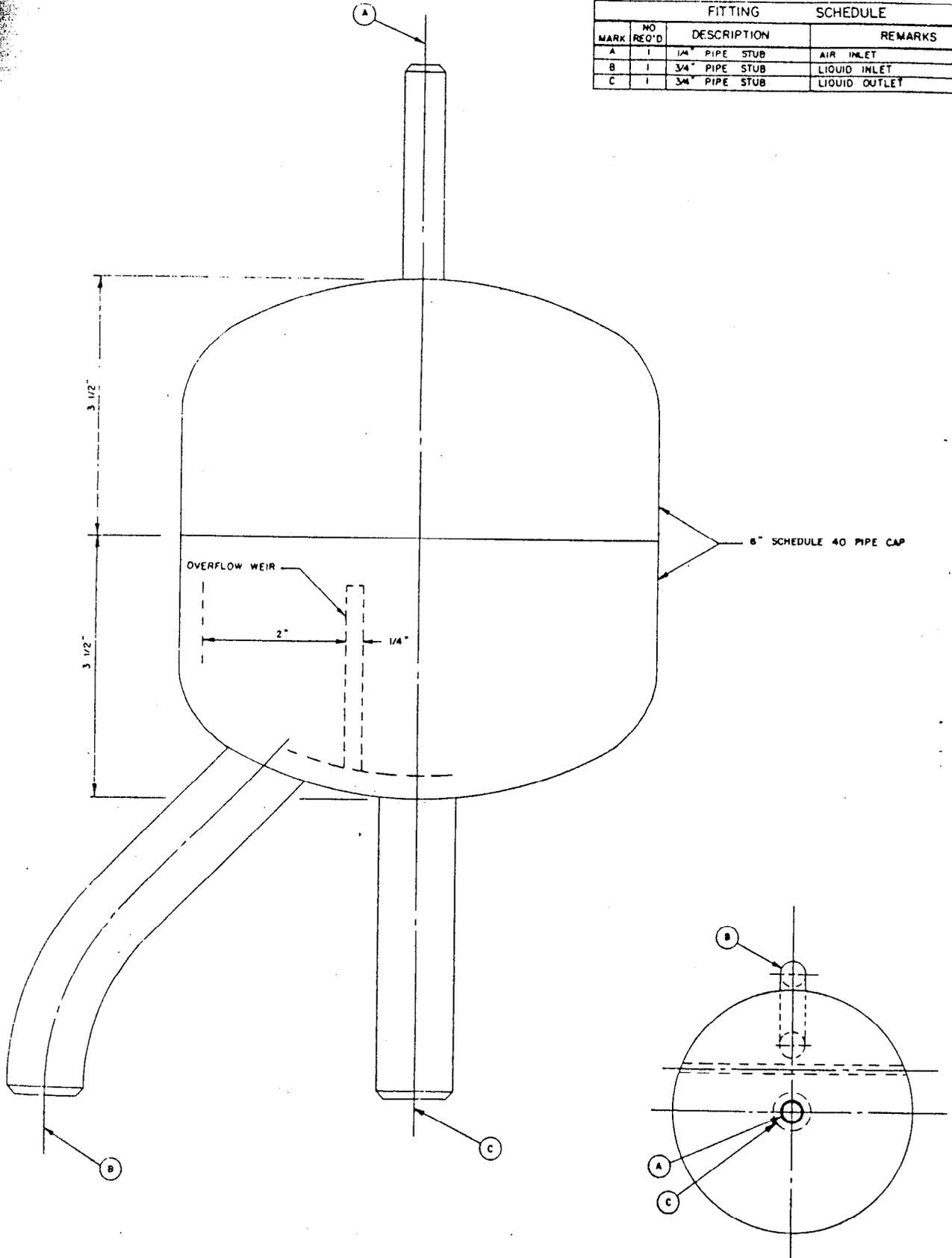
**Figure 4. Vessel H-101 - Jackleg Control Pot**

ACC-A-3793

10

DRCA-H-100

PR-H-101

3:1

Vent
To VOG

Orifice

H-101

H-100

H-102
Via
Jackleg
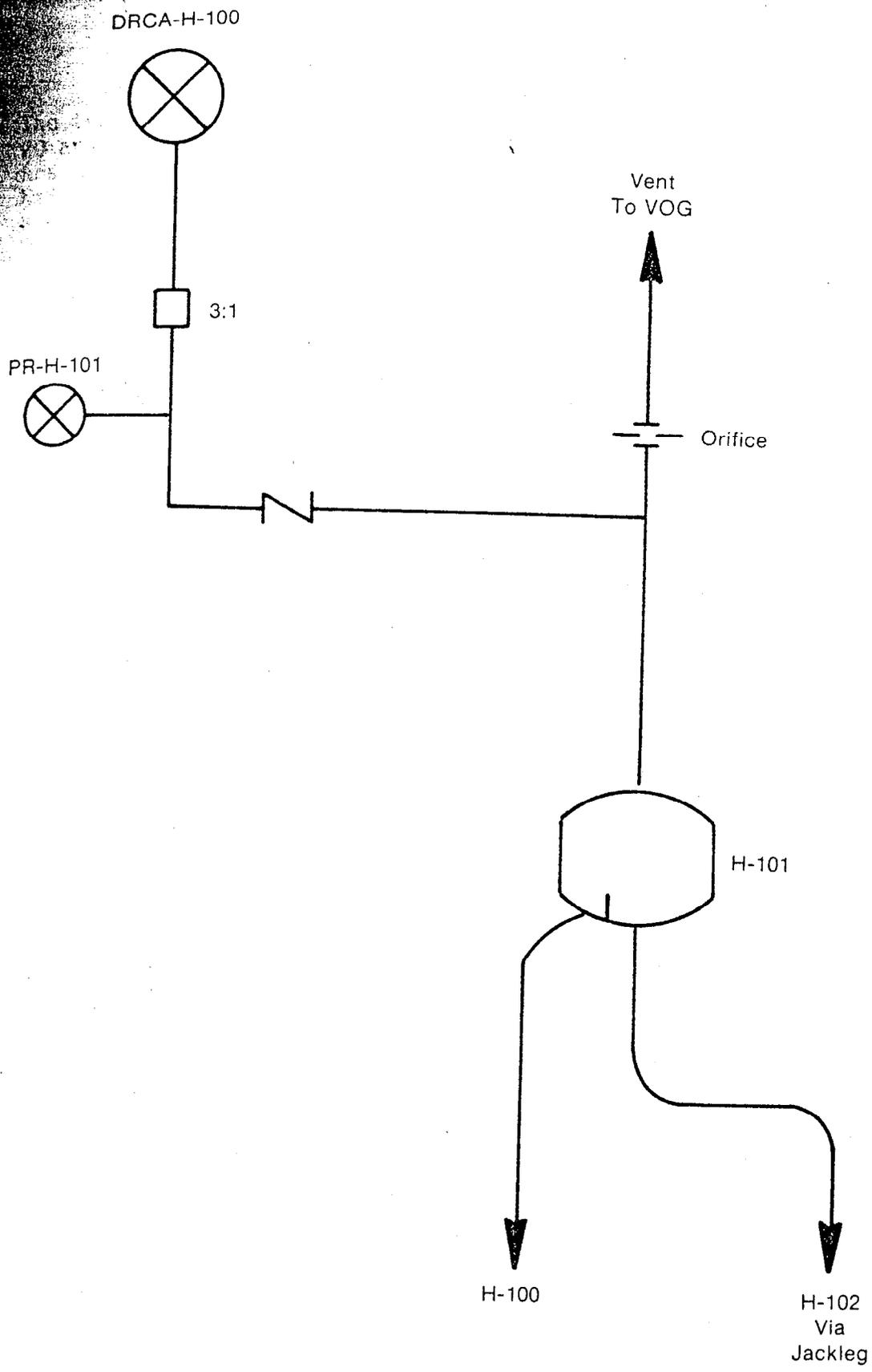
**Figure 5.   Jackleg Control Instrumentation**

ACC-A-3800

11

The test was conducted in four phases during four separate shifts on October 20 and October 21, 1978. The first phase, conducted between 1105 and 1238 hrs on October 20, verified jackleg pressure control to 0.01 psi and column height control to the limit of the accuracy of the water manometer ($\sim$0.05-in. $H_2O$). During this phase of the test, no water was observed to accumulate in U-121, the raffinate receiver to which the jackleg drained.

The P-102 column was filled with water and the initial levels and pressures recorded. With the DRCA-P-102 controller in manual mode, the set point on the controller was slowly decreased in increments of 0.3 to 0.5% at 5-minute intervals. The resulting control point on the controller, the manometer pressures, the pressure reading on the jackleg pressure recorder, and the level in the collection tank (U-121) were recorded.

When it became evident equilibrium conditions were established in less than 5 minutes following a set point adjustment, the time interval between adjustments was reduced to 1 to 2 minutes. The set point on the Foxboro controller was changed from 73.3 to 57.0% during this phase of the test, and the jackleg control pressure was reduced from 112.8 to 94.5 in/Hg. Within the limits of the water manometer, the column level was not changed during this phase of testing.

In the second phase of testing, the set point on the Foxboro controller was reduced from 56.5 to 51% in 0.5% increments at 5-minute intervals between 2240 and 2335 on October 20. The jackleg pressure dropped from 90.3 to 86.2 in/Hg. The level in P-102 column did not change.

The third phase of testing showed the ability to control the discharge rate to 0.12 L/hr. The set point on the Foxboro controller was reduced from 51 to 40% from 0130 to 0320 on October 21. A very slight decrease was noted in the height of liquid in the P-102 column, so the controller was left stationary and the resulting decrease in column level was recorded for the period of 0320 to 0800. The column level gradually decreased 1.8 inches during this period. This corresponds to a volume change of 0.57 L, or 0.12 L/hr.

The fourth phase of testing simulated a proposed procedure to alternately raise and lower the liquid level in the column by injecting borated water, and by removing the aqueous solution from the lower head of the column. During the period of 1306 to 1407 on October 21, the liquid level was slowly decreased from 15.8 inches above the DRCA-P-102 high pressure probe to 13.7 inches above. At this point, solution was injected to the column using a positive displacement pump. The level increased to 15.9 inches at 1425. During this period of 1425 to 1504, the level was again decreased from 15.9 to 15.3 inches, corresponding to a discharge rate of 0.30 L/hr.

## 2.3  Conclusions

The demonstrated control of the jackleg pressure to 0.01 psig or better, was adequate to control H-100 column height to 0.3 inches. The jackleg control pot pressure, at 5.1 psig, was adequate to maintain column

height control to fill the H-100 column to the overflow height, if needed, with any solution of a sp.gr. less than 1.8. The jackleg pressure required to cause the air to evacuate the jackleg and to blow to H-102 was 5.6 psig, assuming a liquid sp.gr. of 1.04.

### 3. Boron Stability

One of the options considered involved the use of poisoned aluminum nitrate solution as a displacement liquid. Such a salted solution would prevent the stripping of uranium from loaded organic phase into the displacement liquid.

A study was made to determine the stability of $H_3BO_3$-$Al(NO_3)_3$ solutions. Fourteen solutions varying in concentration from 0.5 to 0.7M Al and 6 to 10 g/L B were prepared. The appearance of a precipitate, after cooling the solution to room temperature, resulted in the solution being classified as unstable. The following reagents were used:

(1) Solid $H_3BO_3$

(2) Solid $Al(NO_3)_3 \cdot 9H_2O$

(3) $H_3BO_3$ solution, 10 g/L

(4) Plant $Al(NO_3)_3$, 2M (not analyzed)

Samples 1, 2, 3, 4 used reagents 1 and 2.

Samples 5, 6 used reagents 2 and 3.

Samples 9 through 14 used reagents 1 and 4.

Note: The 10 g/L $H_3BO_3$ had to be kept warm to prevent $H_3BO_3$ from precipitation.

Conclusions: The data are plotted (Figure 6) and show the area of stability. Samples (points) represented by Ⓧ took longer to precipitate than samples represented by X. In actual practice, the $Al(NO_3)_3$-$H_3BO_3$ solution should be kept warm (hot) until it is added to H-100. The maximum boron concentration is 6 g/L at 0.5 to 0.7 M Al.

### 4. Determination of Uranium Content in H-100 Column

Information was gathered to determine the uranium content of the H-100 column immediately following the criticality. From two methods of determining the uranium transferred to J-135 with the solutions pumped from the top head, it was calculated there were 8.67 to 8.68 kg uranium in H-100 immediately following the criticality. There were 0.418 to 0.425 kg U in the organic solution transferred to J-135. The organic solution was analyzed to be 6.14 g/L in

13
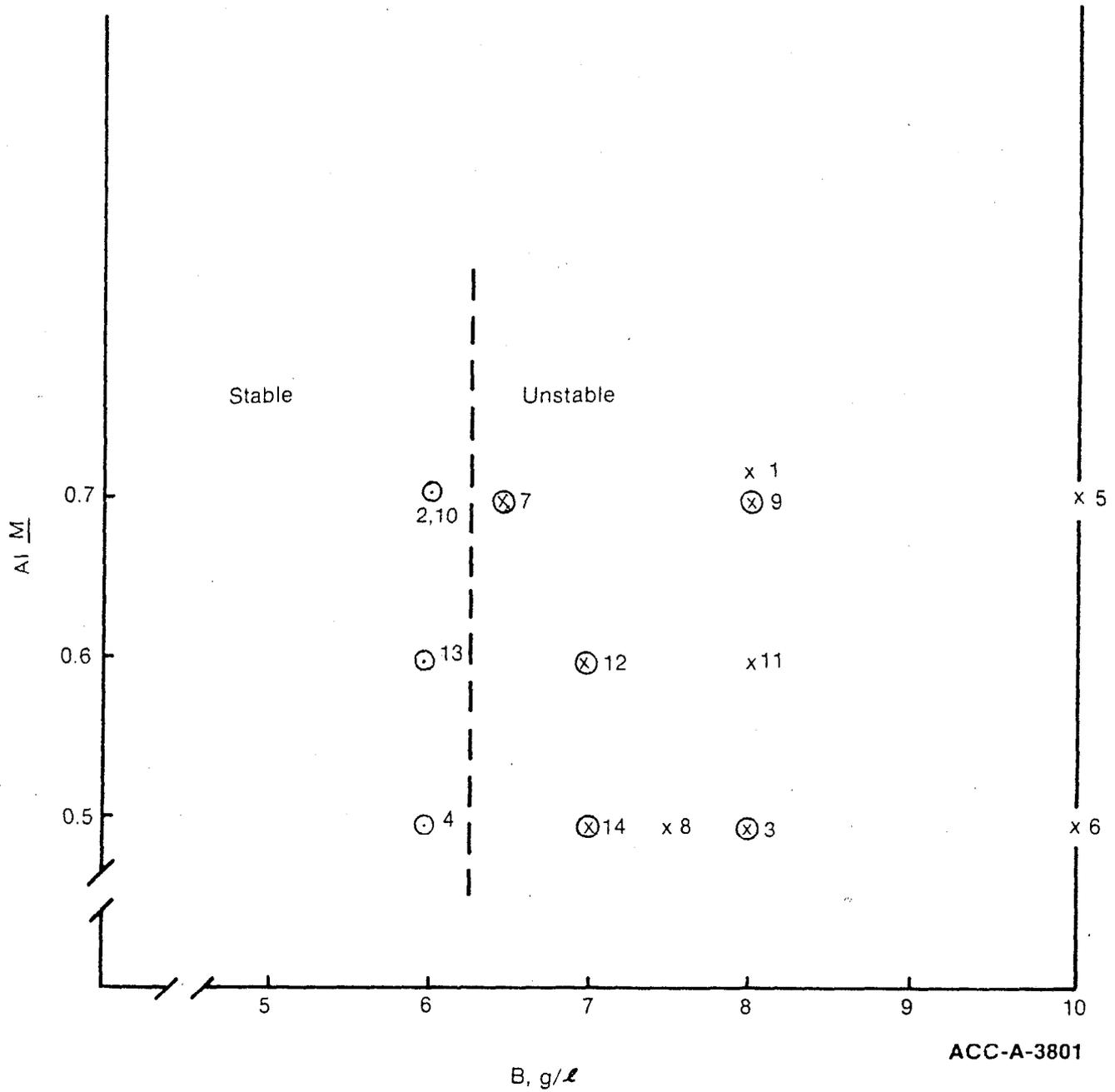
Figure 6. Boric Acid in Aluminum Nitrate Solubility Study

uranium. The aqueous solution contained 8.25 to 8.26 kg U. The aqueous volume was calculated at 364.7 L, which calculates to an average uranium concentration in the aqueous solution of 22.61 to 22.66 g/L total uranium and 18.54 to 18.58 g $^{235}$U/L, assuming an enrichment of 82%.

The uranium content is based on analyses of samples taken from solutions removed from the top and bottom of the H-100 column during recovery operations. Organic and aqueous solutions were removed from the top head of H-100 and transferred to the J-135 tank. Borated water was added to the column in conjunction with uranium removal. When it was verified safe to do so, the remaining contents of H-100 were transferred to G-108 and sampled.

The first removal of uranium from H-100 was 55 L of organic from the top head at 6.14 g/L, 337.7 g U. The second removal was after the addition of 8.7 L of boric acid to the upper head. The liquid level after each removal from the top head was assumed to be identical; therefore, the volume removed would be the same as the volume added. The sample of the organic removed in the second head pumpout was 5.07 g/L U. Thus, 44.1 g U were removed here.

The third removal was 8.5 L at 3.77 g/L = 33.1 g U. The fourth removal was 30% organic and 70% aqueous. The organic phase was not sampled. For the calculation, the uranium content in the organic phase was assumed to be 3.77 g/L. Since 10 L of borated water had been added, 3.0 L organic at 3.77 g/L = 11.3 g U; 7.0 L aqueous at 14.4 g/L = 100.8 g U.

The fifth removal was 10 L at 16.2 g/L    = 162 g U

The sixth removal was 9.8 L at 17.8 g/L    = 174.4 g U

The seventh removal was 9.6 L at 18.3 g/L = 175.7 g U

The eighth removal was 10 L at 18.3 g/L    = 183.0 g U

The ninth removal was 10 L at 18.75 g/L   = 187.5 g U

The tenth removal was 10 L at 17.7 g/L    = 177 g U

The eleventh removal was 10 L at 16.9 g/L = 169 g U.

At this point, the remaining solution in H-100 was transferred to G-108. At the time of the criticality there were 1176 L at 0.0208 g/L U in G-108 or 24.4 g U in G-108. Shortly after the criticality, G-165 was transferred to G-108, leaving 1234 L in G-108 at 0.18 g/L, or 222 g U in G-108 before the transfer from H-100. After H-100 was jetted to G-108, there were 1773 L at 4.026 g/L (average of three samples). Thus, there were 7138 g U in G-108 and subtracting the 222 g U from other transfers gives a net removed from H-100 when transferred to G-108, of 6916 g U. This yields 425.2 g U in the organic and 8245.4 g U removed in the aqueous, or 8670.6 g U total in H-100 following the criticality. To cross-check the assumption of volume removed equaling volume injected, the volume increases in the receiving tank for the transfers from the top head (J-135) were used, and a separate calculation for uranium content was made.

There was a total of 96.6 L of boric acid added to H-100 with corresponding removals of liquid to J-135. Each increment was sampled and the amount of each increment was measured in J-135.

| Removal No. | J-135 Increase | U Conc. | U, grams |
|---|---|---|---|
| 1 organic | 51.1 L | 6.14 g/L | 313.7 |
| 2 organic | 12.4 | 5.07 | 62.9 |
| 3 organic | 8.3 | 3.77 | 31.29 |
| 4 organic | 2.7 | 3.77 | 10.18 |
| 4 aqueous | 5.1 | 14.4 | 74.0 |
| 5 aqueous | 10.3 | 16.2 | 166.4 |
| 6 aqueous | 10.3 | 17.8 | 182.8 |
| 7 aqueous | 11.3 | 18.3 | 207.0 |
| 8 aqueous | 10.3 | 18.3 | 187.9 |
| 9 aqueous | 9.3 | 18.75 | 173.4 |
| 10 aqueous | 10.3 | 17.7 | 181.8 |
| 11 aqueous | 10.3 | 16.9 | 173.6 |
| | | | 1765.0 g |

Total U removed to G-108 = 6916.0 g

Total U in H-100 after the criticality = 8681.0 g U

The maximum concentration of uranium in the aqueous phase that is in equilibrium with the Amsco-tributyl phosphate phase was also calculated. The equilibrium concentration may be calculated from an equilibrium constant relating the uranium concentration in the aqueous phase ($U_a$) to the uranium concentration in the organic phase ($U_o$), to the aqueous nitrate concentration ($NO_3^-$), and to the tributyl phosphate concentration in the organic phase (TBP). The equilibrium expression is given in Equation 1.

$$K_u = \frac{(U_o)}{(U_a)\ (NO_3^-)^2\ (TBP)^2} \tag{1}$$

The equilibrium constant ($K_u$) was estimated from data given in HW-19140 and from the analysis of unpublished data. Concentrations for tributyl phosphate and uranium are from Table II.

16

## TABLE II

### CHEMICAL COMPOSITION OF ORGANIC PHASE

| | |
|---|---|
| TBP | 5.63% |
| URANIUM | |
|    By Colorimetric | $6.00 \pm 0.21$ g/L |
|    By Isotope Dilution | 6.23 g/L |
| ENRICHMENT | 81.9% |

Certain assumptions were necessary to calculate a conservatively large $U_a$:

(1) TBP = 5.55%. This is two standard deviations lower than the reported 5.63%.

(2) $U_0$ = 6.23 g/L. This is the highest uranium analysis reported.

(3) The only source of nitrate in the aqueous stream is uranyl nitrate.

(4) There are no other extractable materials in solution.

(5) Enrichment of uranium in the plate section of the extraction column is 82% $^{235}U$, and the average atomic weight is 235.5.

$K_u$ was evaluated at more than 4.0. To support this value, the equilibrium constant was estimated at 5.6 from data presented in the thesis, "Equilibria in Extraction of Nitrates from Aqueous Solution by Tributyl Phosphate," by Lucien Donadieu, 1956, from the Massachusetts Institute of Technology. A value of 4 was used to give the highest aqueous uranium concentration. The calculations are summarized below:

$$K_u = 4 = \frac{(U_0)}{(U_a)(NO_3^-)^2(TBP)^2} \tag{2}$$

$$4 = \frac{(6.23/235.5)}{(U_a)(2 \times U_a)^2 (0.2285 - 2 \times 6.23/235.5)^2}$$

$$U_a^3 = 0.05366 \ \underline{M}^3$$

$$U_a = 0.3772 \ \underline{M} = 89 \text{ g/L uranium}$$
$$= 73 \text{ g/L } ^{235}U$$

Maximum uranium concentration in Aqueous Phase

87 g/L total, or
73 g/L $^{235}U$

# IV.  SAFETY JUSTIFICATION

Using information gathered in support activities, a model was developed and
an endpoint for the removal operations determined.  This was defined as the
point at which sufficient boron had been introduced into the column and dis-
tributed and/or the uranium so diluted that criticality was incredible either
in the column or in the receiving vessel.  Subsequently, the implementation
of the plan of action was carefully monitored; samples were taken at each
step to verify that conditions within the H-100 column corresponded to those
identified during support activities and mockup.

## 1.  Model of H-100 Recovery

During the first step, the organic solution above the lower DRCA probe will
be removed.  Nothing will hapen in the column below this probe during this
step.

Next, boric acid solution tagged with lithium will be added to the top of
the column in 10-L batches.  After each addition of 10 L, a hold time of
30 minutes should be allowed for the boric acid to finish flowing through
the organic in the plate section.  Then a 10-L batch of organic will be
removed through the lower DRCA probe.

It is estimated that a maximum 46.2 L of organic solution is present in
the column, and therefore, approximately five 10-L withdrawals will be
necessary to remove all the organic.  Removing the organic solution, using
the procedure described above will take about 20 hours.  This procedure
allows adequate time for complete separation of the phases.  Some aqueous
solution will be present in the fifth 10-L withdrawal, indicating that all
but a very small amount of organic has been removed from H-100.

At this point an 8.5 g/L boric acid solution with 1.45 g/L cadmium as tracer
will be added to the bottom of H-100 in 10-L batches at the rate of 15 L/hr.
Then the solution from the top of H-100 will be removed down to the lower
DRCA probe.  This solution from the top of H-100 will be analyzed for Cd, B,
and U.  Based on the Cd analysis, the Cd-to-B ratio in the solution fed to
the bottom of H-100; the minimum boron with Cd in the sample is to be cal-
culated.  This addition and withdrawal procedure will be repeated until
the boron concentration has passed through a minimum and the B/U ratio
(based on minimum calculated boron) shows that remaining aqueous solution
is safe at any location in H-100 (Figure 7).  If significant organic appears
in any of these 10-L withdrawals, the procedure will be halted until the
sparging of the level probe separates the phases.  Using the criteria
established in Table I will result in a criticality-safe solution for trans-
fer to G-108.

Figure 7 shows the anticipated trends in the concentrations of uranium, boron,
cadmium, and lithium in the solution removed from the top of H-100 with time.
As boric acid and lithium are added to the top of the column, they will strip
a small amount of uranium from the organic.  Therefore, the concentration of
uranium in the organic should decrease slightly for the first 20 hours.

18

## 1.1   Uranium Trends

There will be a sharp decrease in U concentration when aqueous is first being removed from the column. The concentration will be low due to the 50 L of boric acid solutions added to the top of the column. Any uranium in this solution is due to diffusion of uranium upward. Once this 50 L of solution is removed, there will be a sharp increase in the uranium concentration. The U concentration will continue to increase until the solution from the middle section of H-100 is removed. This concentration will be slightly lower than the maximum concentration prior to boron addition of boron solutions at both ends of the column. Then the concentration of U will decrease steadily as the boric acid added into the bottom of the column difuses into the aqueous and eventually forces all the uranium in H-100 to the top.

For the first 20 hours (organic removal time) the boron concentration at the top of H-100 will be zero, because only organic will be removed from the column. Once aqueous is removed from the top of the column, the boron concentration will jump to a concentration of approximately 9 g/L. This concentration of boron will steadily decrease to a minimum as poorly mixed solution from the middle of the column is removed. By this time, boron will have been added to the bottom of the column and will be diffusing upward. This will result in an increasing boron concentration until the concentration of boron fed to the bottom of the column is reached.

Lithium will be added with the boric acid to the top of H-100, so it will peak as soon as the aqueous phase begins to exit the column. Then it will steadily decrease as more of the column contents are removed. The concentration of Li will eventually fall to an extremely low level.

Cd tracer will be added to the B-solution added to the bottom of the column as a cross-check. When the B concentration begins to climb after the dip in the curve shown in Figure 8, the Li concentration should be decreasing asymtotically to zero, while the Cd concentration should be increasing to a B/Cd ratio equal to that added to the bottom of the column. Thus, one will know conclusively that the high B concentration is not B from the additions to the top, but B from the additions to the bottom of H-100, and can assume that there is B poison throughout the plate section.

A safe concentration of uranium and boron concentration in the head of H-100 must be determined before boric acid can be added continuously to the bottom of H-100 while aqueous solution is removed from the top head. The critical U concentrations as a function of B concentration for 150 L of solution in the top head were calculated.

> (1) When the H-100 column is uniformly poisoned with 2.5 g B/L, the system will be subcritical for the aqueous saturation loading of 89 g U (82)/L. This is based on the effect of boron on an infinite system. For this conservative basis, the Safety Margin Limit would be 2.5 g B/L and a limiting condition for operation of 3.0 g B/L would allow a margin of over 15% in $K_{eff}$.

> (2) For 100 g $^{235}U$/L or less, an infinite system of boron and uranium will be subcritical if the B/$^{235}U$ ratio is greater than 0.8.

19

89 g/ℓ

Concentration

Organic Removal

U235

8-9 g/ℓ

B

6 g/ℓ

Cd

Li

← 20h →

Time →

ACC-A-3802
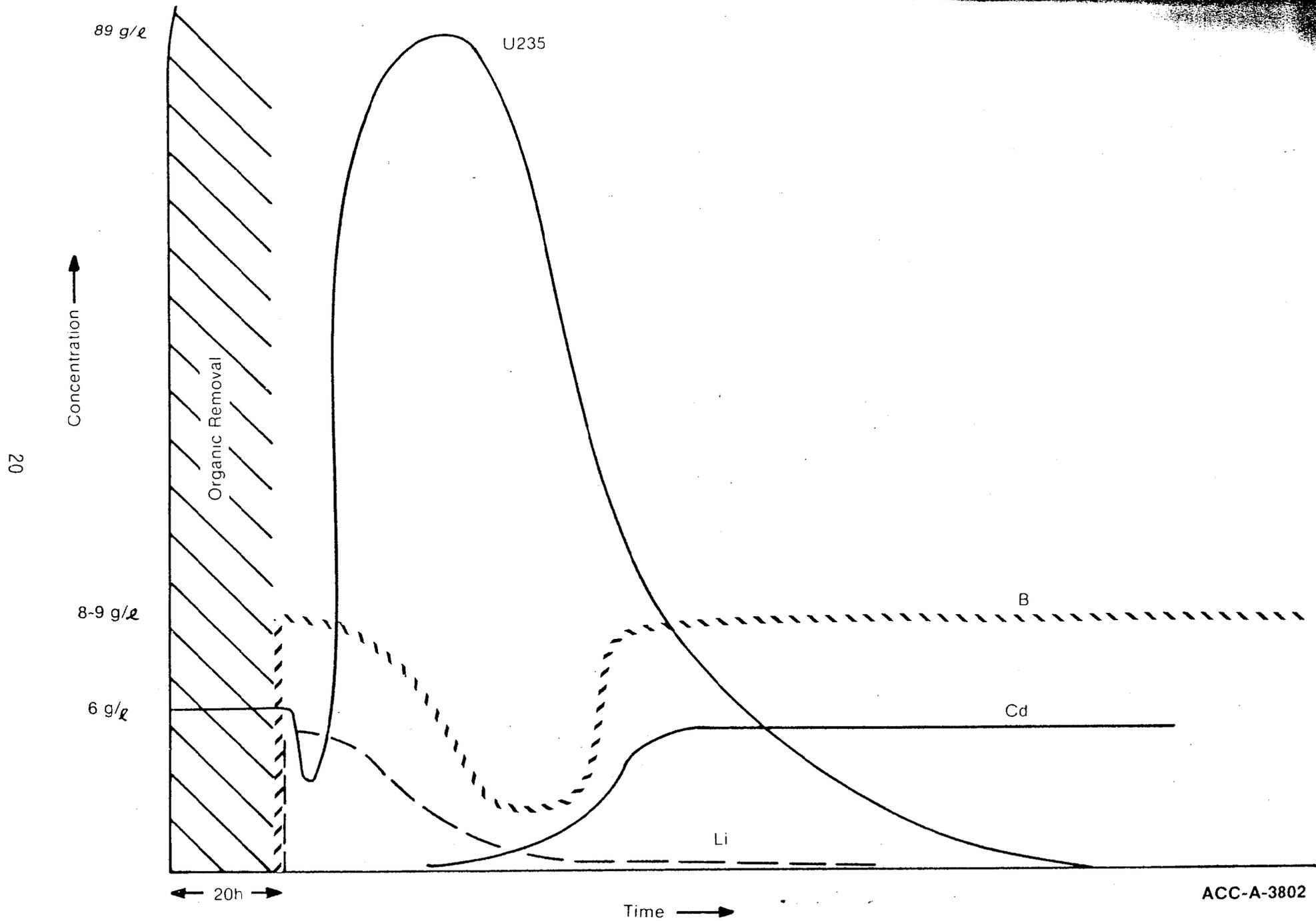
Figure 7.   Qualitative Model of Solution Composition During Recovery of Uranium From H-100

(3) For a 160-L system (Upper Head: H-100) less than 43 g $^{235}$U/L and 1 g B/L; >68 g $^{235}$U/L and 2 g B/L; and 82 g $^{235}$U/L with 2.5 g B/L should be subcritical. This is from an extrapolation of unpublished data.

(4) Note that after 10 additions of 10 L each to the bottom head, the aqueous solution in the column, which might have the higher $^{235}$U loadings, will be in the top head. At this point, the highest $^{235}$U concentration would be under 20 g/L, and a safe B loading would be under 1 g B/L. This assumes no removals from the bottom head.

To assure that the critical concentrations are not exceeded, critical values for uranium concentrations for 0.5 g/L less in boron concentrations were plotted against boron concentrations (Figure 8). The following paragraphs explain how to use this graph and the general procedure to follow for uranium addition.

Add boric acid solution, for which the Cd and B ratio has been determined, in 10-L increments to the bottom of H-100. After each 10 L has been added to the bottom of H-100, pump 10 L of liquid from the bottom DRCA probe. The aqueous solution is pumped from this probe, analyze it for Cd, B, and $^{235}$U. Based on the cadmium analysis and the Cd-to-B ratio in the feed to the bottom column, calculate the boron concentration in the sample. If the analysis for $^{235}$U is less than the $^{235}$U concentration obtained from Figure 8 at that boron concentration, continuous addition of boric acid at the bottom of the column at 15 L/hr may be started; however, the pumpout ratio from the top must be equal to or greater than the feed rate to the bottom of H-100. Sample the aqueous solution being removed from the bottom DRCA probe every 2 hours and determine Cd, Li, B, and $^{235}$U. When the B concentration as determined by Cd analysis exceeds 2.5 g/L, the contents of H-100 may be jetted to G-108.


## 2. Sampling

After implementing the plan of action, careful monitoring was necessary to ensure that the operation proceeded according to expectations. Sampling of the solution removed from H-100 provided data that demonstrated the validity of the course of action. Concentrations of boron, lithium, cadmium, and uranium conformed with those expected as a result of support activities and modeling. The sampling also provided appreciable information about the dispersing of the boric acid and about the distribution of the aqueous and organic solutions within the H-100 column.

### 2.1 Uranium

The uranium concentration in the solution removed from the top of H-100 followed the expected trends. The initial concentration decreased with each removal of organic solution due to the stripping action of the boron solution added to the top of the column. The concentration in the aqueous solution

21
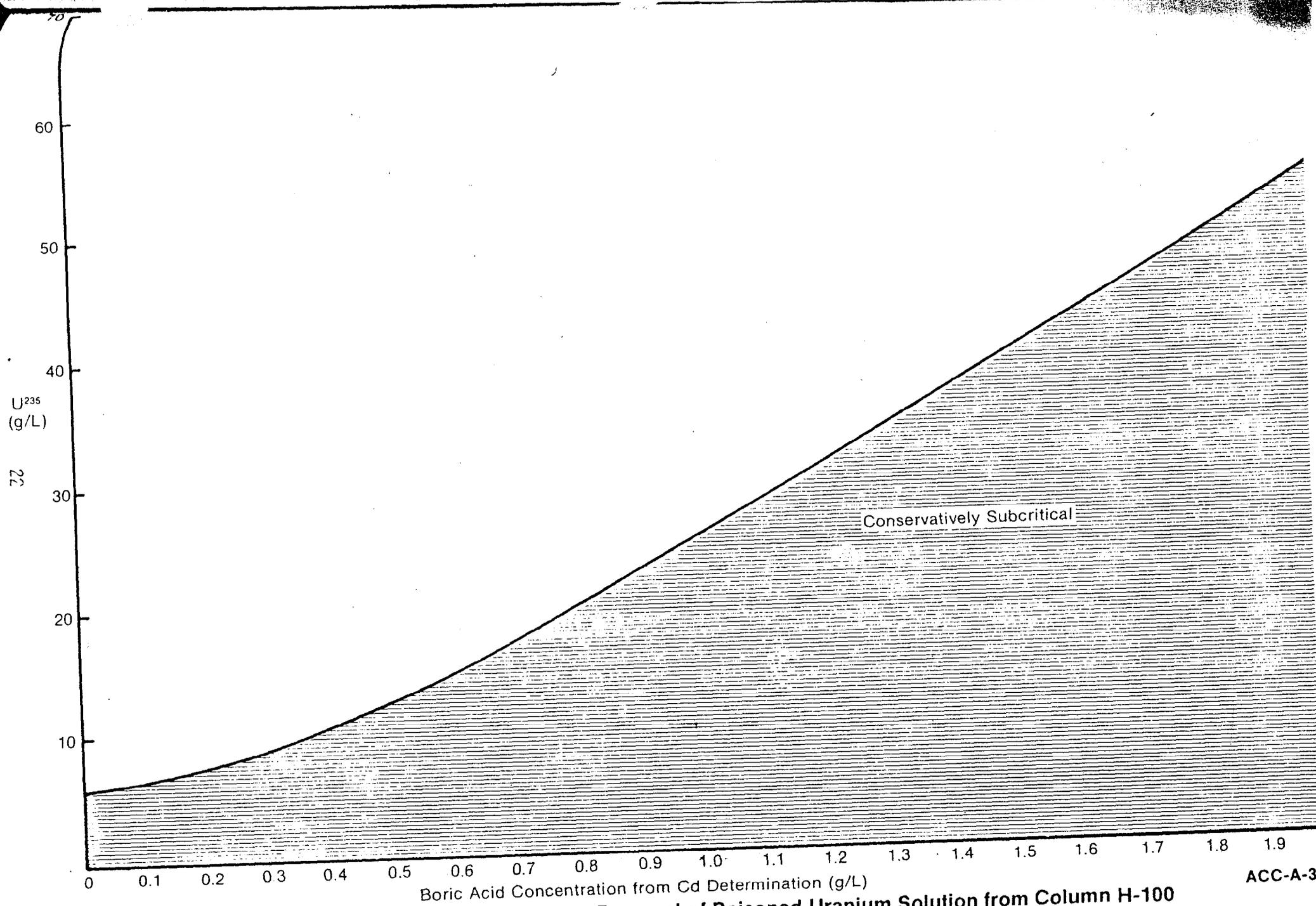
**Figure 8.** Criticality Control Diagram for Removal of Poisoned Uranium Solution from Column H-100

started at about 14.4 g/L and slowly increased, leveling off at about 19 g/L (Figure 9), and then slowly decreased with successive removals. The uranium concentration change was small for the aqueous solution removed, indicating the column was well mixed before addition of the boron solutions to the top and bottom of H-100. The maximum uranium concentrations occurred in the same solutions as the minimum boron concentration as would be expected. This shows that uranium and boron mixed and diffused through the column in a similar manner.

## 2.2  Lithium

The lithium concentration in the solution removed from the top of H-100 followed the expected trends. The concentration of lithium was not determined in the organic solution removed from H-100. The first aqueous solution removed had a lithium concentration of one-third the lithium concentration in the boron solution added to the top of H-100. This shows that significant down-mixing occurred in the column during the time between the first addition of boron solution to the top of H-100 and the first removal of aqueous (3-1/2 hours). The lithium concentration dropped off steadily as more aqueous was removed from the column, leveling off at about 0.06 g/L with the tenth and eleventh removals (Figure 10). Good mixing is again demonstrated by the presence of lithium in the tenth batch of solution removed from the column after the initial lithium addition.

## 2.3  Cadmium

The cadmium concentration in the solution removed from the top of H-100 followed the expected trends. The concentration of cadmium was not determined in the organic solution or the first aqueous solution removed from H-100. Cadmium was detected in minute amounts in the first solution removed that contained only aqueous. This indicates that a very small amount of boron added to the bottom had moved to the top in 30 minutes. The concentration then increased steadily as more solution was removed from the top showing that more and more of the boron added to the bottom was mixing to the top of the H-100 (Figure 11).

## 2.4  Boron

The boron concentration in the solution removed from the top of H-100 followed the expected trends. The first aqueous solution removed contained the highest concentration (4.14 g/L) due to the 27.2 L of 9.0 g/L boron solution added to the top. The fact that the concentration more than halved from its original value indicates that good down-mixing in H-100 took place as predicted. The concentration decreased with the next three removals and leveled off at 1.24 g/L (Figure 12). The concentration then rose slowly with further removals, indicating that boron added to the bottom of H-100 had mixed upward.

## 2.5  Organic Removal

Since no significant aqueous solution was reported in the three removals from the top of H-100, and since no significant organic was reported in the subsequent removals, phase separation in H-100 was virtually complete as expected from pilot-plant mockup studies (Figure 13).

## 2.6  Distribution of Solutions within the H-100 Column

Figures 14 through 28 show the H-100 column and its contents during the sequence of the plan of action.
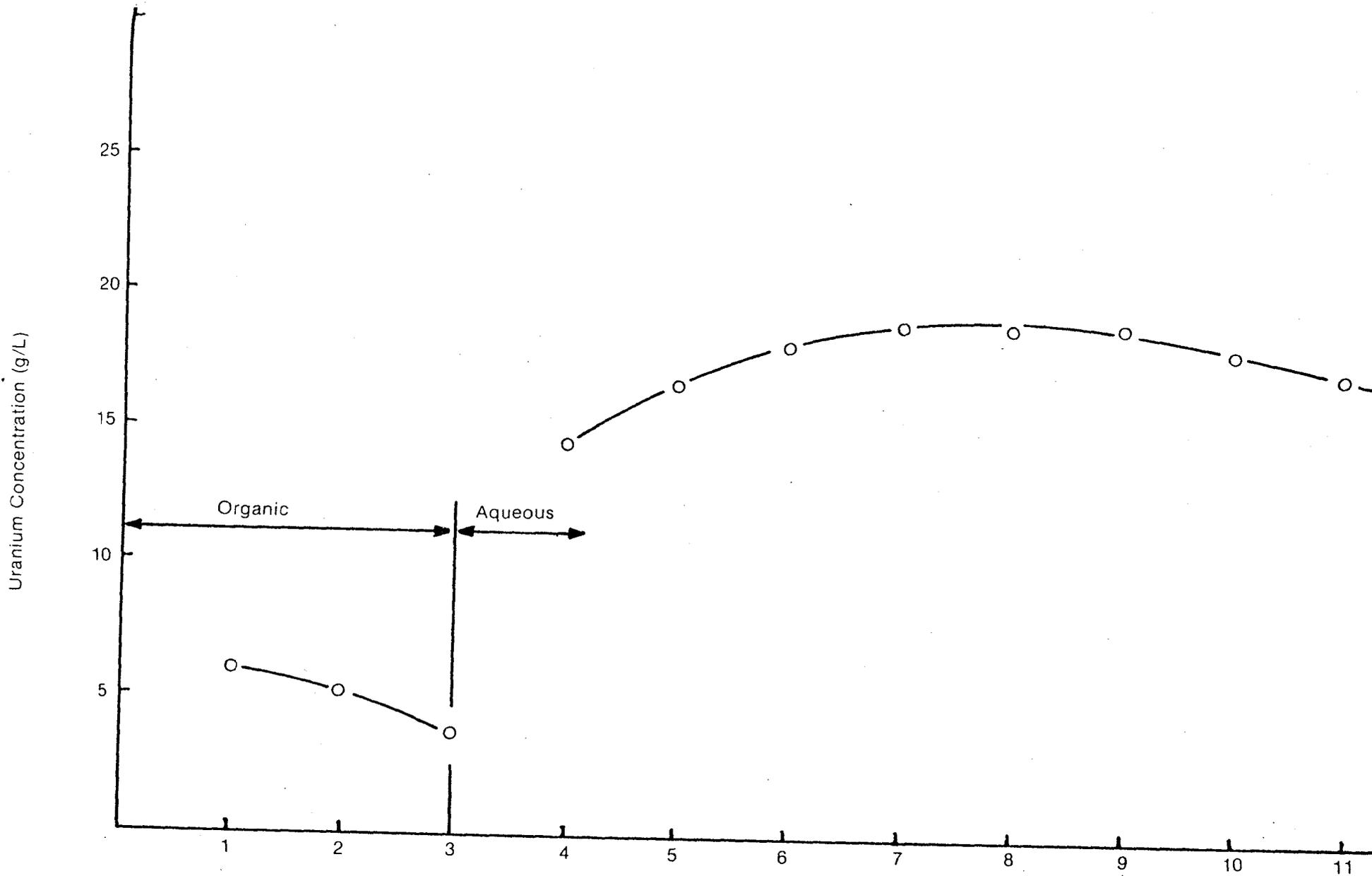
Figure 9.   Uranium Concentration in Solution Removed From Top of H-100

ACC-A-3803
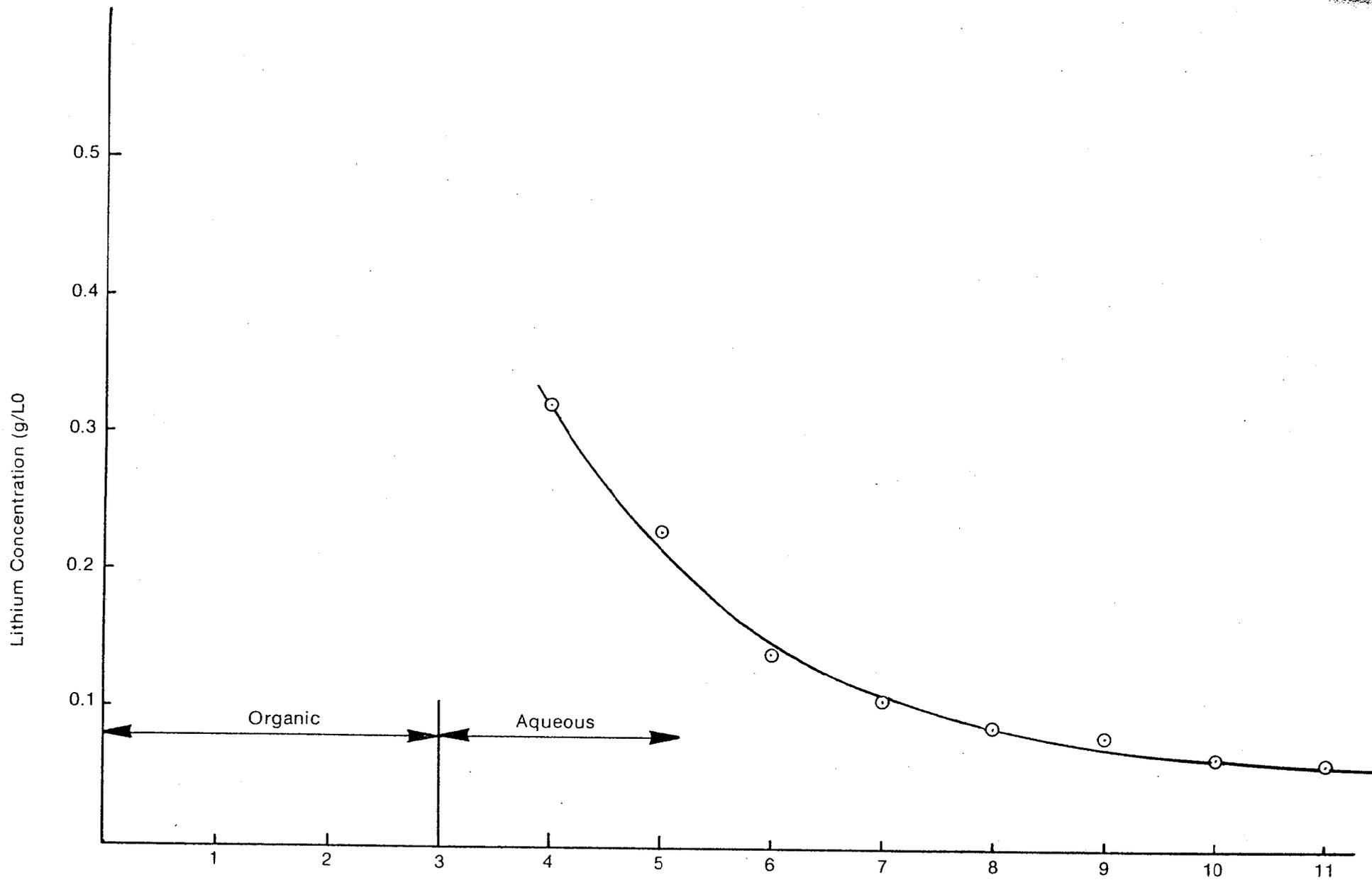
Figure 10.   Lithium Concentration in Solution Removed From Top of H-100

25
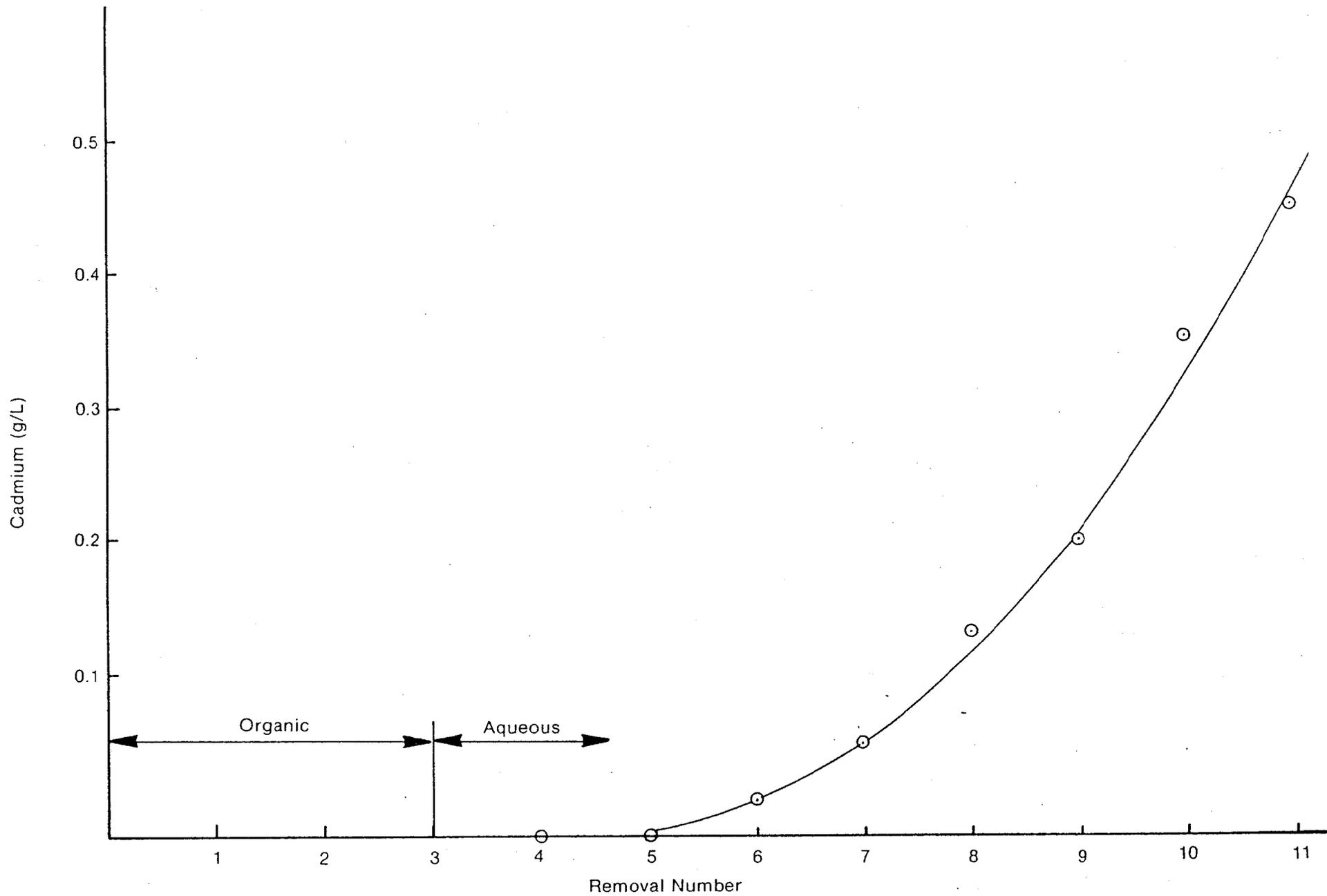
ACC-A-3795

Figure 11. Cadmium Concentration in Solution Removed From Top of H-100
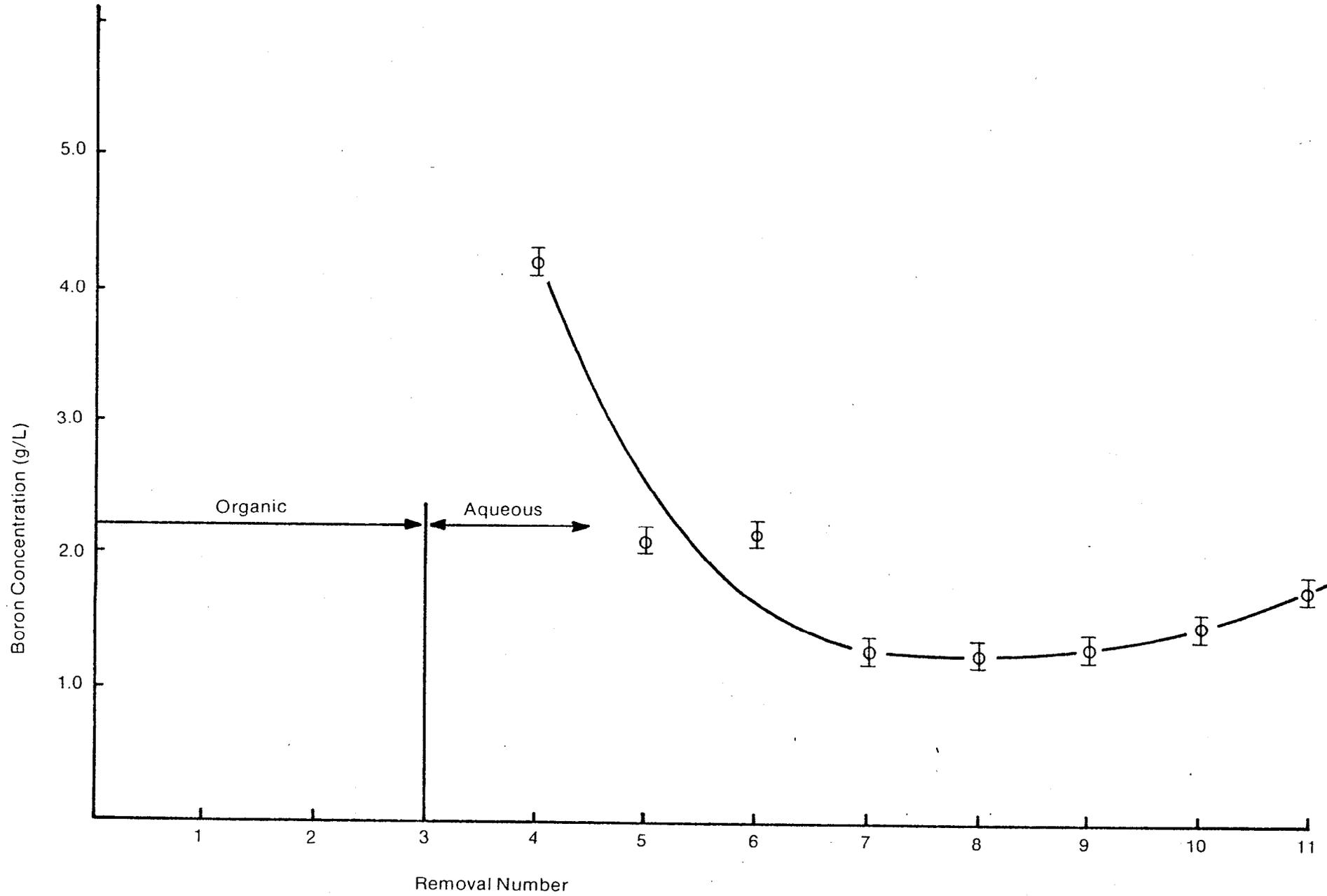
ACC-A-3796

Figure 12.  Boron Concentration in Solution Removed From Top of H-100
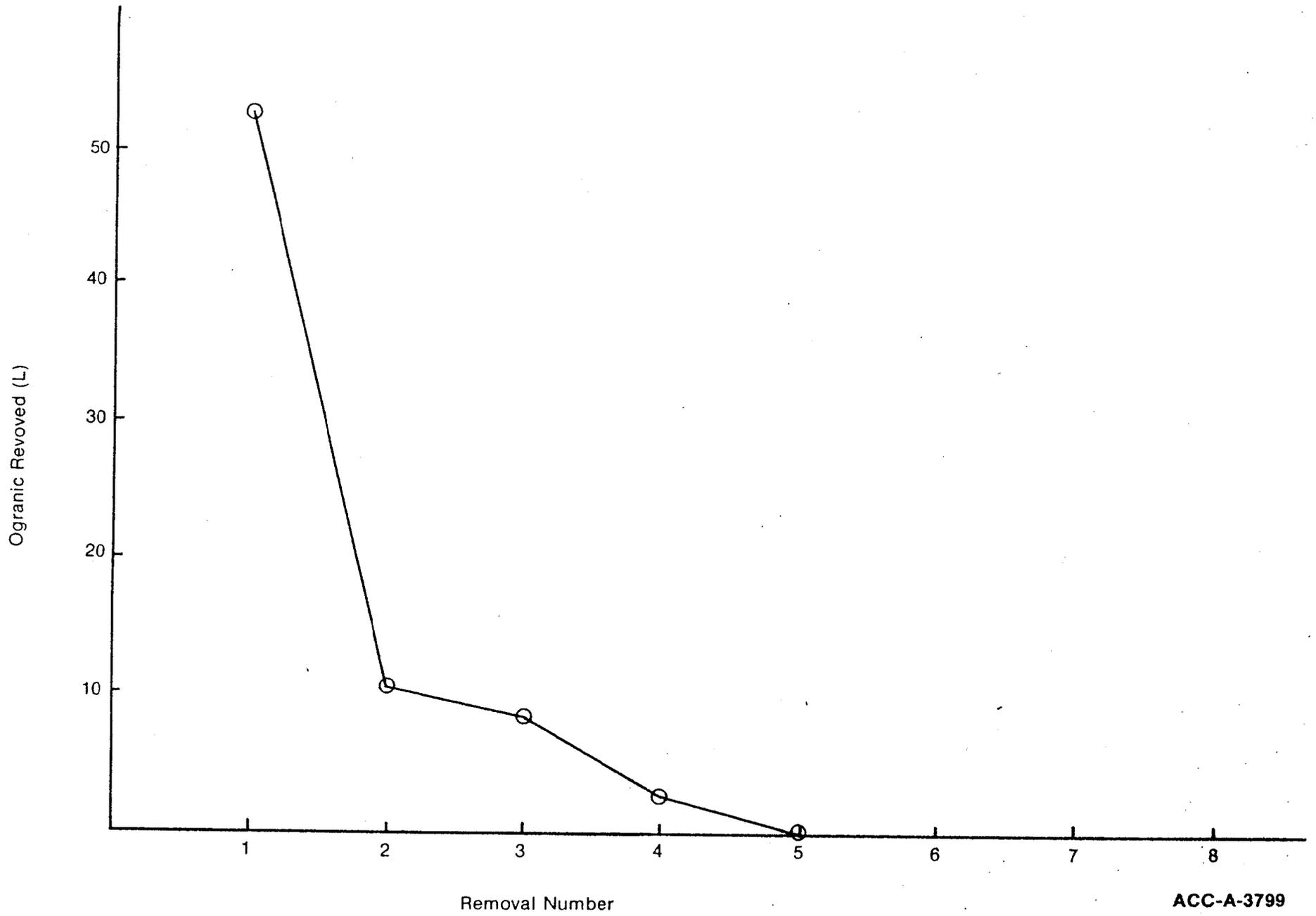
Figure 13.   Organic Removal From H-100

ACC-A-3799

28

174 s.q. organic)

H-100
(1B Column)

Volume Organic = 81 liters

DRCA

6.4"

3"

Organic

28.7"

162"

Organic

Liquid Level

Upper Tangent

Interface

Aqueous

Volume Aqueous
= 362.5 liters Aqueous

92.3'

121"

181"

LR

ACC-A-3804
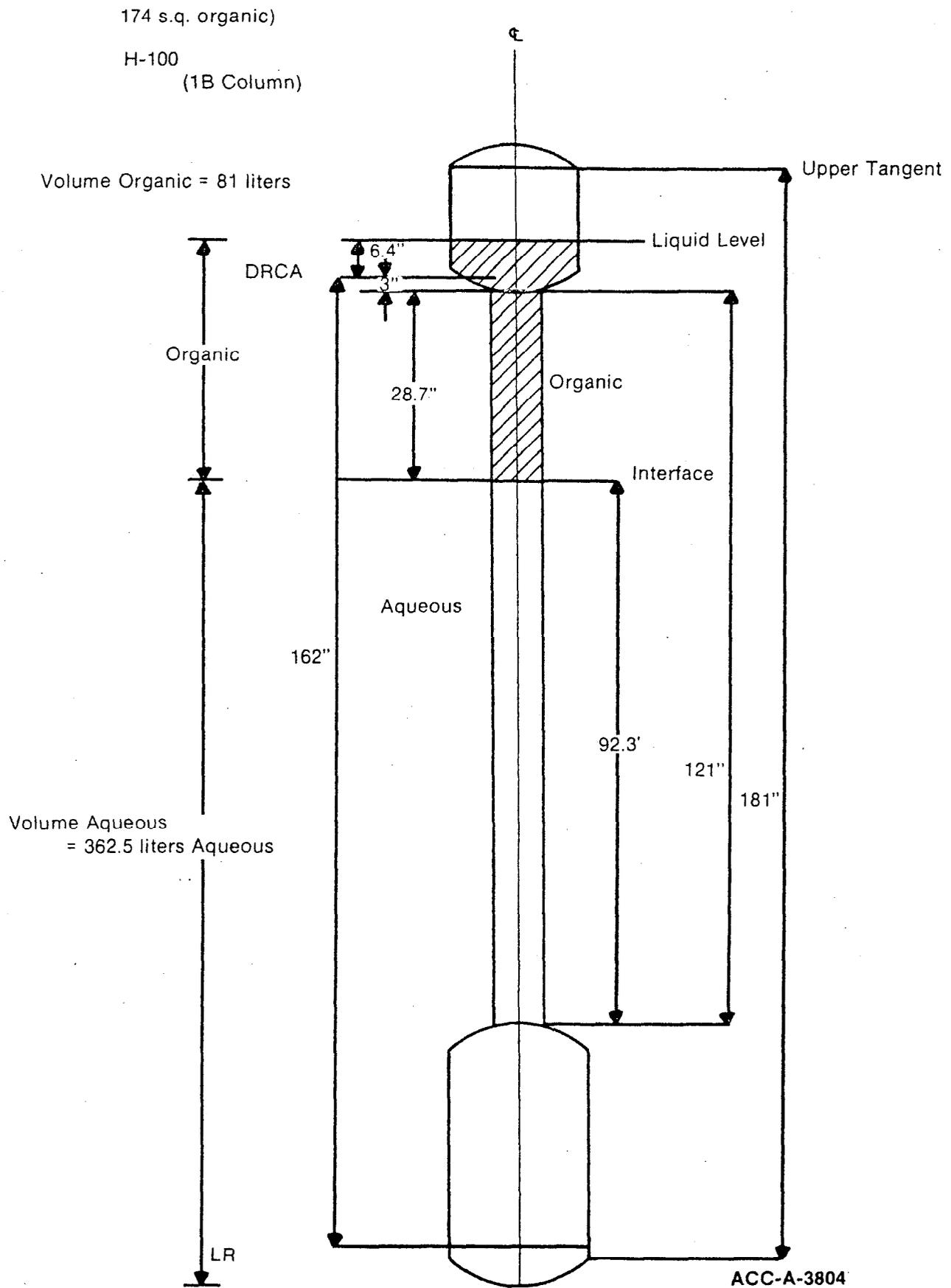
**Figure 14    Relation of Organic to Aqueous in H-100 Prior to First Injection**

29

(10 Liters Borated $H_2O$, 82.6 g Boron)

Volume Organic = 80 liters

Tangent

Liquid Level

7.6"

DRCA

3"

28.5" Organic

≥ 17.9

Interface

169.6"

103"

141" Aqueous

121"

181"

162"

Volume Aqueous = 371

38"

LR

ACC-A-3805
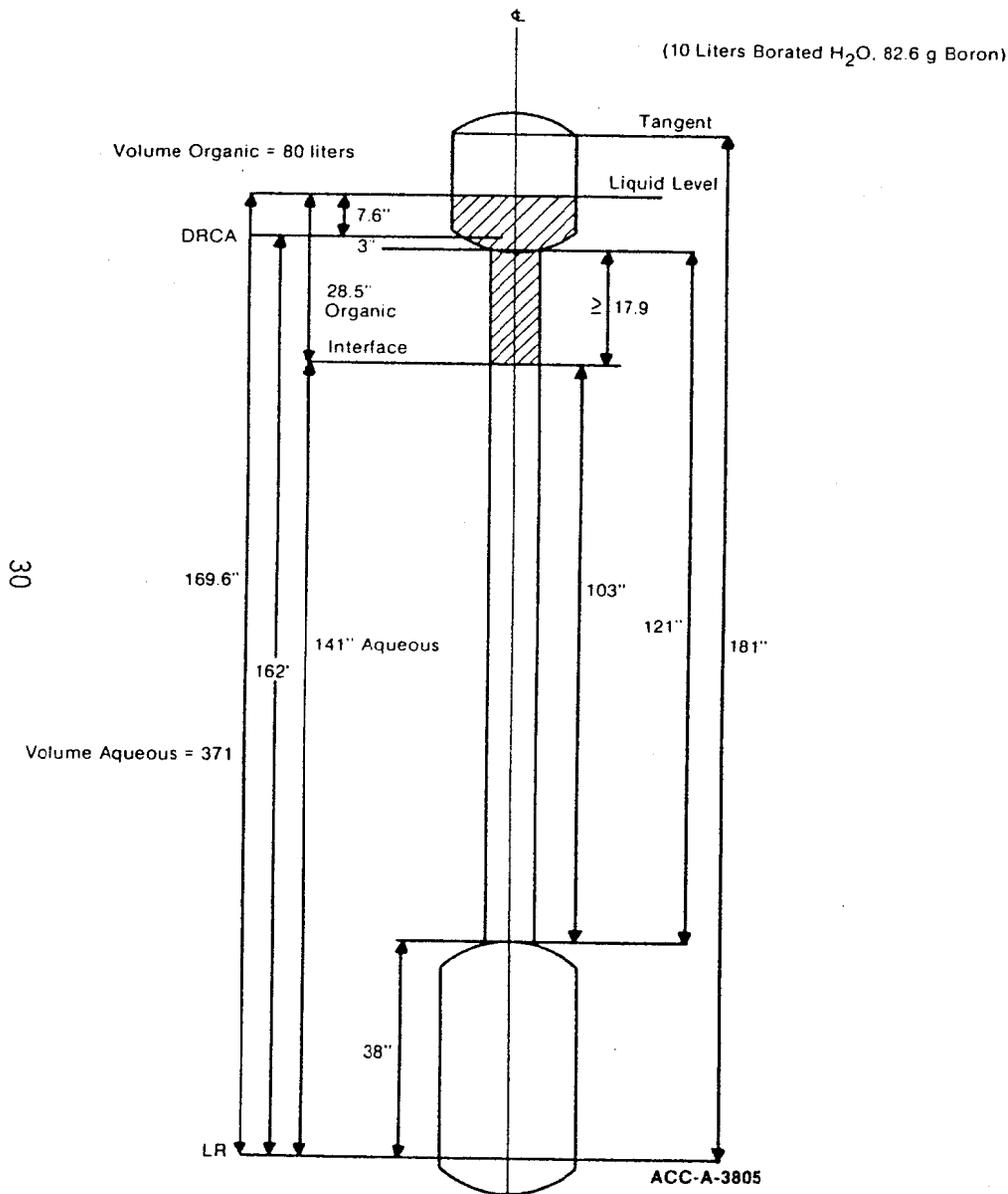
**Figure 15   Relation of Organic to Aqueous in H-100 After First Injection**

DRCA

Liquid Level

Organic

Interface

Aqueous

LRA

ACC-A-3806
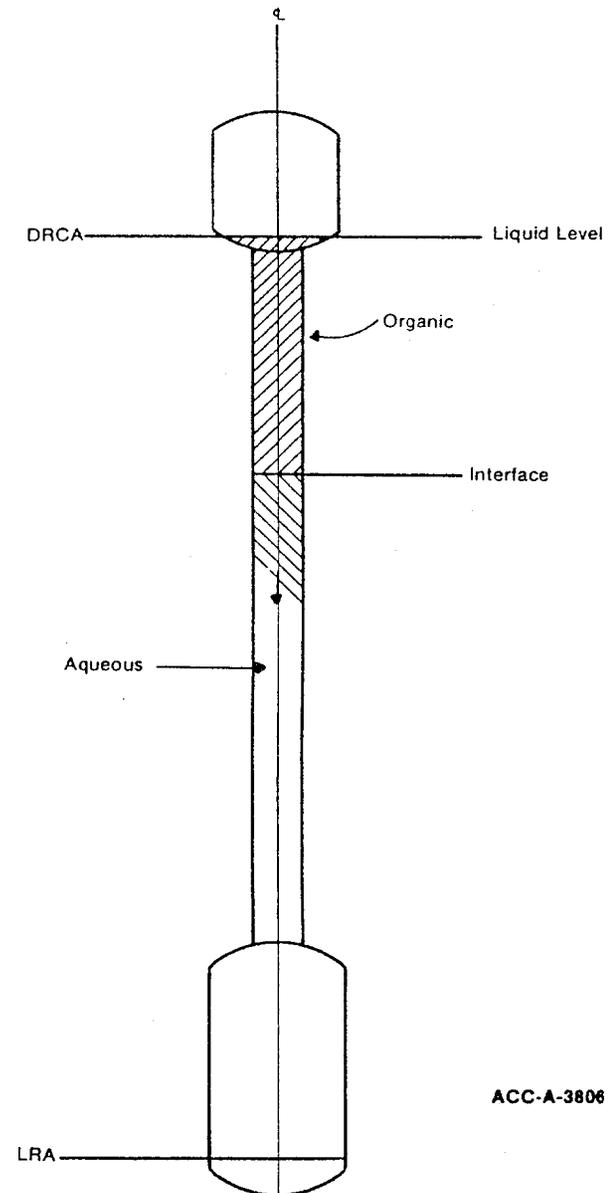
**Figure 16   Relation of Organic to Aqueous After First Organic Pump-Out**
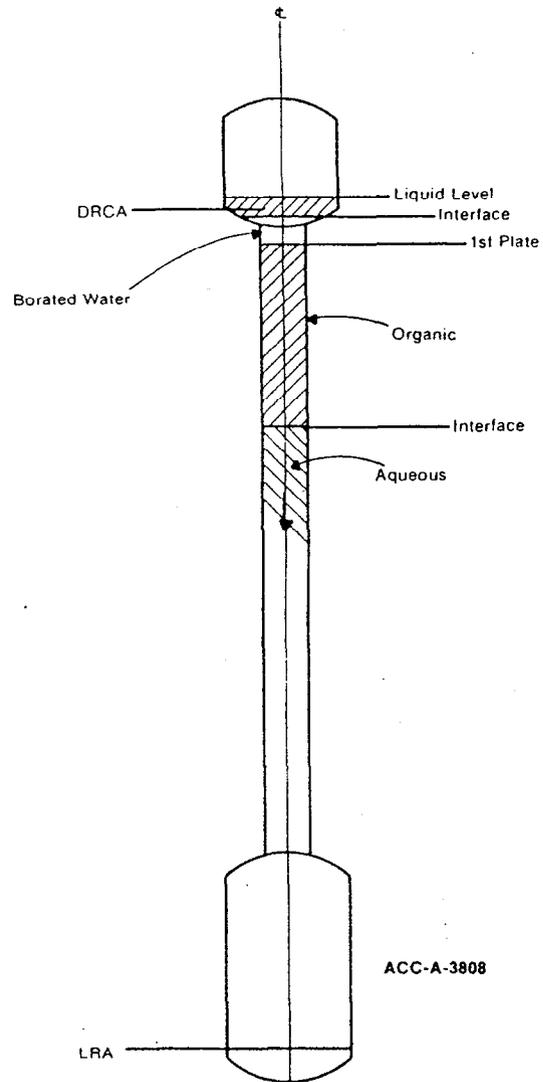
Figure 17   Relation of Borated Water, Organic, and Aqueous After First Borated Water Addition to Top
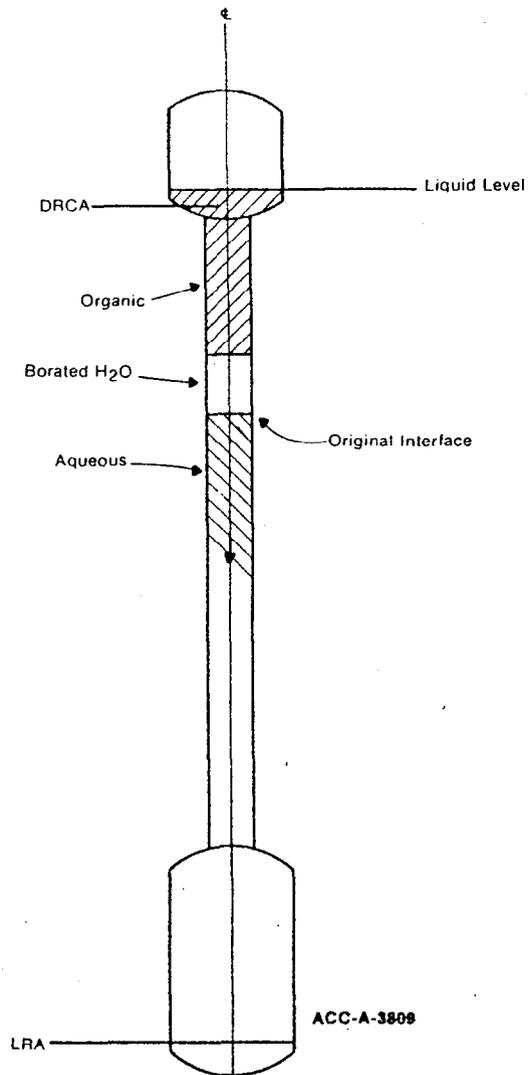


Figure 18   Relation of Organic, Borated Water, and Aqueous After the First Borated Water Addition to Top Reached the Aqueous Interface
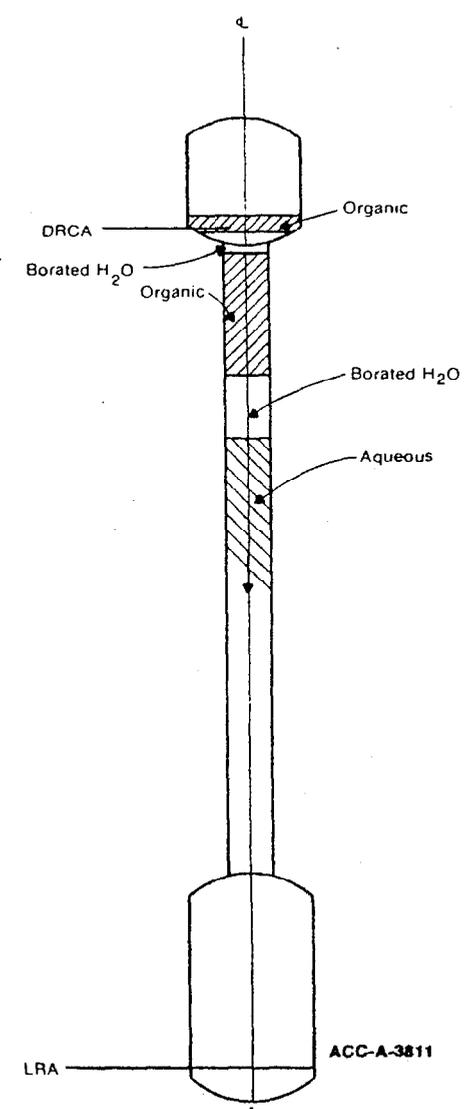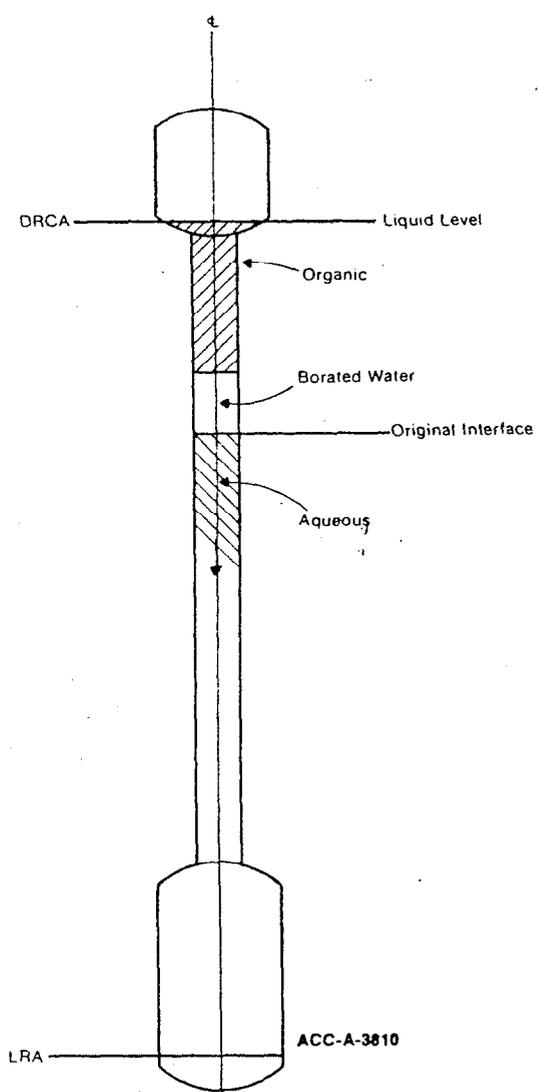
Figure 19   Relation of Organic, Borated Water, and Aqueous After Second Organic Pump-Out
From Head



Figure 20   Relation of Borated Water, Organic, and Aqueous After Second Borated Water
Addition to Top
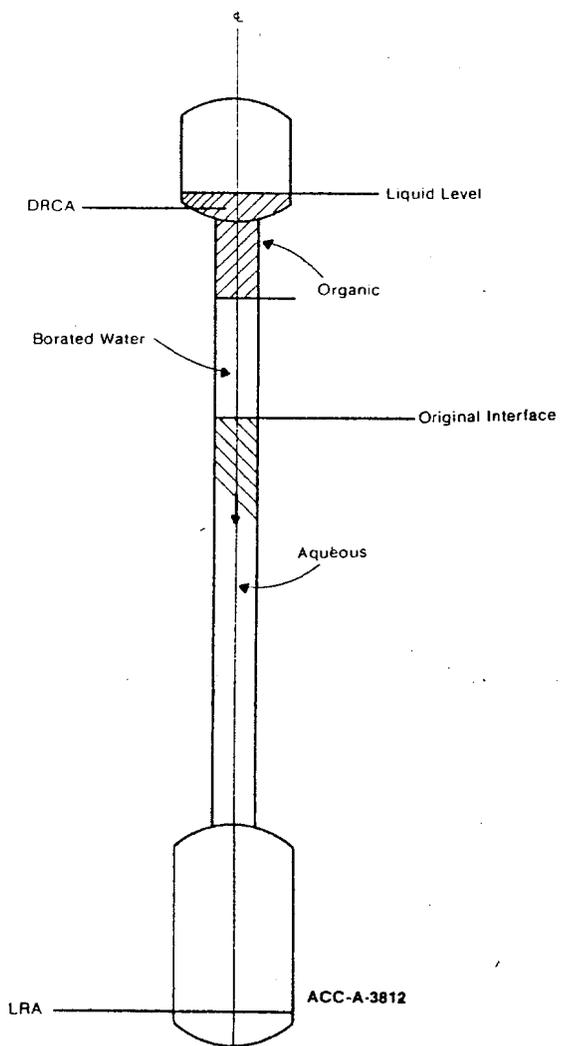
**Figure 21  Relation of Organic, Borated Water, and Aqueous After the Second Borated Water Addition to Top Reached the Aqueous Interface**
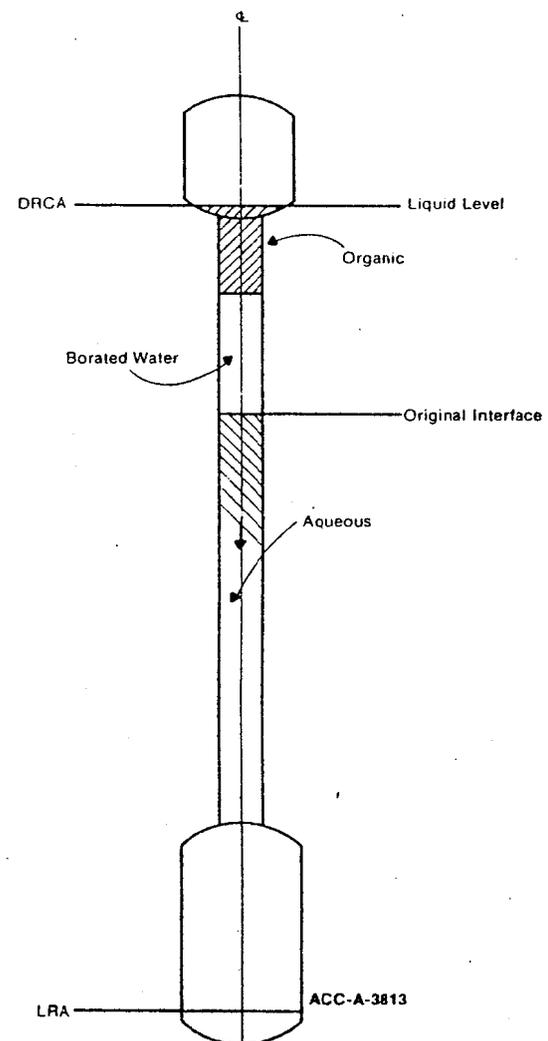
**Figure 22  Relation of Organic, Borated Water, and Aqueous After Third Organic Pump-Out from Head**
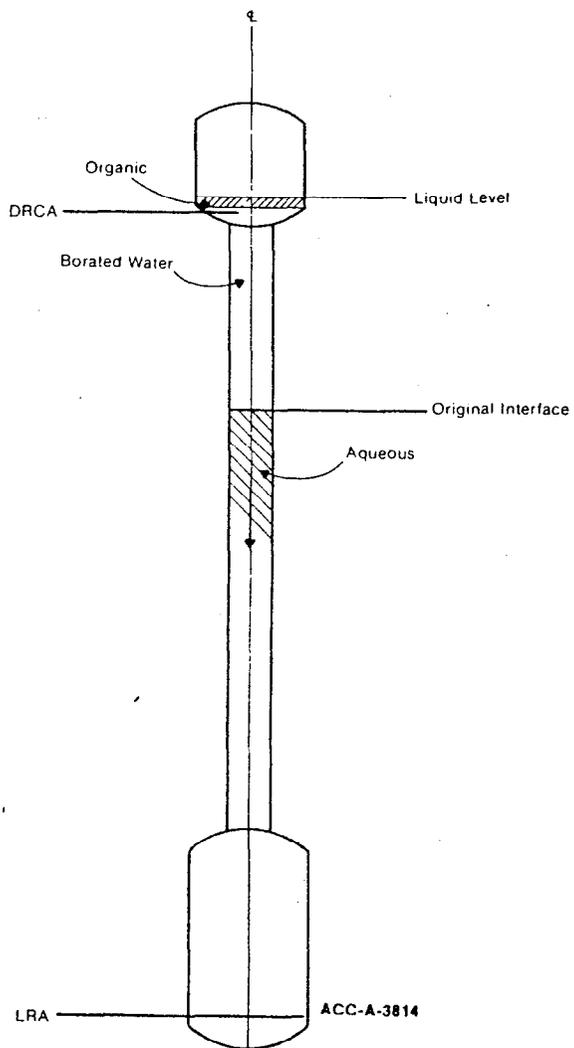
**Figure 23   The H-100 Column After the Final Borated Water Adddition to the Top Head**
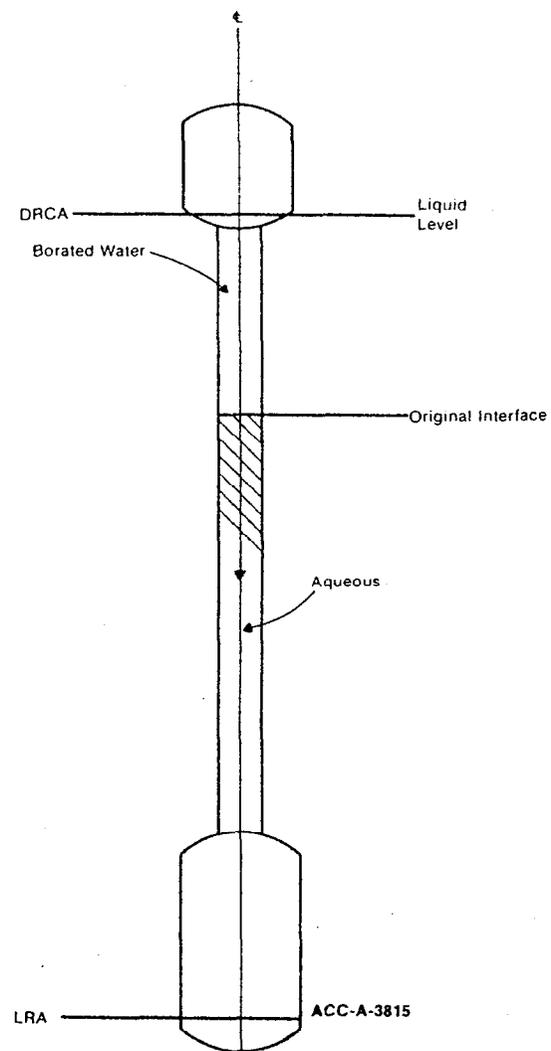


**Figure 24   Pump-Out After Final Borated Water Addition to the Top Head**

Organic Layer
(trace)

Liquid Level

DRCA

Borated Water

Uranium Interface
(Raised 12" by 10L
Addition of Borated
$H_2O$ at Bottom)

Aqueous

LRA

ACC-A-3816

**Figure 25   Relation of Borated Water, Uranium Interface, and Aqueous After
First Borated Water Addition to the Bottom**

DRCA

Liquid Level

Borated Water

Uranium Interface

Aqueous

LRA

ACC-A-3817

**Figure 26   Relation of Borated Water, Uranium Interface, and Aqueous Following Pump-Out
After First Addition of Borated Water to Bottom**

Organic Layer
(trace)

Liquid Level

DRCA

Borated Water

Uranium Interface
(Raised 12" by 10L
Addition of Borated
$H_2O$ at Bottom)

Aqueous

LRA

ACC-A-3816

**Figure 25   Relation of Borated Water, Uranium Interface, and Aqueous After
First Borated Water Addition to the Bottom**

DRCA

Liquid Level

Borated Water

Uranium Interface

Aqueous

LRA

ACC-A-3817
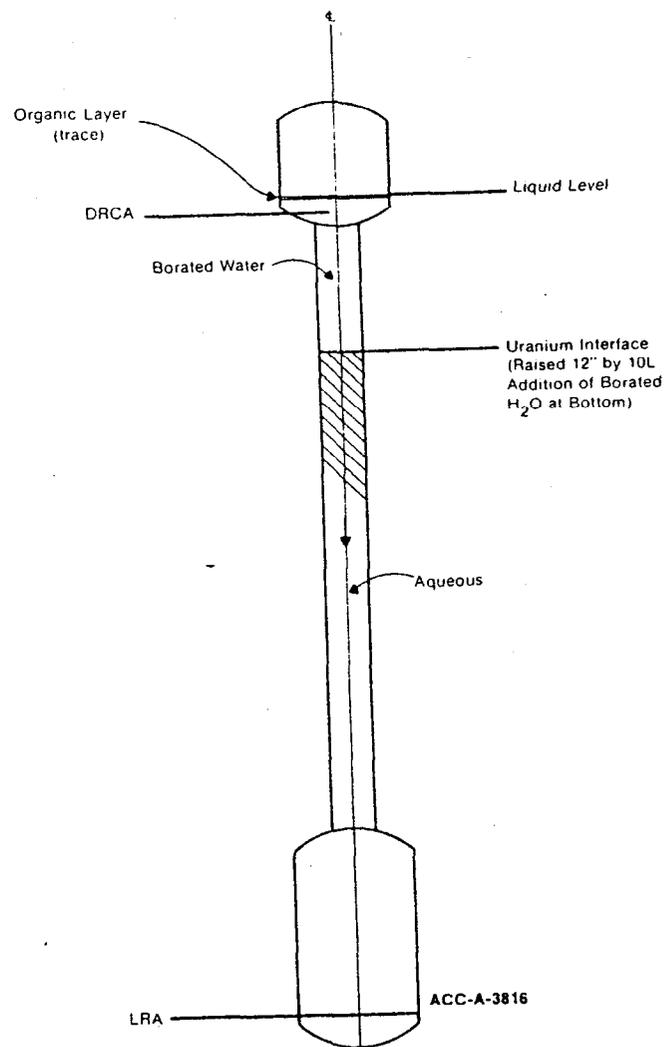
**Figure 26   Relation of Borated Water, Uranium Interface, and Aqueous Following Pump-Out
After First Addition of Borated Water to Bottom**
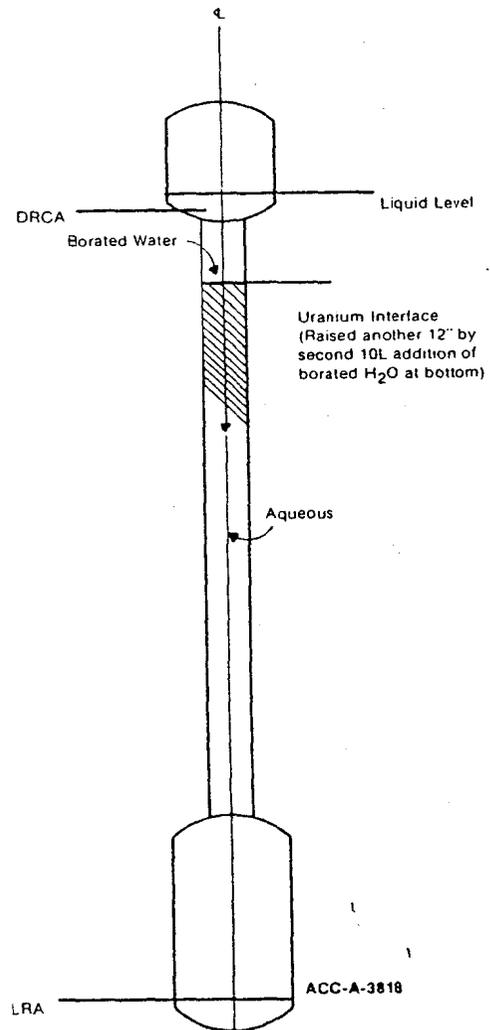
Figure 27  Relation of Borated Water, Uranium Interface, and Aqueous After Second Borated Water Addition to Bottom
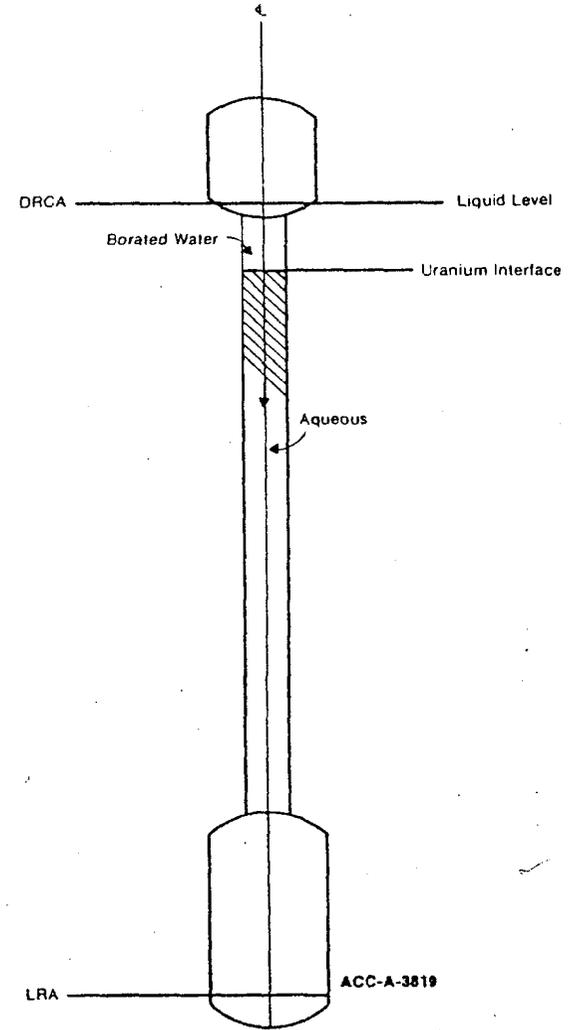


Figure 28  Relation of Borated Water, Uranium Interface, and Aqueous Following Pump-Out After Second Borated Water Addition to Bottom

# V. APPENDIX

Should an alternate plan of action be required to prevent subsequent criticalities, two contingency plans were developed:

(1)  to jet H-100 to G-108;

(2)  to add boronated water rapidly to top and bottom heads.


## 1.  H-100 Criticality Contingency Procedure (1)

SCOPE:  To establish method and requirements needed to jet H-100 to G-108 in event of new criticality.

CONCEPT:  Poison G-108 with adequate boron, outline preparatory steps and outline steps for use of procedure.

INFORMATION:

(1)  Figure 29 is a schematic of the related equipment.

(2)  Jet H-501 is a criticality control jet.  It has the jet vent header disconnected and the steam supply valve is sealed.

(3)  Jet H-501 has been used during the past month without difficulty.

(4)  A jet usually takes 30-60 seconds to start up and set at proper operating pressure.  However, if an operator was stationed at the jet valves, he could get them opened in 5-10 seconds.  Opening Valve 4-H requires flipping the lock handle of the actuator plunger and pulling the plunger open.  This could be done by a separate operator in 1-2 seconds after notification.

(5)  H-100 currently holds 451 L (aqueous and organic).  Estimates show the total U concentrated in H-100 is 17 kgs.  Assuming 20 kgs at 85% enriched gives a total $^{235}U$ mass in H-100 = 17 kg.

(6)  G-108 currently holds 1217 L of solution with 178 g $^{235}U$ total.

(7)  Using the curves shown in Figure 30, another curve of $^{235}U$ conc. vs. boron conc. can be established at $K_{eff}$ = 1.  This is shown in Figure 31. Assuming 17 kgs $^{235}U$, the following table is established from Figure 31.

| Boron (g/L) | $^{235}U$ (g/L) | Maximum L for $K_{eff}$ = 1 |
|---|---|---|
| 0 | 11.8 | 1694 |
| 1 | 38.3 | 527 |
| 2 | 67.5 | 299 |
| 3 | 101.0 | 200 |
| 4 | 134.0 | 151 |
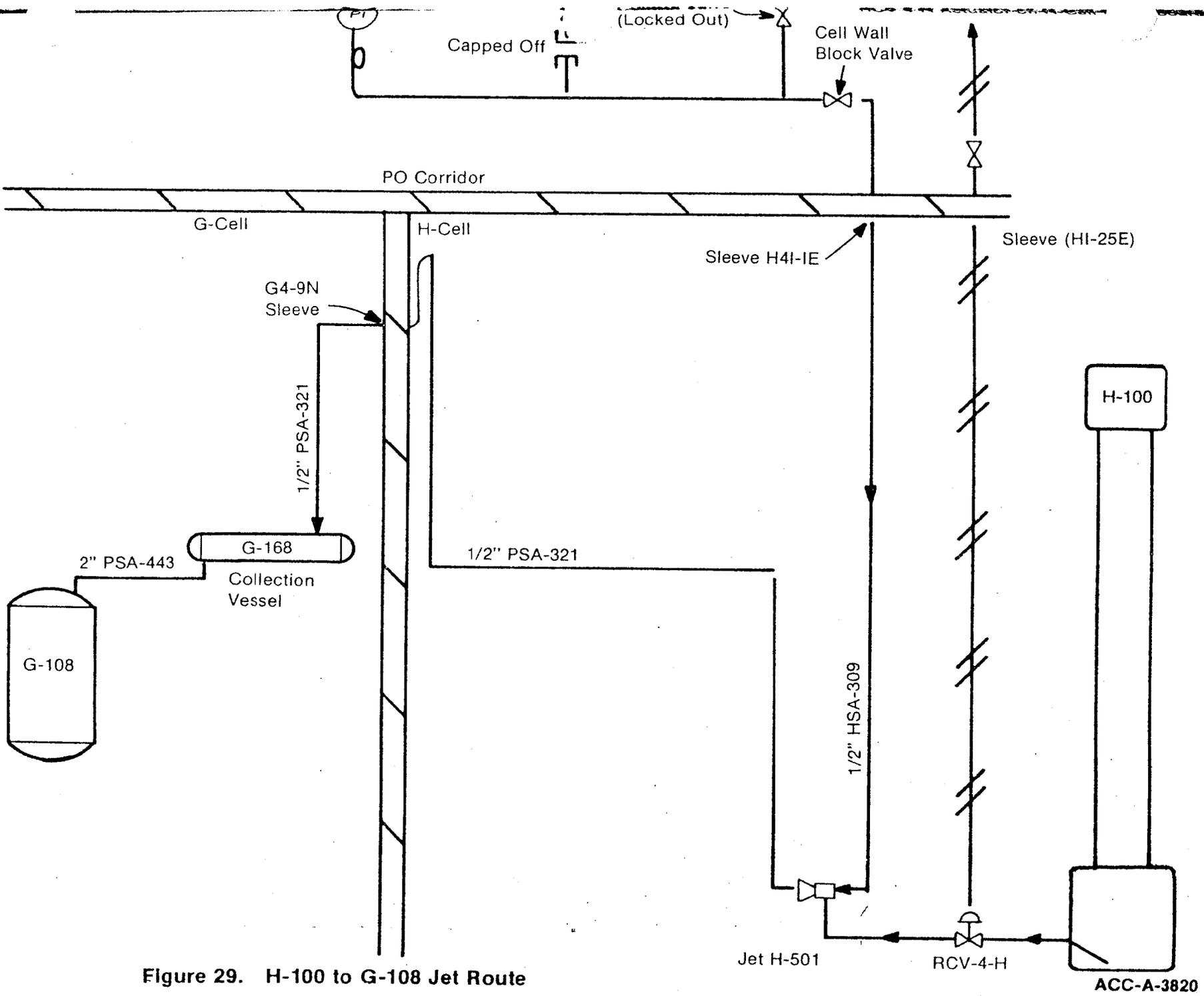
**Figure 29.   H-100 to G-108 Jet Route**

ACC-A-3820

38

300 mm $H_2O$ Reflector

3 gBoron/1

2 gBoron/1

4 gBoron/1

1 gBoron/1

O gBoron/1

ACC-A-3780

Uranium Concentration, kg/1

0.01    0.02    0.03    0.05    0.07    0.01    0.2    0.3    0.5    0.7    1
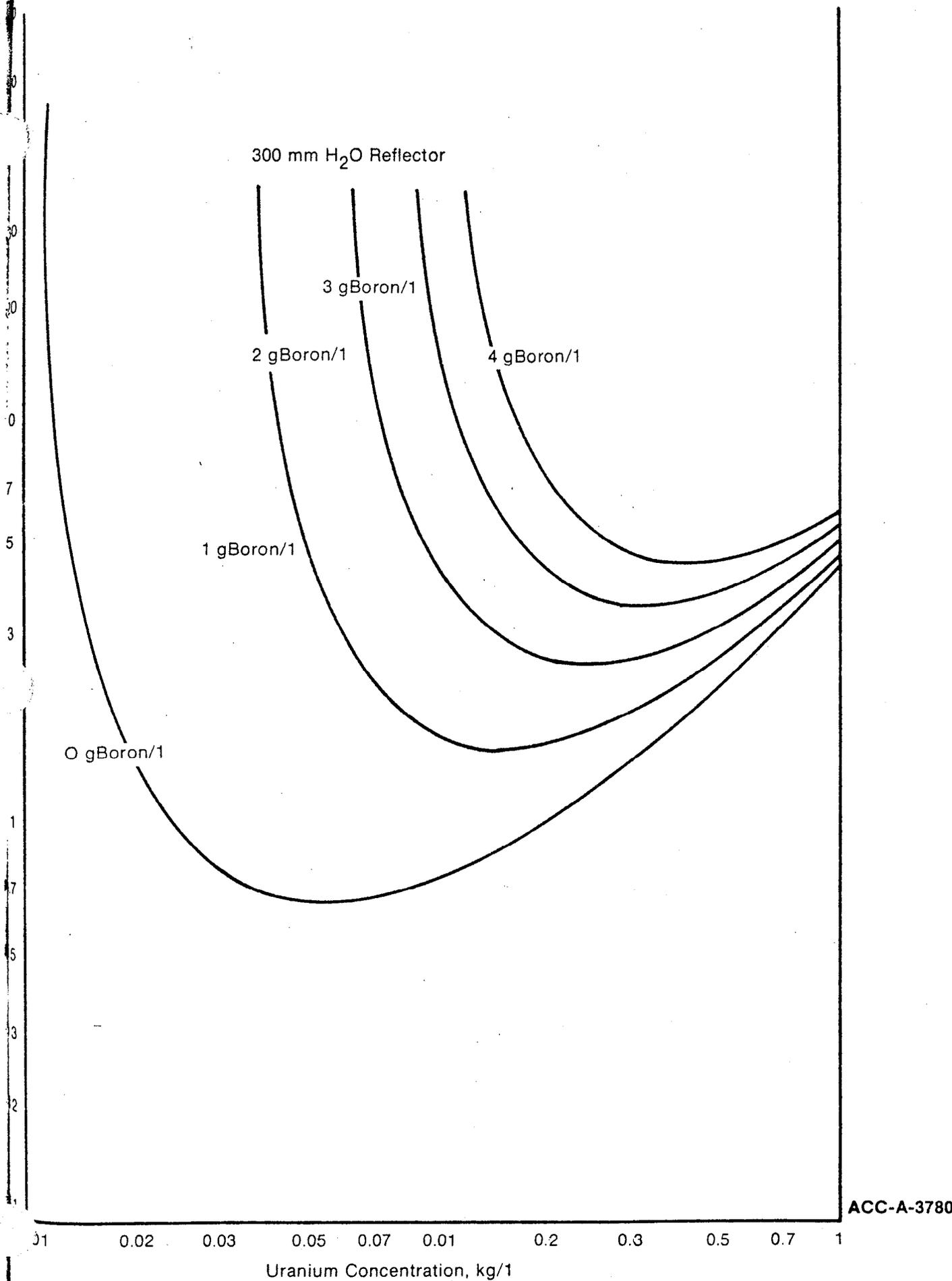
**Figure 30   Effect of Boron on Subcritical Mass Limits for Homogeneous Water Reflected and Moderated $^{235}U$ Spheres**

39
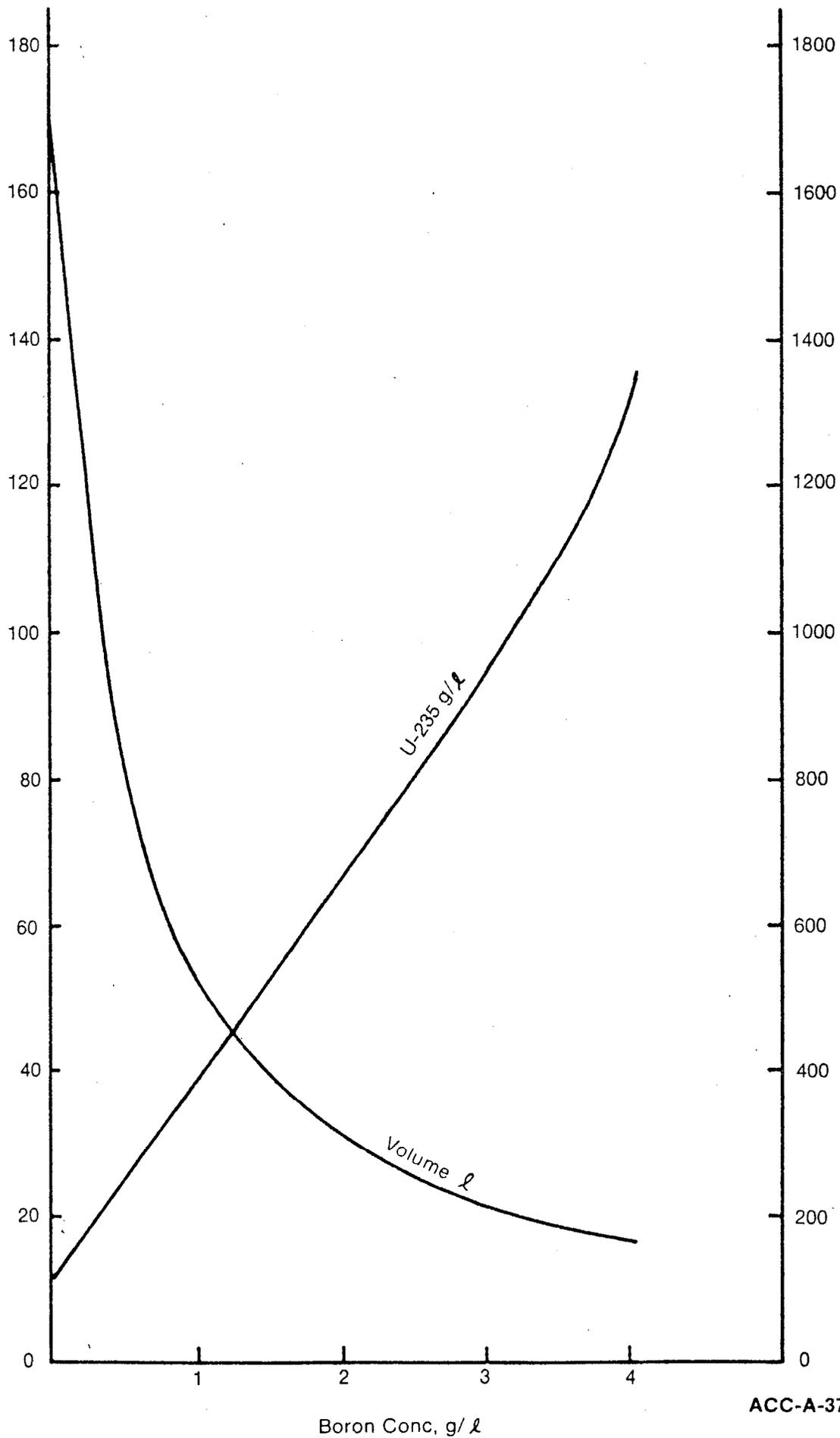
Figure 31    Plot of Required $^{235}U$ Conc. and Maximum Volume Required in G-108 vs. Boron Conc. for 17 kg $^{235}U$ Mass From H-100 to Produce $K_{eff}$ = 1

ACC-A-3797

(8)  The maximum boron concentration available is $\sim 8$ g/L in makeup solutions.

(9)  If all U in H-100 were averaged, the net assuming 17 kg $^{235}U$, would be 37.7 g/L.

(10) Using Figure 31, if 17 kgs of $^{235}U$ at a conc. of 37.7 g $^{235}U$/L solution were dumped into empty vessel, just under 1 g B/L would provide $K_{eff} = 1.0$. If the solution were dumped into the 1217 L in G-108, the net $^{235}U$ concentration would be 11.78 g/L. The required boron concentration would be 0.0 to provide a $K_{eff} = 1.0$.

(11) Therefore, if 2.0 g boron/L were to be picked as the net concentration after jetting, the solution should be significantly subcritical.

(12) The required boron to be added is calculated to be 4.6 kgs in 570 L.

$$1217(0) + 451 \ (1.1 \text{ for jet dilution}) \ (0) + X(8) =$$
$$(1217 + 451 \ (1.1) + X) \ (2)$$
$$X = 571 \text{ litres}$$

## PROCEDURE BEFORE H-100 SOLUTION IS TO BE MOVED

1.  Make up 570 L of 8 g boron/L and add to G-108 via decontamination inlet. This can be done in PM-121 and pumped via P-PM-221 to the G-108 inlet at sleeve G2-8N. The line number is 1/2-inch DCA-334. Sample PM-121 before pumping to ensure all boron is in solution and at the right concentration. All other valves to other vessels must be checked to ensure all solution is sent to G-108 from PM-121.

2.  Sample G-108. The required boron concentration must be at least 2.58 g boron/L. Adjust as necessary.

3.  Prevent further addition to G-108 by tagging out all jets and valves into the vessel except H-501.

4.  Prevent removal of solution from G-108 by tagging out all jets and valves on outgoing routes.

5.  Attach highly visible tags on the steam supply valve and cell wall block valve for jet H-501 to ensure easy location.

6.  Provide independent verification of Step 5.

7.  Issue MJR to reconnect jet vent header to H-501. Ensure valve is closed.

8.  Hang a highly visible tag on the plunger used to actuate RVC-4-H.

9.  Crack the steam supply valve and cell wall block valve to jet H-501 separately and then reclose lightly. This ensures they can be opened quickly and by hand.

10. Train the designated operator in case procedure is needed:

    a. Open cell wall block valve wide open.

    b. Open steam supply valve to provide pressure between 30 and 60 psi.

    c. Open RVC actuator 4-H on panel board.

    d. Get out.

11. When activities begin in H-100, station trained operator by H-501 valves with gloves on. Ensure he knows location of valves and actuator.

## 2. H-100 Criticality Contingency Procedure (2)

SCOPE: To establish the method and requirements for the very rapid, emergency addition of boronated water into both the base and head of column H-100.

CONCEPT: Boronated water can be added rapidly to both the top and bottom heads of H-100 via lines not currently being designated for re-covery operations. This procedure develops the requirements necessary for getting the equipment established.

INFORMATION:

(1) Routes into top include:

    a. 1/2-inch DCA-309 (leaves cell via sleeve H2-7R) capped off in PM Area.

    b. 1/2-inch AA-354 (leaves cell via sleeve H3-15E). This line is the IBS feed line. It comes from PM-107-0 through 80 feet of 1/2-inch pipe to a rotameter in the PO corridor. It then enters the cell. The rotameter has a bypass around it which must be removed. In addition, the ANN in the line would need to be drained by breaking a flange in PO corridor. Use of this line is not required.

    c. The upper DR probe (Sleeve No. H1-23E) leaves H-100 and enters PO corridor.

    d. The lower DR probe (Sleeve No. H1-22E) leaves H-100 and enters PO corridor.

(2) Routes into bottom include:

    a. 1/2-inch DCA-308 (leaves cell via sleeve H2-1R). This is the common line for lower LR probe. The PM-121 vessel is already piped to this line.

    b. The column pulser line (1-inch PSH-559) connects to organic feed line to H-100. This line exits the cell via sleeve H4-1R and can be connected via the Sonoprobe outlet.

42

(3) Locations where boronated water could be stored for this contingency are:

    a.  PM-121 is full of boronated water. PM-121 is already connected to the lower LR probe on H-100.

    b.  The weigh tank is full of boronated water and can be easily connected to 1/2-inch DCH-309. The weigh tank needs a high capacity pump installed to push solution into top of H-100.

    c.  PM-107-0 is empty. Boronated water could be made up here and drained into H-100 via the IBS route. A pump to push the solution would be needed.

(4) If this procedure is required, the expected routing of solution out of H-100 is as follows:

    a.  To H-103 from organic outlet at top of column.

    b.  To G-108 via G-165 from aqueous outlet at bottom of column if jackleg pressure has been released.

    c.  To G-111 organic inlet at bottom of column.

    d.  To vessel off-gas outlet on H-100 and various disengaging pots.

    e.  To G-108 if RCV-4-H is opened.

    f.  To operating corridor if cell wall block valve is open on H-105 jet.

    g.  To PM Area via inelt line being used by boronated water-adding crew.

    h.  To PO corridor via DR line being used by uranium-removal crew.

(5) G-108 should be poisoned to 2.58 g boron/L as contingency.

## PROCEDURE

1. Determine what procedure will be used for removal of uranium from H-100. This will enable determination of vessel inlets available for use.

2. Determine which vessel will be used for adding boronated water. This will determine which vessels are available.

3. Write MJRs for connecting a vessel to a top inlet, and one to a bottom inlet. If PM-102-0 is used, it must be flushed thoroughly as will all lines which could possibly be plugged.

4. Make up 8 g/L boronated water in both vessels. Sample each and verify concentration of boron.

5.  If the IBS feed line is to be used, drain the line to the PO corridor, and valve the bypass into the line. Valve out the rotameter.

6.  Add boronated water to G-108. 570 litres at 8 g/L would be adequate.

7.  A single valve close to the pump will be the only one closed for each method of addition. Ensure that all other valves on each line are open into H-100.

8.  Identify the pump switches and valves identified in Step 7 with highly visible tags.

9.  Ensure power is connected to the pumps.

10. Train the operators needed at each station on procedure to be followed and exit route to take.

11. Train an operator how to open RVC-4-H and to release pressure on H-101 jackleg. Establish his exit route.

12. Station operator as required just before uranium removal procedure is started.