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January 6, 1971

HANFORD ATOMIC PRODUCTS OPERATION - RICHLAND, WASHINGTON

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TITLE

CHEMICAL MILLING OF COUNTERPORE RECLUSIONS
IN THE URANIUM WALL OF ZIRCALOY-2 CLAD
URANIUM TUBES - PROGRESS REPORT NO. 1
(HAPO Contract CA-264)

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AUTHOR

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Manhattan Beach, Calif

ISSUING FILE

KLINGMAN, J. H.

SEP 20 1952

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PR-24, 4-19-94

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Verified By J E Savely 5-16-94

January 6, 1961

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Mr. W. L. Hampson
Senior Research Engineer
General Electric Company
Hanford Atomic Products Operation
Richland, Washington

Dear Walt:

Enclosed is a copy of Charlie's progress report concerning your project. In addition to the information presented in this report, I would like to invite your attention to some additional comments.

At the present time our pilot line bath is at the following composition ranges:

U	900#/M gallons	} — Current status purpose to explore high U range
NO ₃	1300#/M gallons	
SO ₄ ²⁻	4200#/M gallons	
Cu	160#/M gallons	

Our next experiment will be to explore the high (900 to 1200#/M gallons) dissolved uranium range.

This study will be conducted at 165 ± 5° F. since confirmatory tests indicate that this is the optimum temperature. Again, we note that at 140° F. there is a slope problem toward the center of the metal, apparently similar to that reported in your studies.

Subsequent to these current studies, it is intended to variate the nitrate and then the sulfate concentrations as we have discussed.

The most recent formula which gives optimum results is offered below:

	%	Lbs.	Gals.
H ₂ O	39.9	4437	531.7
HNO ₃ 42° Baume	17.1	1910	162.5
CuSO ₄ ·5H ₂ O	5.6	629	-
H ₂ SO ₄ 66° Baume	37.4	4178	-
		11,154	1000 gallons

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Mr. W. L. Hampson
General Electric Company

January 6, 1961
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[REDACTED]

Also enclosed, for your information, are some copies of the most recent test data.

Charlie, of course, is back on the job and we are proceeding on schedule.

Very truly yours,

UNITED STATES CHEMICAL MILLING CORPORATION

Don C. Atkins, Jr.
Technical Director

DCA:er
Enclosures

cc C. Vinton

[REDACTED]

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CHEMICAL MILLING OF COUNTERBORE RECESSES IN
THE URANIUM WALL OF ZIRCALOY-2 CLAD URANIUM TUBES

PROGRESS REPORT NO. 1

FOR

THE GENERAL ELECTRIC COMPANY

UNITED STATES CHEMICAL MILLING CORPORATION

1700 Rosecrans Avenue

Manhattan Beach, California

Don C. Atkins, Jr.
Technical Director

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CHEMICAL MILLING OF COUNTERBORE RECESSES IN
THE URANIUM WALL OF ZIRCALOY-2 CLAD URANIUM TUBES

PROGRESS REPORT NO. 1

REFERENCE

Consultant Agreement CA-264.

SCOPE OF WORK

The general scope of the work as set forth in Article II of the referenced document has been divided into several phases. The first phase is concerned with development of analytical procedures suitable for analyses of the ingredients present in the basic Etchant 24-1. This first progress report is a description of the status of the work on this first phase and, also, contains an outline of planned experiments for the subsequent phase.

RESULTS AND CONCLUSIONS

Laboratory analytical procedures have been developed and adapted to Etchant 24-1. Equations have been derived which will permit adjustment of the etchant bath to conditions approaching the initial charging of the etchant, at least with respect to the acid components. It is possible that as the work progresses it may be desirable to modify the analyses and computations.

DISCUSSION

The work conducted to date has been primarily concerned with the development of analytical procedures which permit the adjustment of the acid components of Etchant 24-1 to any desired concentration. The analysis of acidic etchants for nitrate and sulfate content has led to the development

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of standard methods presented as part of this report. The computations presented below represent a tentative means of controlling the nitrate and sulfate ion concentrations in the etchant. It should be noted that the starting values have been arbitrarily selected as the reference point since it is not yet known over what range these concentrations may be permitted to vary.

TENTATIVE

COMPUTATIONS FOR ADJUSTMENT OF ACIDIC CONSTITUENTS

ETCHANT 24-1

I. When concentrations are too low:

Nitrate Ion

$$\left(\begin{array}{l} \text{Gallons of } 42^{\circ} \text{ Be' HNO}_3 \\ \text{to be added} \end{array} \right) = \frac{1100 - \left(\begin{array}{l} \text{Lbs. NO}_3^-/\text{M gal.} \\ \text{determined by} \\ \text{analysis} \end{array} \right)}{8} \times \frac{\text{Gals. etchant in tank}}{1000}$$

Where: 1100 = Lbs. NO_3^- /M gals. in initial charge of Etchant 24-1
 8 = Lbs. NO_3^- /gal. of $42^{\circ} \text{ Be' HNO}_3$

Sulfate Ion

$$\left(\begin{array}{l} \text{Gallons of } 66^{\circ} \text{ Be' H}_2\text{SO}_4 \\ \text{to be added} \end{array} \right) = \frac{4550 - \left(\begin{array}{l} \text{Lbs. SO}_4^{--}/\text{M gal.} \\ \text{determined by} \\ \text{analysis} \end{array} \right)}{14.5} \times \frac{\text{Gals. etchant in tank}}{1000}$$

Where: 4550 = Lbs. SO_4^{--} /M gals. in initial charge of Etchant 24-1
 14.5 = Lbs. SO_4^{--} /gal. of $66^{\circ} \text{ Be' H}_2\text{SO}_4$

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II. When concentrations are too high:

Nitrate Ion

$$\left(\begin{array}{l} \text{Adjusted volume of} \\ \text{etchant in gals.} \end{array} \right) = \frac{\left(\begin{array}{l} \text{Lbs. NO}_3^-/\text{M gals.} \\ \text{determined by} \\ \text{analysis} \end{array} \right) \times \left(\begin{array}{l} \text{Present volume} \\ \text{etchant in gals.} \end{array} \right)}{1100}$$

Sulfate Ion

$$\left(\begin{array}{l} \text{Adjusted volume of} \\ \text{etchant in gals.} \end{array} \right) = \frac{\left(\begin{array}{l} \text{Lbs. SO}_4^{--}/\text{M gals.} \\ \text{determined by} \\ \text{analysis} \end{array} \right) \times \left(\begin{array}{l} \text{Present volume} \\ \text{etchant in gals.} \end{array} \right)}{4550}$$

- Note: (1) Water may be used to dilute etchant to adjusted volume.
- (2) If etchant tank is reasonably symmetrical, the depth of solution may be substituted for "present volume" and "adjusted volume".
- (3) It must be recognized that unless a correction is made for the effect of one of the above equations on the other, a slight error will result.

The second part of this phase of the work is concerned with the development of procedures for analysis of copper and uranium. A few concluding tests are necessary to confirm initial results, but it is believed that suitable procedures will be available shortly.

In addition to these procedures, other aspects of the work to be undertaken immediately will be the actual milling to determine the depletion point of the bath. There has been some indication that as the dissolved

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uranium content increases there may be a slight acceleration of the etch rate. Alternatively, it is conceivable that if some minimum dissolved uranium content is maintained, the concentration of dissolved copper may be reduced proportionately. The results of this and other tests will be reported in subsequent reports.

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STANDARD METHOD "A"

URANIUM ETCHANT 24-1

Etchant Control Limits

(A-1) PREPARATION OF SAMPLE

Object: To prepare a diluted sample of uranium etchant for control analysis.

Apparatus: 1 - 25 ml pipet equipped with suction bulb
1 - 250 ml volumetric flask

Procedure: 1. Pipet exactly 25 ml of uranium etchant into the 250 ml volumetric flask and dilute to volume with distilled water.

2. Use samples of this diluted solution as required in the following procedures.

(A-2) NITRATE ION

Object: To determine the amount of nitrate ion in Etchant 24-1.

Apparatus: 2 - 250 ml Erlenmeyer flasks
1 - 50 ml graduated cylinder
1 - 5 ml pipet
1 - 25 ml pipet
1 - 50 ml burette

Reagents: Ferroin indicator, 0.025 M.

Ferrous ammonium sulfate solution:

Prepare a stock solution by dissolving 393 grams of ferrous ammonium sulfate, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, in 1300 ml of distilled water plus 500 ml of concentrated sulfuric acid, H_2SO_4 . Cool and dilute to two liters.

Dilute one liter of stock solution to 2-1/2 liters with distilled water for standard solution.

0.2000 N potassium dichromate solution:

Dissolve exactly 19.614 grams of primary standard grade $\text{K}_2\text{Cr}_2\text{O}_7$ in sufficient distilled water to make two liters in a volumetric flask at 20° C.

Sulfuric acid, concentrated.

Procedure: 1. Pipet exactly 5 ml of the diluted sample (Standard Method A-1) into a 250 ml Erlenmeyer flask containing a number of glass beads.

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STANDARD METHOD "A" (Continued)

2. Add, via a pipet, exactly 25 ml of ferrous ammonium sulfate solution.
3. Slowly add, while swirling, 25 ml of concentrated sulfuric acid.
4. Add 30 ml of distilled water.
5. Boil the solution at least ten minutes.
6. Cool, add 50 ml of H₂O, 3 drops of ferroin indicator and titrate with standard potassium dichromate solution.
7. At the same time a sample is run, run a blank in the same manner as above except substitute 5 ml of distilled water for the sample.
8. Record the burette readings for both blank and sample.

Calculations: (blank titration - sample titration) x 69.0 = lbs
NO₃⁻/M gallons

(A-3) SULFATE ION

Object: To determine the amount of sulfate ion in Etchant 24-1.

Apparatus: 1 - 2 ml pipet
1 - 50 ml graduated cylinder
1 - 10 ml graduated cylinder
1 - 250 ml beaker
1 - 250 ml Erlenmeyer flask
1 - 3 inch 60° funnel

Reagents: Barium chromate:
Add 167 ml concentrated hydrochloric acid, HCl, to approximately one liter of distilled water. Add 20 grams of barium chromate BaCrO₄, and mix to dissolve. Dilute to 2000 ml with distilled water.

Sodium thiosulfate - 0.2N, standardized.
Sodium hydroxide - 20% solution.
Ammonium hydroxide - reagent grade.
Hydrochloric acid - reagent grade.
Potassium iodide - reagent grade.

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STANDARD METHOD "A" (Continued)

Starch indicator:

Dissolve 150 grams of sodium chloride in approximately 800 ml of water. Add 100 ml of acetic acid and dilute to one liter. Bring solution to a boil. Make a paste of 5 grams of starch in 25-30 ml of water and pour into boiling solution. Allow to boil 2-3 minutes before cooling.

Whatman filtering paper #30.
Filtering tablets.

- Procedure:
1. Pipet exactly 2 ml of the diluted etchant (A-1) into a 250 ml beaker.
 2. Add 50 ml of BaCrO_4 and heat to boiling.
 3. Cease heating and then make definitely basic with NH_4OH ; (a curdy yellow precipitate will form and not go back into solution when basic. Then add 4 ml of NH_4OH in excess).
 4. Add a filtering tablet, heat to boiling and filter through Whatman #30 paper into a 250 ml Erlenmeyer flask.
 5. Wash out the beaker with small portions of boiling distilled water onto the precipitate until the solution coming from the funnel is clear.
 6. Add 10 ml of concentrated HCl to the filtrate. Discard the precipitate.
 7. Cool the filtrate to room temperature and then add about 2 g of KI . Let stand five minutes, stoppered and titrate with sodium thiosulfate to a straw color.
 8. Add 5 ml of starch indicator and finish the titration. The end point is a sudden change from purple to light green.

Calculations: $(\text{Normality of } \text{H}_2\text{S}_2\text{O}_3) \times (\text{mls used}) \times 1336.1 = \text{lbs. } \text{SO}_4^{2-}/\text{N gallons}$

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