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ELECTROLYTIC RECOVERY OF URANIUM AND VANADIUM FROM CLIMAX LEACH LIQUORS

Topical Report

By
Paul F. Kirk

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December 31, 1952

Research Laboratories
Rohm and Haas Company
Philadelphia, Pennsylvania

Technical Information Service, Oak Ridge, Tennessee

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Electrolytic Recovery of Uranium and Vanadium from Climax Leach Liquors

TOPICAL REPORT

By

Paul F. Kirk

December 31, 1952

Rohm and Haas Company
5000 Richmond Street
Philadelphia, Pennsylvania

Contract AT(49-1)-535

A B S T R A C T

An electrolytic method has been investigated for the recovery of uranium and vanadium from the pregnant leach liquors of the Climax Uranium Co. This method, employing anion-permeable membranes, has been found capable of effecting virtually complete recovery of both metals and a fair separation of the two. A recovery of the acid value of the leach liquor is also achievable. The leaching of Climax ore in the anode chamber was investigated and shows some promise.

TOPICAL REPORT

ELECTROLYTIC RECOVERY OF URANIUM AND VANADIUM FROM CLIMAX LEACH LIQUORS

By

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INTRODUCTION

The method currently employed by the Climax Uranium Company for the recovery of uranium from their acidic leach liquors involves the addition of metallic iron. This reagent reduces the uranium to the (IV) valence state resulting in the formation of insoluble uranous phosphate.

This method presents several problems. First, the "barren" liquors routinely contain about 0.3 grams per liter U_3O_8. This fact necessitates that the entire "barren" be recirculated, along with all the impurities, to the leaching process to avoid large losses. The leaching solutions thus become fouled rather readily. Second, the iron employed becomes coated and fails to react completely leading to mechanical handling problems in filtration, etc., and much of the iron reports in the uranium cake.

OBJECT OF INVESTIGATION

The object of this investigation was the determination of the feasibility and economy of an electrolytic method for the recovery of uranium from acidic leach liquors of the Climax Uranium Company.

SUMMARY OF CONCLUSIONS

The electrolytic recovery of uranium was found to proceed readily from Climax leach liquors at an average cost of 32 kwh per lb. U_3O_8. The average recovery efficiency was 99%.

The cost of precipitation depends largely on the original concentration of uranium as well as on the initial pH.

The grades of the precipitates are fairly low averaging about 18% U_3O_8. About 20% of the vanadium reports in the uranium cake. A simple up-grading procedure has been evolved and consists of redissolving the precipitate in fresh liquor and re-electrolyzing the resultant solution. This procedure was found capable of increasing the grade two to three fold. Doubtless the vanadium and uranium will have to be separated further as is currently done at Climax.

It was found that lead cathodes give better reduction early in the electrolysis than the graphite cathodes.

The initial pH of the liquor was found to be critical. An initial pH of less than 0.6 was found necessary for good reduction and complete recovery.

Since the emf changes with time along with the pH and since the rate of reduction is dependent on the pH, it is virtually impossible to evaluate the effect of final pH on completeness of recovery. If the final pH is viewed as an independent factor, then, in general, a higher pH gives more complete recovery.

Fluoride addition prior to electrolysis was attempted and gave good grades. However, the recovery was only 90 to 95%.

Vanadium can be recovered from the barren filtrates by further application of this electrolytic process. The costs are low (about 5 to 6 kwh per lb. V_2O_5) at grades of about 40 to 50%. Recovery is complete at a pH of about 6.

Two runs were made in which raw, ground Climax ore was slurried in the anolyte. In one run 99.9% of the uranium was leached and in the other, 82% was leached. The presence of the ore should help reduce costs by increasing the ampere efficiency of the electrolysis.

Lead appears to be quite stable in sulfate anolytes while the presence of chlorides will cause some corrosion. Graphite anodes are fairly good but would represent a considerable expense item if employed.

Initial work was begun on continuous systems. While design problems are considerably greater for flowing systems, the type of cell used for the reduction of commercial phosphoric acids (R (H report RMO-2509) seems adaptable to this process. A single run gave 99% recovery of the uranium.

FUTURE WORK

This work will be continued both in the laboratory and at the Climax Company.

Evaluation of various cathode materials should be conducted to determine their effect on completeness of recovery and degree of separation of uranium and vanadium. Various anode materials should be thoroughly tested in life-studies.

A critical study of optimum conditions such as P_2O_5 concentration and pH (initial and final) should be carried out.

The further testing of anodic leaching should be carried out at the Climax plant site.

NOMENCLATURE

1. Membranes - The ion-permeable membranes referred to in this report are the Rohm & Haas products, Amberplex A-1 and Amberplex C-1. The A-1 membrane is selectively permeable to anions while the C-1 membrane is selectively permeable to cations. These membranes function to increase the "transport number" of ions of one sign to a value approaching unity while preventing virtually any diffusion of dissolved electrolyte.

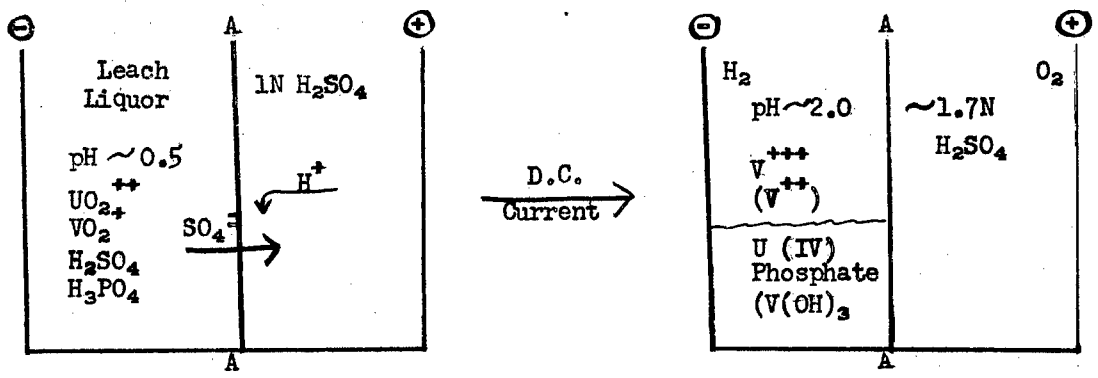
2. Anolyte and Catholyte are the electrolyte solutions at the anode and cathode respectively.

3. Current Density is regarded in this report as the average current divided by the exposed membrane area and is expressed in amperes per sq.ft.

4. Ampere Efficiency in this process is calculated as the ratio of equivalents of acid produced in the anolyte per faraday of current consumed and is expressed as percentage.

Theoretical

The function of the membranes in this process can best be explained by reference to Figure 1.



(A - A represents Amberplex A-1)

FIGURE 1.

As is indicated, the anion permeable membrane permits the passage of sulfate ions from the catholyte to the anolyte while restricting, to a great extent, the migration of H^+ ions in the reverse direction. (Amberplex C-1 would be unsatisfactory in this process since the current would be carried almost exclusively by the H^+ ions). As one sulfate ion migrates through the membrane, two H^+ ions are discharged as H_2 gas at the cathode, resulting in an increase of the pH of the

catholyte. At the anode, two OH^- ions are discharged (as O_2 gas) leaving behind two H^+ ions. The net effect in the anolyte is the generation of H_2SO_4 while in the catholyte, H_2SO_4 has been lost. At the same time, uranyl (UO_2^{+2}) ions in the catholyte are reduced to uranous (U^{+4}) ions according to equation I

$$UO_2^{+2} + 2\,e + 4\,H^+ \longrightarrow U^{+4} + 2\,H_2O \qquad (I)$$

Since some phosphate is present in the leach liquors, a precipitate of uranous phosphate forms.

The vanadium present is also reduced -

$$VO_2^+ + e + 2H^+ \longrightarrow VO^{+2} + H_2O \qquad (II)$$

$$VO^{+2} + e + 2H^+ \longrightarrow V^{+3} + H_2O \qquad (III)$$

Some $V(OH)_3$ also precipitates along with the uranium.

Results of Investigations

The first phase of these investigations involved a batch-type electrolysis. The cells used had a capacity of one gallon in each chamber with a membrane area of approximately 0.6 sq.ft. (See accompanying photograph and drawings). The cell was constructed of Plexiglas and employed neoprene gaskets. The electrodes used were fabricated of both graphite and lead.

Procedures

Both chambers of the cell were filled and the electrodes inserted as close to the membrane as possible. Both chambers were mechanically agitated during the entire course of the electrolysis. Voltage was applied to give the desired current, the latter being held constant throughout the run. As the electrolysis proceeded, the pH and emf were measured periodically. Samples were withdrawn, filtered and acidified to prevent further precipitation prior to analysis.

The first shipment of leach liquor consisted of three carboys which differed considerably in uranium content. The results of tests on these liquors are summarized in Table I (Several runs employed composite samples of the original liquors).

TABLE I

Batch Electrolyses of Pregnant Climax Liquors

#	Orig. Assay U_3O_8 g/l.	pH	Final Assay U_3O_8 g/l.	pH	% Rec'y	Time (min)	Av. Volt.	Amp.	Vol.(l.)	kwh/#U_3O_8	Ppt. Grade % U_3O_8
1	2.78	0.27	0.008	2.7	99.7	170	5.2	56	3.6	37	12
2	2.80	0.27	0.025	2.0	991.	166	5.6	56	3.4	41	14
3	3.47	0.18	0.007	2.3	99.8	266	4.5	56	3.6	40	10
4	3.49	0.18	0.000	3.1	100	184	6.2	56	3.6	38	18
5	3.68	0.18	0.013	1.9	99.6	137	6.8	56	3.6	30	18
6	3.15	0.18	0.005	1.8	99.8	141	5.6	56	3.6	29	15
7	3.20	0.25	0.027	1.8	99.2	130	6.2	56	3.6	30	13
8	3.51	0.25	0.110	1.8	96.9	133	5.5	56	3.6	25	37
9	5.70	0.24	0.050	1.8	99.1	132	5.8	56	3.6	16	28
10	5.70	0.24	0.073	1.9	98.7	118	6.0	56	3.6	15	18
11	5.60	0.24	0.049	1.8	99.1	130	6.1	54	3.6	17	23
12	1.60	0.29	0.005	1.9	99.7	151	5.8	56	3.6	64	14
13	1.60	0.29	0.016	1.8	99.0	131	5.8	54	3.5	55	14
14	5.70	0.25	0.028	2.0	99.5	160	6.4	58	3.5	19	23
15	3.68	0.18	0.004	1.9	99.9	130	6.7	56	3.5	29	21
Average			0.030 g/l		99.2%					32 kwh/#U_3O_8	18%

These results were achieved using graphite cathodes. As can be seen, virtually complete recovery of uranium was effected in these initial tests. The cost in kilowatt hours per lb. of U_3O_8 varies considerably and depends to a great degree, of course, on the initial concentration of uranium in the leach liquor. Other factors affecting the cost are the initial pH and the voltage required. (In some of the above runs, fresh membranes were employed which show a lower conductivity than membranes which have been used previously).

Precipitate Grade

The grades of the uranium cake also show wide variation. To some extent, the grade has been shown to vary with the initial concentration; a richer liquor giving the higher grades. (The grades reported in Table I are based on cakes that have been dried at 110°C.). For this reason, a simple up-grading procedure was attempted. The precipitate from one electrolysis was dissolved in a fresh batch of leach liquor by agitation in the cell prior to applying the current. This "enriched" liquor was then electrolyzed in the usual manner and the precipitate again collected and treated with another batch of leach liquor. (The first dissolution occurred quite rapidly while the second required about one-half hour.) This further enriched liquor was also electrolyzed and the final cake collected. The initial cake analyzed about 10% U_3O_8 while the final cake analyzed 27% U_3O_8. The recovery of uranium in each of the electrolyses was greater than 99.5% at an average final pH of 2.0. While much further work remains to be done on this procedure, it seems possible to achieve grades higher by a factor of two or three by this method.

No complete analyses of the cakes were performed. However, the chief contaminants are probably iron, aluminum and vanadium. For normal runs, approximately 20% of the vanadium reports in the uranium cake. The factors affecting the separation of these two metals such as final pH and extent of reduction are to be studied in the future.

Effect of Cathode Material

It was felt that a metal having a higher hydrogen overvoltage than graphite should give better reduction of the uranium and thus give complete recovery at lower pH's. For this reason, cathodes were employed which were fabricated of lead. It was found that recovery was "complete" at a lower pH using the lead electrodes.

A comparison of typical runs using graphite and lead can be seen in Table II.

Table II

Sample pH	U_3O_8 in filtrate Graphite Cath.	Lead Cath.
1.52	0.153 g./l.	0.025 g./l.
1.85	0.011 g./l.	0.008 g./l.
2.19	0.008 g./l.	0.005 g./l.

The filtrates from electrolyses employing graphite electrodes were green, indicating reduction of the vanadium to V^{+3}. Using lead cathodes, the filtrates were ordinarily violet in color which would indicate that the vanadium reduction had actually proceeded to the V^{+2} state. (The original leach liquor is green and passes through a sky-blue color shortly after the electrolysis is begun. This blue color corresponds to the VO^{+2} valence state.)

Effect of Initial pH

According to equation I, the rate of reduction should be critically dependent on the initial pH of the liquor. This effect was strikingly demonstrated when further batches of the liquor were received. While the original lots had pH's near 0.3, a subsequent lot showed pH's of 0.6 to 0.8. This new lot was run "as is" and with H_2SO_4 added to a pH of 0.5. In both cases, the runs were repeated with the addition of 1 ml. per gallon of H_3PO_4 to eliminate any possible phosphate deficiency. The results of these runs are summarized in Table III.

Table III

Effect of Initial pH

Run #	Initial pH	Final pH	Final emf	U_3O_8 in filtrate
1 "as is"	0.64	1.90	-137 mv.	0.260 g./l.
2 (H_2SO_4 added)	0.50	1.72	+345 mv.	0.000 g./l.
3 (H_3PO_4 added)	0.62	2.15	- 46 mv.	2.26 g./l.
4 (H_3PO_4,H_2SO_4)	0.50	1.84	+392 mv.	0.000 g./l.
5 (H_3PO_4,H_2SO_4)	0.30	1.50	+400 mv.	0.000 g./l.

Lead Cathodes; Vols = 1 gal.
All runs at 60 amps.

It is obvious from these runs that the initial pH is an **all-important factor.** For this reason, a thorough study of any factors affecting optimum conditions such as cathode material, current density, final pH, cell design, etc., must be carried out on the site of production where large volumes of liquor are available which can be subject to more precise controls.

The addition of phosphate apparently hinders the precipitation but not the reduction. All the liquors received apparently contain sufficient P_2O_5 values.

These results do indicate that a pH of about 0.5 or less is required for complete recovery by this method. Of course, a lower initial pH requires additional electrolysis time thereby increasing the cost. However, if complete recovery in a single pass is required, this additional expense becomes quite necessary.

Effect of Final pH

The effect of final pH is inherently difficult to evaluate. The completeness of precipitation depends on the extent of reduction. The extent of reduction depends, inter alia, on the elapsed time of electrolysis. The pH of the catholyte changes also with time. Further, the rate of reduction is dependent on the pH. The results in Table II would show that an increasing pH results in more complete recovery. However, the pH per se may not be the important factor.

A study of the dependence of the solubility of pure uranous phosphate on pH alone would probably not be very useful for this process investigation since the emf and pH are constantly changing. (Plots of pH and emf vs. ampere minutes appears in Figure 2.)

Effect of Fluoride Addition

In an effort to determine the feasibility of plating UF_4 from the liquor on the cathode, electrolysis was performed in which NaF was added to the catholyte. Only two runs were tried. In one, the initial pH was 0.7 and in the other 0.5. Two grams of NaF per liter were added in both cases. The electrolyses were carried to pH 2.0 (catholyte). The filtrates in both cases contained 0.1 to 0.2 g./l. U_3O_8. However, the grades were high (40-50%). This method will be investigated in future work.

Vanadium Recovery

Since some of the vanadium was reporting in the uranium cake, it was felt possible to recover all of the metal by continuing the electrolysis further to pH near 6. This should effect the quantitative removal of vanadium as $V(OH)_3$.

The procedure used to electrolyze the barren filtrates after uranium recovery is precisely the same as that previously described.

Table IV summarizes the results of vanadium recovery runs.

Table IV

Run #	Original Assay V_2O_5(g/l)	pH	Final Assay V_2O_5	pH	% Rec'y	% V_2O_5 (Grade)	kwh/#V_2O_5
1	7.5	2.3	2.0	4.4	74	45	6.2
2	5.4	1.9	0.05	5.1	99	35	10.6
3	9.6	1.8	0.00	6.1	100	41	5.6
4	8.6	1.7	0.00	5.8	100	44	5.6
5	9.8	1.8	0.12	5.7	99	47	5.4
6	9.5	1.8	0.29	5.4	97	57	5.6
7	12.5	2.1	0.00	6.4	100	63	4.4

Graphite cathodes employed.

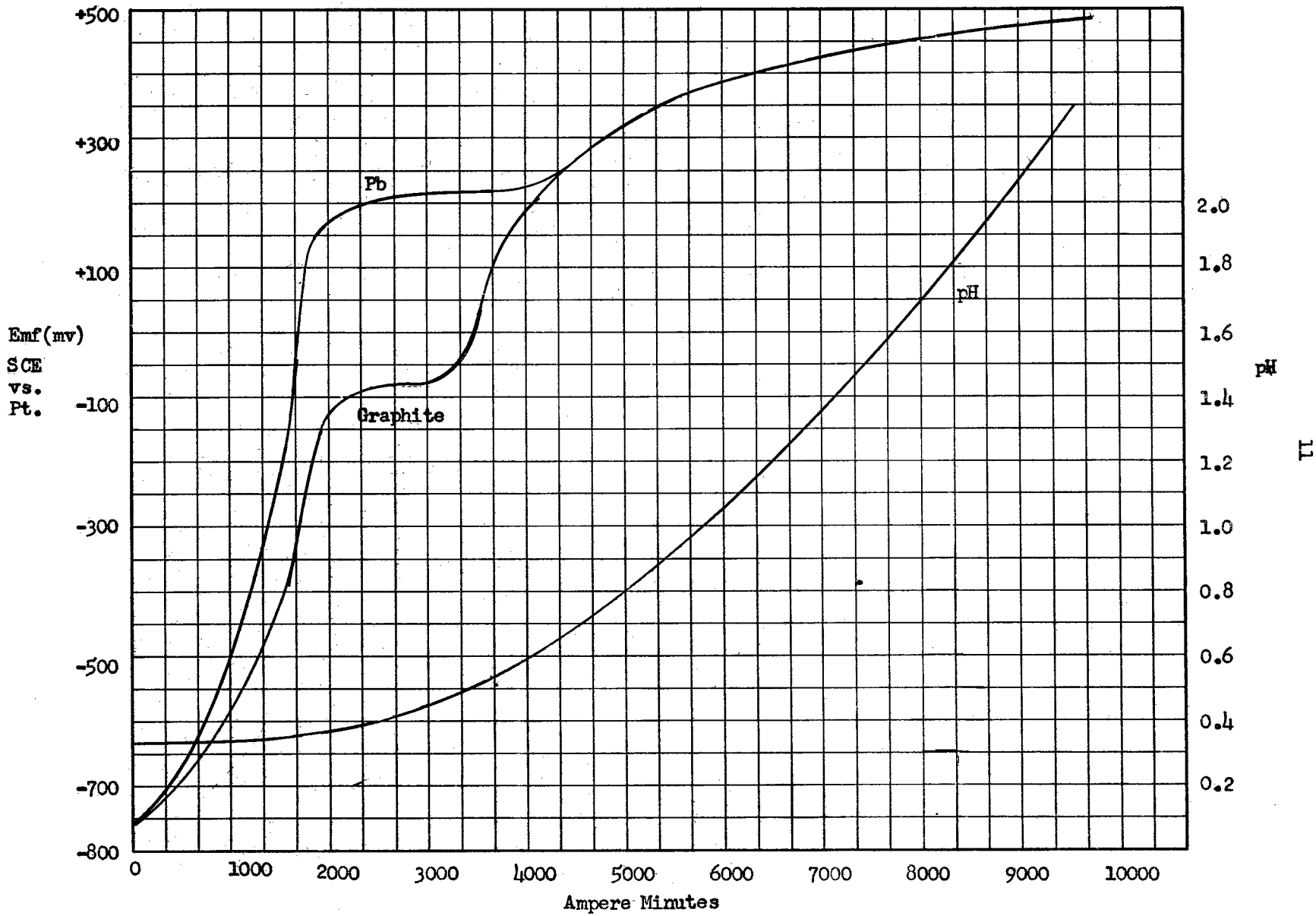


Figure 2. Emf and pH vs. Ampere Minutes

These results are more uniform than those for uranium recovery. The cost per lb. V_2O_5 is clearly a function only of the original vanadium concentration. With graphite cathodes, the recovery is virtually complete above a pH of about 5. The precipitates were ignited at about 800°C and were ordinarily powdery and grey-green in color. No attempt at up-grading these precipitates was made.

A single run using a lead cathode gave interesting results. At a final pH of 6.2 about 0.5 g./l. V_2O_5 remained. The emf of the filtrate was +600 and was pale violet in color. Apparently the lead cathode had reduced the vanadium too far. The (III) valence state is the least soluble while the (II) state is quite soluble. The filtrate turned brown on standing but no further precipitate formed. Vanadium in the (II) state is known to be a powerful reducing agent, capable of decomposing water. Doubtless this reaction occurred on standing. The precipitate from this run was ignited in the usual manner but gave a very hard and brittle red cake. The ignited cake had bright, shiny crystal-like structures throughout. It was partially insoluble in H_2SO_4, HNO_3 and HCl on prolonged heating.

Anodic Leaching

The small sample of Climax ore which was available was ground in a ball mill and sieved through a 60 mesh. A slurry consisting of 2800 ml. of 1N H_2SO_4 and 2,100 g. of the ore was employed as the anolyte in an ordinary electrolysis of leach liquor. Graphite electrodes were used. The original analyzed 0.39% U_3O_8. When the leach liquor electrolysis was complete (pH 2.0, 3 hrs.) anolyte was drained off and filtered. The residual ore then contained 0.07% U_3O_8, representing an 82% recovery. The filtrate analyzed for 3.3 g./l. U_3O_8 and was pale yellow in color. Apparently little of the vanadium had been leached.

Sufficient ore remained for a smaller run employing 800 ml. of 1N H_2SO_4 and 500 g. of the ore. After one hour of electrolysis, a sample of the anolyte slurry was withdrawn and the solid analyzed. The ore then contained 0.0004% U_3O_8 representing 99.9% recovery. The filtrate analyzed 1.8 g./l. U_3O_8. The reason for the great difference in the two runs is unknown, except perhaps better anode contact in second case employing the thinner 1 liter cell.

It is felt that the oxidative conditions in the anolyte will serve much the same as the usual oxidizing agents employed in leaching. Doubtless some persulfuric is formed at the anode.

Since the ampere efficiency of the anion membrane is inversely proportional to the average hydrogen ion concentration in the two chambers, the presence of the ore in the anolyte will increase the efficiency by neutralizing some of the acid as it is formed. Thus, even if the leaching is incomplete in the anode chamber and must be continued outside the cell, lower costs in U_3O_8 recovery from the liquor should result from this addition.

Much work remains, obviously, on this phase of the process. Evaluation of various anode materials, membrane abrasion, etc. must be studied in the future when further ore samples are available.

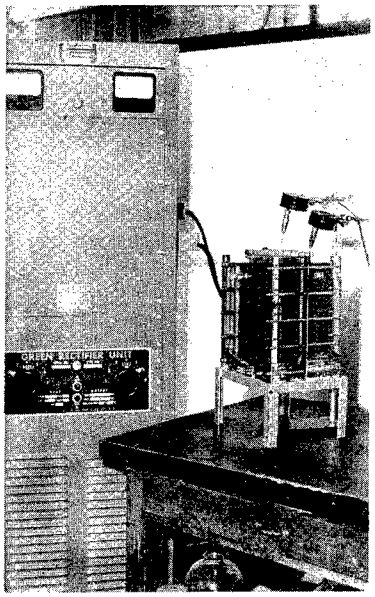
Anode Materials

Both graphite and lead were employed as anodes. The graphite is attacked considerably by the oxygen being evolved. A more satisfactory anode material is ordinary chemical lead. This metal corrodes to only a very slight extent in pure sulfate solutions. The presence of chlorides in leaches seems to accelerate this corrosion somewhat. Future work will include thorough corrosion studies on a variety of anode materials.

Continuous Operation

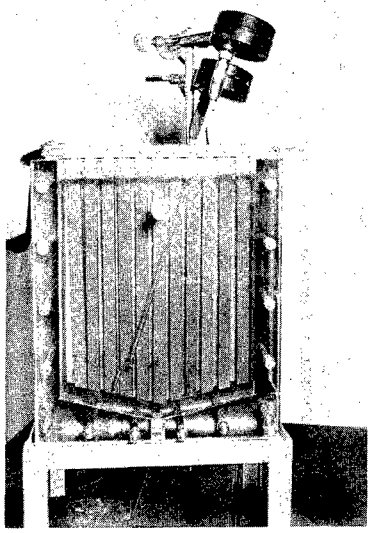
The initial work on flowing systems was begun. A cell was constructed which resembled the cell used for phosphoric acid reduction (R & H report RMO-2509). The cell measured 4" x 16" in membrane area and had a corrugated, perforated cathode. The stream was upflow. Precipitation occurred in the cell but was washed out with the stream. At a final pH of 2.0, the recovery was routinely 95% or better. One run at a final pH of only 1.4 showed a recovery 99% after standing several days. Originally, only 70% recovery was noted for this run.

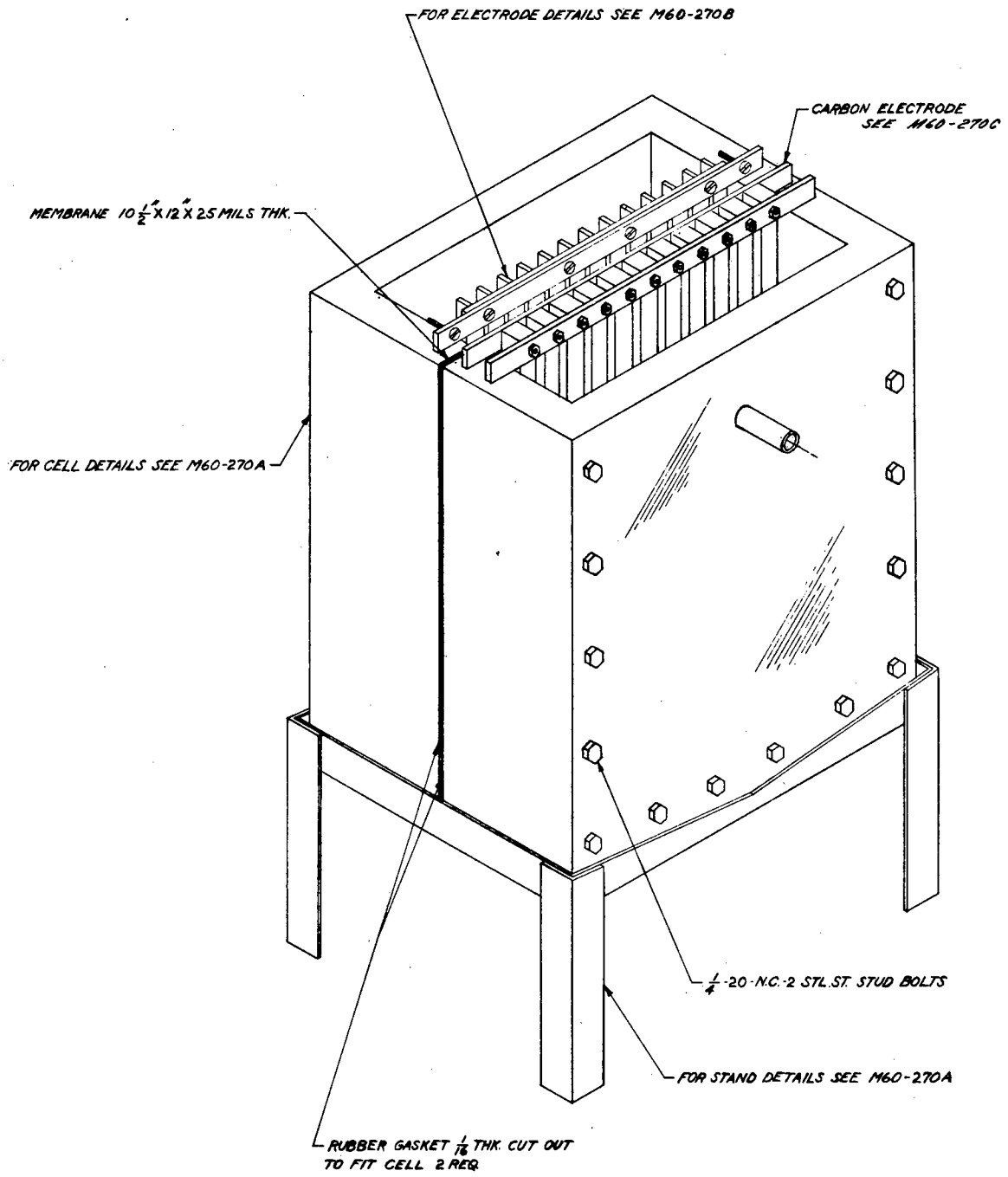
Some difficulty was experienced in regulating the flow of both chambers (water was dripped into the anolyte) and hence cost calculations are not meaningful. A larger unit will be built and tested in future work.



(Left) Gallon Batch Cell and Rectifier

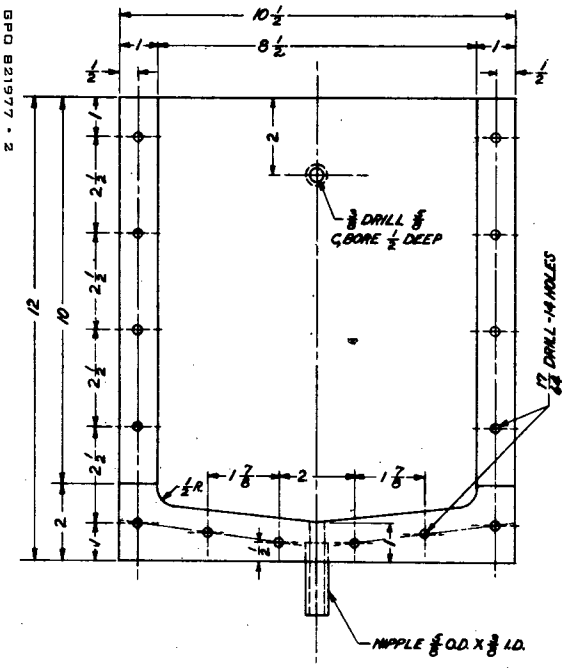
(Right) Gallon Batch Cell (Detail)

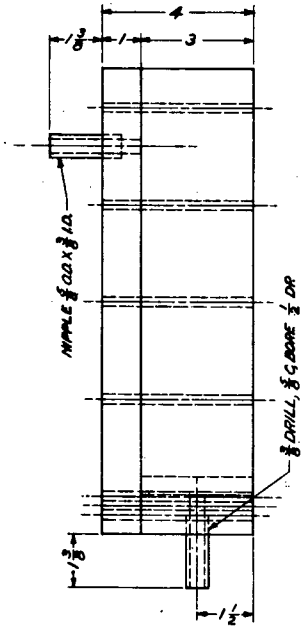


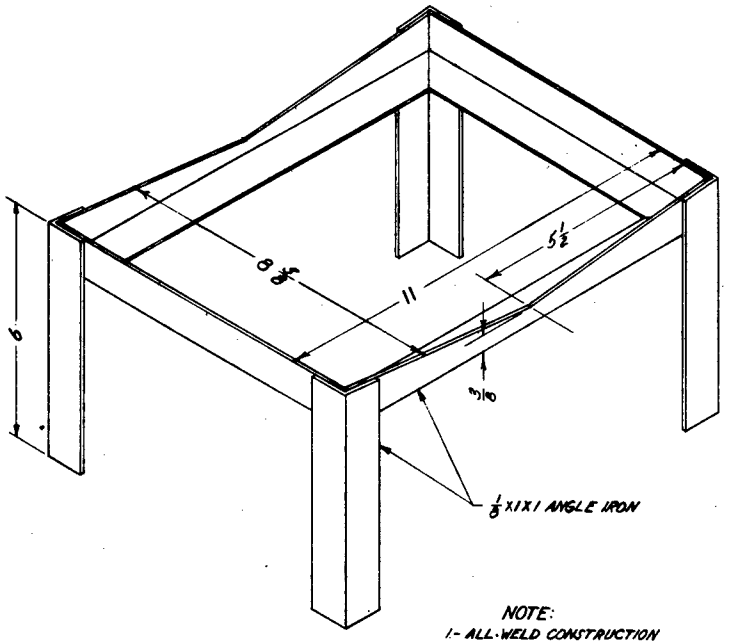


M60-270. Two Chamber 1 Gal. Electrolysis Cell.
Scale 3/8" = 1". Rev. 12-8-52.

GPO 821777 - 2





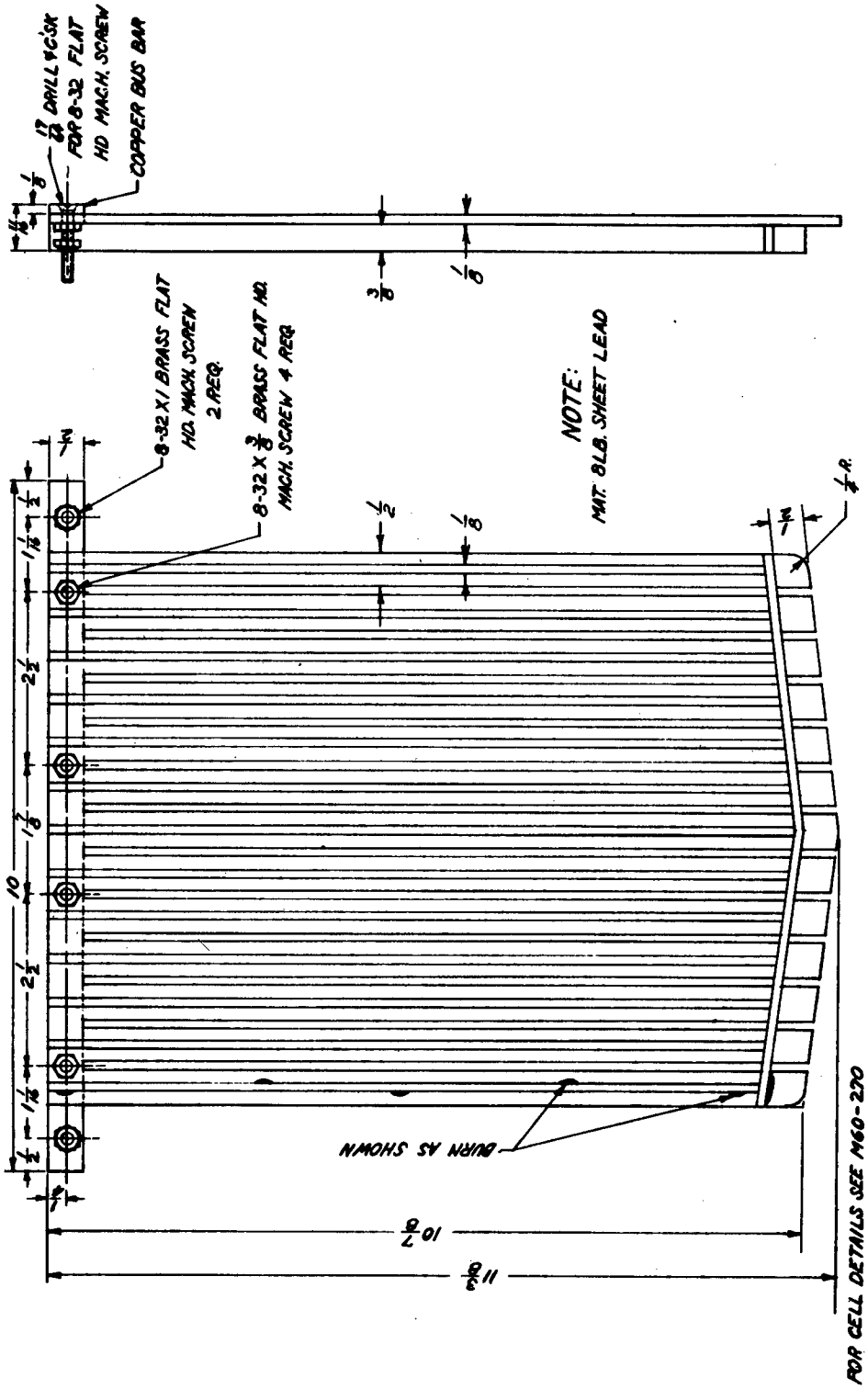


NOTE:
1.- MATERIAL - PLEXIGLAS
2.- ASSEMBLE ALL PCS. WITH PLEXIGLAS CEMENT
3.- TWO REQUIRED
4.- BOLT HOLES TO BE DRILLED AFTER ASS'Y PROVIDE 14 - 1/4 - 20 X 9 LG. STL. ST. STUD BOLTS

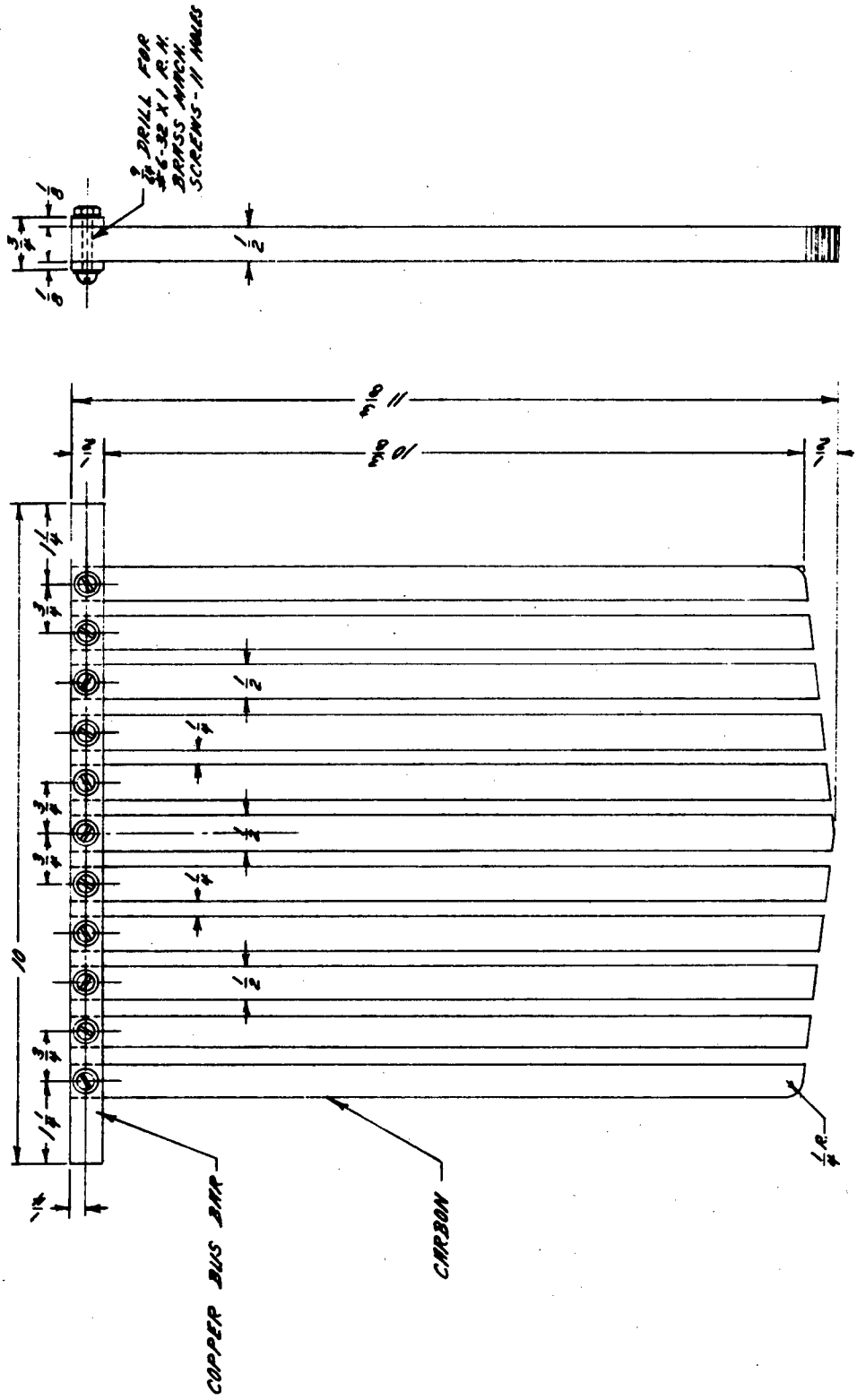
NOTE:
1.- ALL-WELD CONSTRUCTION
2.- GRAY HAMMER FINISH
3.- MATERIAL 1/8 X 1 X 1 ANGLE IRON

NOTE:
FOR ASS'Y DWG. SEE M60-270

M60-270A. Electrolysis Cell Detail. Scale 3/8" = 1". Rev. 12-8-52.



M60-270B. Lead Electrode for 1 Gal. Electrolysis Cell. Scale 1/2" = 1".



M-60-270C. Carbon Electrode for 1 Gal. Electrolysis Cell. Scale 1/2" = 1".