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A STUDY OF MERCURY-CATHODE MEMBRANE CELLS FOR THE ELECTROLYTIC REDUCTION OF URANYL SOLUTIONS

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EXTRACTION METALLURGY DIVISION

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A STUDY OF MERCURY-CATHODE MEMBRANE CELLS FOR THE ELECTROLYTIC REDUCTION OF URANYL SOLUTIONS

by

J. W. Kim[*] and R. Simard[**]

SYNOPSIS

Bench-scale horizontal cation-permeable membrane cells were constructed to study the effect of cell dimensions on the efficiency of electrolytic reduction of uranyl sulphate solutions flowing continuously over a mercury cathode. Current efficiencies were determined for various cells having length-to-width ratios of 10/1 to 40/1, and for catholyte solutions containing from 20 to 100 g U_3O_8/l in sulphuric acid. Optimum current density and solution flowrate were determined under these conditions. The effects of the nitrate and chloride ions were briefly examined.

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Direction des mines

Rapport de recherches R-70

ÉTUDE DE CELLULES À MEMBRANE ET À CATHODE DE MERCURE, POUR LA RÉDUCTION ÉLECTROLYTIQUE DE SOLUTIONS D'URANIUM

par

J. W. Kim* et R. Simard**

RÉSUMÉ

On a construit, à l'échelle expérimentale, des cellules horizontales à membrane perméable aux cations, afin d'étudier l'effet des dimensions de la cellule sur l'efficacité de la réduction électrolytique de solutions de sulfate d'uranyle en courant continu au-dessus d'une cathode de mercure. On a déterminé le rendement du courant dans le cas de diverses cellules dont le rapport longueur/largeur variait de 10/1 à 40/1, avec des solutions contenant de 20 à 100 g de U_3O_8/l en présence d'acide sulfurique. On a déterminé les valeurs optima pour la densité de courant et le débit de la solution dans ces conditions. On a examiné brièvement les effets des ions nitrate et chlorure.

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INTRODUCTION

A study of new methods of preparation of high-purity uranium dioxide pellets directly from uranium leach plant products is a continuing project of this Division. As part of this program it was considered of interest to study a special design of an electrolytic cell for the reduction of purified uranyl solutions to the uranous state.

"Wet process" reduction of uranyl sulphate or chloride for the production of UO_2, UF_4 and uranium metal is an alternate route to the currently used "dry process" whereby UO_3, U_3O_8 or ammonium diuranate are reduced at temperatures ranging from 600°C - 900°C with hydrogen or cracked ammonia. Applications of the "wet process" are limited at present to one semi-commercial scale installation in Japan,(1) where purified uranium solutions are treated in Excer cells (2, 3) to produce the tetrafluoride. Other wet methods of reduction have been studied however. Thus, purified uranyl chloride has been successfully reduced in zinc-packed columns (4) to produce the double salt $NaUF_5$, and by the cupric sulphate-sulphur dioxide couple (5) to produce dense tetrafluoride for subsequent metal production. Crystalline uranous sulphate has been obtained by the reduction of strong sulphuric acid solutions of uranyl sulphate in the Excer cell.(6)

While most of the above studies were directed towards the precipitation of the tetrafluoride salt for metal production, the current interest in UO_2 in the form of high-density pellets for use in nuclear reactors has directed our work to the production of ammonium diuranate or some form of reactive uranium oxide from which suitable fuel elements can be made. While the diuranate can be readily precipitated from purified uranyl salt solutions, a subsequent hydrogen reduction step is required to produce a UO_2 powder that will press and sinter to a high-density pellet. The "wet process" reduction of uranyl solutions from ion exchange or solvent extraction circuits, to be later followed by the precipitation, filtering and drying of an equally suitable UO_2 powder, was our final objective in the present study.

This report describes some basic design relationships determined for a horizontal mercury-cathode, permeable-cation-membrane cell, of simple construction, to be used in the reduction step. Previously, a laboratory-size Excer cell, manufactured by Ionics Inc., Cambridge, Mass., had been tested for this type of work, but the design was relatively complex and required high circulating loads of solution to carry off the small volumes of hydrogen and oxygen gas inherent to an electrolytic reduction process.

The simplicity of the horizontal mercury-cathode cell appeared to justify a preliminary examination of its operating characteristics as affected by the general design.

EQUIPMENT

Electrolytic Cell

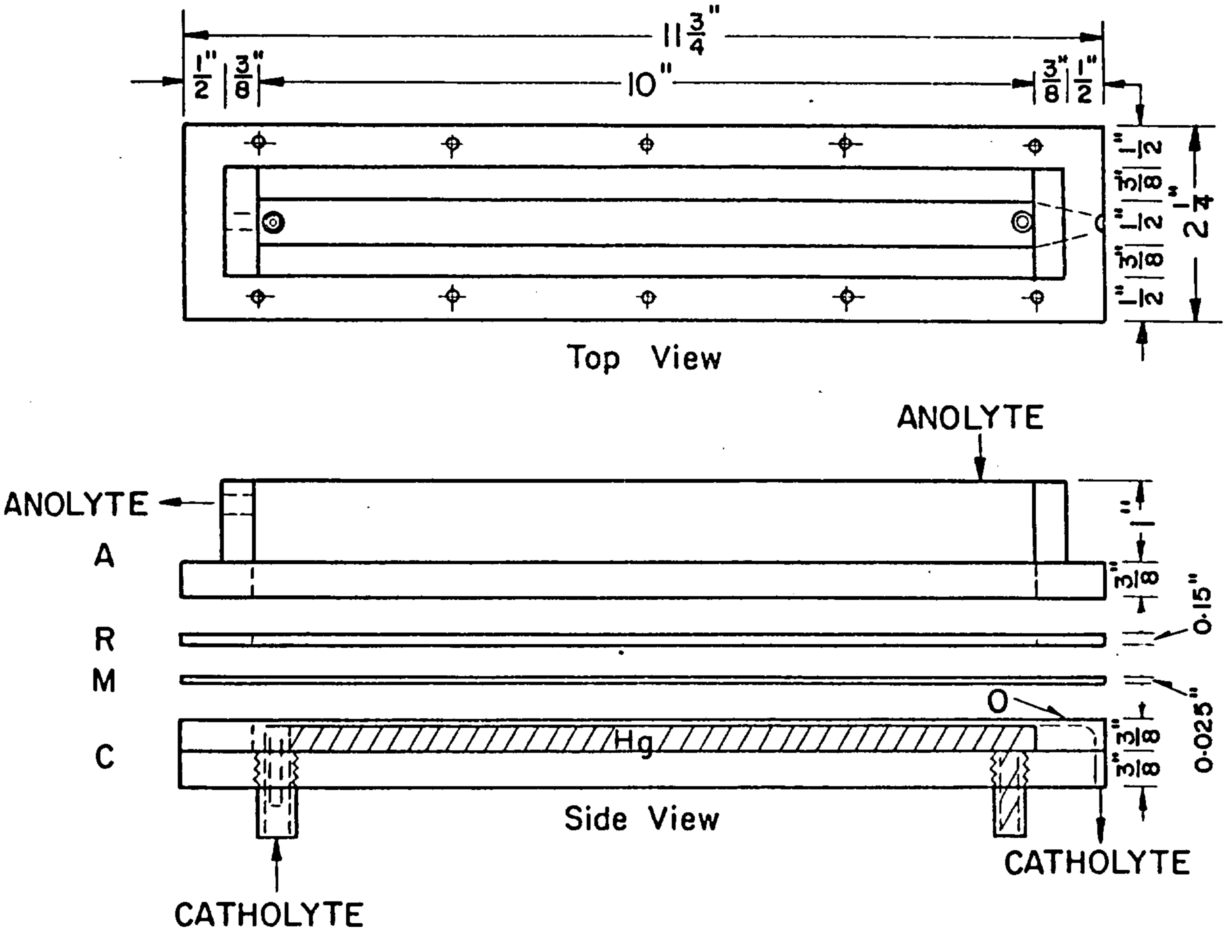
In electrolytic reduction of acid solutions, where a mercury cathode is used to take advantage of the high hydrogen overvoltage of mercury, a horizontal cathode cell is normally adopted. For alkaline solutions, mercury-wetted vertical cathodes have been developed, taking advantage of the amalgamating property of mercury in such a system, but with acid solutions amalgamated cathodes have not worked well. The necessity of a diaphragm between anode and cathode for efficient uranium reduction has also been well established and the development of ion-selective membranes by ion exchange resin manufacturers has made a great improvement over canvas, asbestos or porous ceramic plate, in controlling the diffusion of the electrolytes.

The main problem in the operation of horizontal membrane cells is the trapping of hydrogen gas underneath the horizontal membrane surface, and the consequent high cell resistance and poor current distribution. Mechanical agitation through a central hollow shaft was provided in the development of the Excer cell.(2) This design was effective but led to a complicated construction which would probably result in maintenance problems. The alternative is a long and narrow cell with a shallow catholyte space to achieve fluid flow at high linear velocities so that the hydrogen formed will be continuously swept out of the cathode comparment. The sweeping action of the flowing catholyte would be assisted by inclining the membrane, but the inclination angle is limited by the depth of the catholyte compartment which must be kept small to reduce cell voltage.

The choice of materials and general cell dimensions was governed by these considerations. Cathode areas were chosen to suit the proposed scale of operation, with an available D. C. supply of 30 amp and a possible maximum current density of 3 amp per sq. in. (46.5 amp per dm^2). Four cells, having widths and lengths respectively of 1 in. by 10 in., 3/4 in. by 15 in., 1/2 in. by 10 in. and 1/2 in. by 20 in., were constructed from 3/8-in. Plexiglas. Construction features are shown in Figure 1. The mercury level could be varied by an adjustable glass sleeve in a Saran nipple to obtain from 0.08 in. to 0.2 in. of catholyte depth. The cation permeable membrane, Zerolit C-20 Permaplex, was used for all tests and was supplied in sheet form by the Permutit Co. of England. The anode was made from pure lead sheet 0.1 in. thick, and the mercury of the cathode was of high purity.

Accessory Equipment

Direct current was supplied from a 12-volt battery or from a Northern Electric 550-V, 3-phase selenium rectifier with three-step D. C. supply rated at 6 V-100 amp, 12 V-50 amp and 120 V -10 amp.



A - ANODE COMPARTMENT
R - RUBBER GASKET
M - CATION EXCHANGE MEMBRANE
C - CATHODE COMPARTMENT
O - OVERFLOW TROUGH

FIGURE I

ELECTROLYTIC REDUCTION CELL

A coarse rheostat control at the rectifier or battery was supplemented by a high capacity Ni-chrome wire with sliding contact. The flow-rate of catholyte was measured with a suitable Fischer-Porter rotameter.

PROCEDURE

Electrolytes

The catholyte was prepared from refined UO_3 dissolved in sulphuric acid to obtain various concentrations of uranyl ion and free acid. One mole of sulphuric acid is theoretically required per mole of uranyl ion for reduction to the uranous sulphate. In these experiments, however, an excess was used since it was known that some acid would be consumed through hydrogen discharge and that this could cause hydrolysis of the reduced salt. Any precipitate forming at the surface of the mercury would decrease its hydrogen overvoltage. On the other hand, too high an acidity would cause a decrease in current efficiency and increase the ammonia required for the subsequent neutralization.

The anolyte used was 1.0 $\underline{M}$ H_2SO_4, at which concentration the cell resistance is near the minimum.

In all experiments the rate of flow of catholyte is expressed as a fraction of theoretical flow. Theoretical flow is defined as the rate of flow at which, under conditions of 100% current efficiency, 100% of the contained uranium would be reduced from U^6 to U^4.

The fraction of theoretical flow is calculated by the formula:

$$\frac{(\text{g } U_3O_8/\text{l catholyte}) \times (\text{flowrate, l/min})}{0.0872 \times (\text{current, amp})}.$$

The electrochemical equivalent for reduction of U^6 to U^4 is 0.0872 g U_3O_8 per amp min (See Appendix 2 for calculations).

Cell Operation (see Figure 2)

The cell was placed horizontally and the cathode compartment filled with mercury to the overflow point. The lead anode was then placed on the diaphragm and the anode compartment filled with 1 M H_2SO_4. The electrolytes were then fed by gravity at a constant rate and the current adjusted. The anolyte overflow was collected, and cooled before recycling to the feed end. The catholyte was sampled at intervals and the samples kept in bottles under nitrogen until analyzed for U^6, U^4 and U^3. The analytical procedure is briefly described in Appendix 1.

The temperature of the anolyte was maintained at near 30°C by external cooling, while that of the catholyte ranged from 30 to 45°C according to the current density and flowrate used. Current density in all cases was calculated as amperes per sq. in. cathode area.

These experiments were first designed to determine the preferred cell dimensions for maximum current efficiency of the uranium reduction. Following these experiments, the effect on

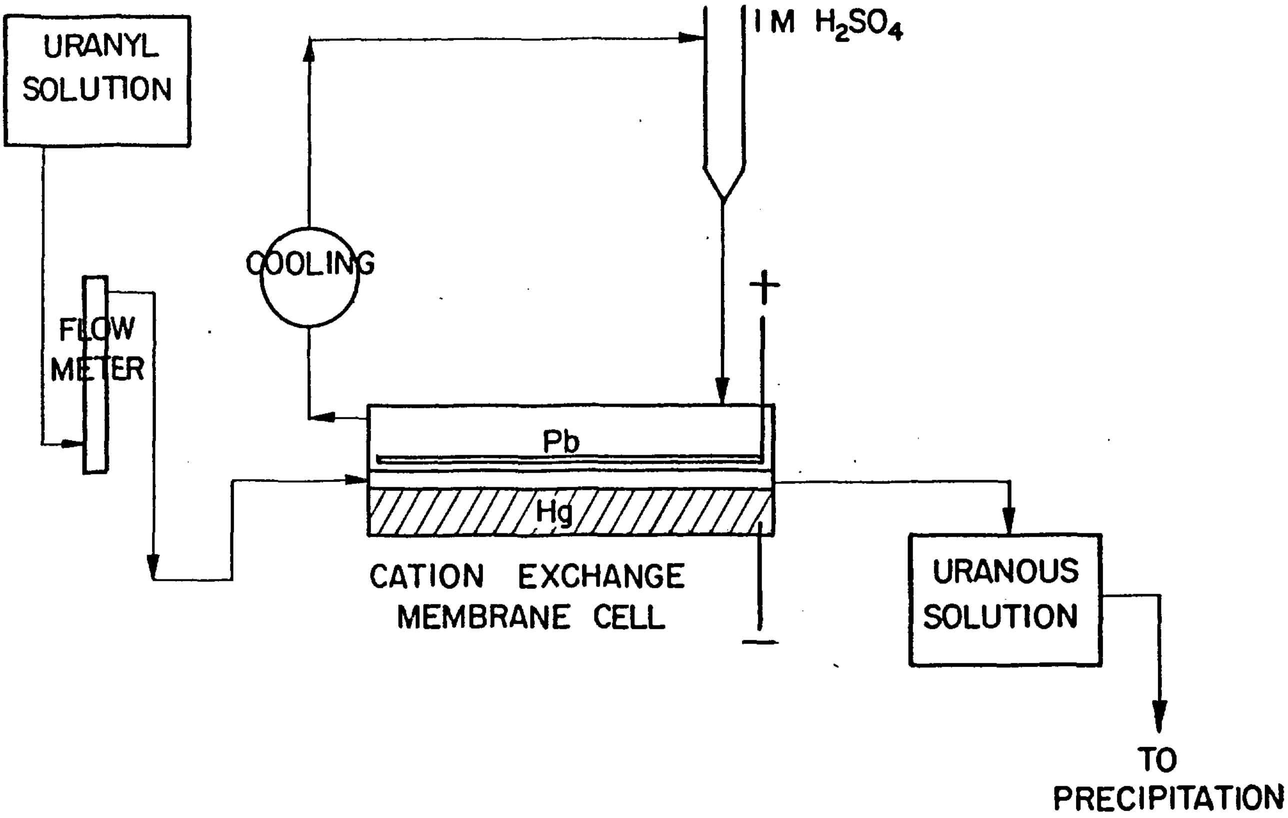


FIGURE 2

FLOW DIAGRAM OF ELECTROLYTIC CIRCUIT

current efficiency of varying current density at various concentrations of uranyl sulphate in sulphuric acid was examined, using the preferred cell design. A few experiments were made with uranyl chloride in hydrochloric acid, and uranyl nitrate in nitric acid, to compare the behaviour of these salts with that of uranyl sulphate.

RESULTS

Reduction of Uranyl Sulphate Solutions

Effect of Cell Dimensions

A series of tests was first completed at the relatively high uranium concentration of 98 g U_3O_8/l and 51.7 g H_2SO_4/l, with the four cells of different shapes described earlier, the current density being maintained at 2 amp per sq. in. The results are summarized in Table 1 and Figures 3 and 4, from which it will be seen that the cell with 1/2 in. width and 20 in. length gave the highest current efficiency. However, because of the difficulty of maintaining an even current density at the long and narrow lead anode, the 1/2 in. by 10 in. cell was chosen for subsequent experiments. As shown in Figure 4, the loss in current efficiency in going from a 40 to a 20 length-to-width ratio is only 3 to 4%.

The reduction values of Table 1 were calculated from the following expression:

$$\% \text{ reduction} = \frac{\text{Current efficiency}}{\text{Fraction of theoretical flow}}$$

TABLE 1

Effect of Cell Dimensions

Catholyte:	98 g U_3O_8/l, 51.7 g free H_2SO_4/l
Anolyte:	1 M H_2SO_4
Current Density:	2 amp per sq. in.
Temperature:	30° - 45°C in catholyte 30°C in anolyte

Cell Type W x L (inches)	Fraction of Theoretical Flow	Current Efficiency (%)	Reduction (%)	Cell Voltage (volts)
1/2 x 20	1.35	97.5	72	4.9
"	1.20	96.5	80	5.0
"	0.97	95.5	98	5.1
"	0.74	82.5	98.5	5.2
1/2 x 10	1.37	94	67	5.4
"	1.20	92.5	77	5.6
"	0.99	94	94.5	5.8
"	0.87	86.5	99	6.0
3/4 x 15	1.35	90.5	68.5	5.8
"	1.05	90.5	86	5.9
"	0.89	88.	98.5	5.9
"	0.78	79.5	99.	6.0
1 x 10	1.31	83	62	5.8
	1.15	84	72	5.9
	0.94	79	84	6.0
	0.79	71.5	91	6.0

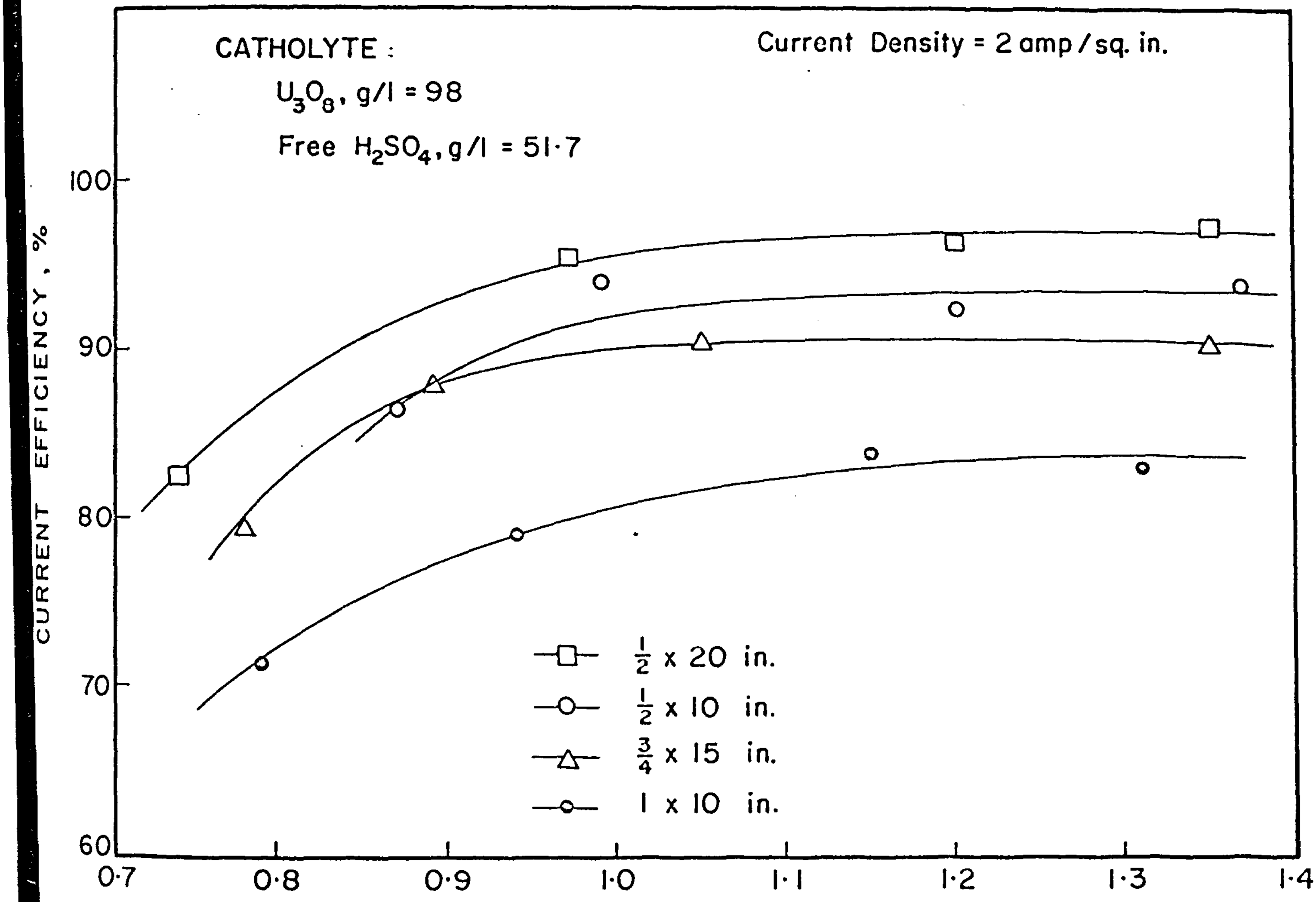


FIGURE 3

EFFECT OF CELL DIMENSIONS

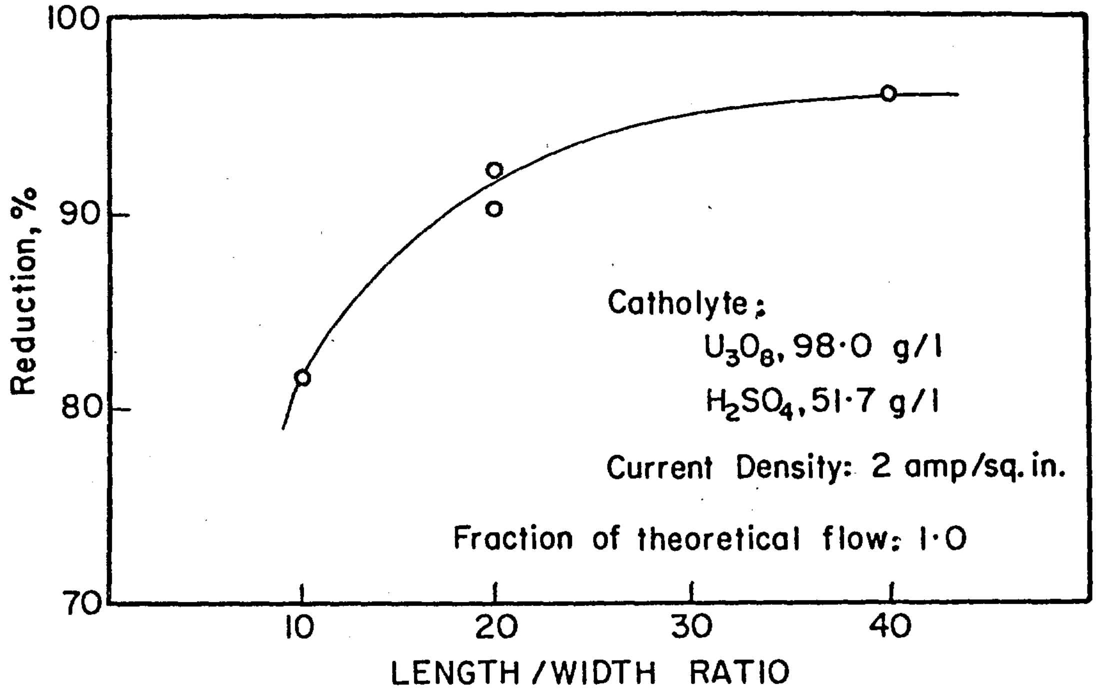


Figure 4
EFFECT OF CELL DIMENSIONS
AT MAXIMUM CURRENT EFFICIENCY

Effect of Depth of Catholyte

A third dimension, the depth of catholyte, was also varied in a series of tests reported in Table 2 and Figure 5. The results show that the depth of the catholyte has no appreciable effect on current efficiency within the range tested. However, as expected, a slightly higher voltage accompanied the increase in depth of catholyte.

TABLE 2

Effect of Depth of Catholyte

Catholyte:	20.3 g U_3O_8/l, 32 g free H_2SO_4/l
Anolyte:	1 M H_2SO_4
Current Density:	0.7 amp per sq. in.
Temperature:	30°C

Depth of Catholyte (in.)	Fraction of Theoretical Flow	Current Efficiency (%)	Reduction (%)	Cell Voltage (volts)
0.08	1.26	83.5	52	4.3
"	1.05	84.0	80	4.4
"	0.87	81	92.5	4.5
"	0.6	63.5	99	4.6
0.17	1.24	82	65.5	4.5
"	1.08	83.5	77	4.6
"	0.88	84	95	4.7
"	0.65	65.5	99	4.8

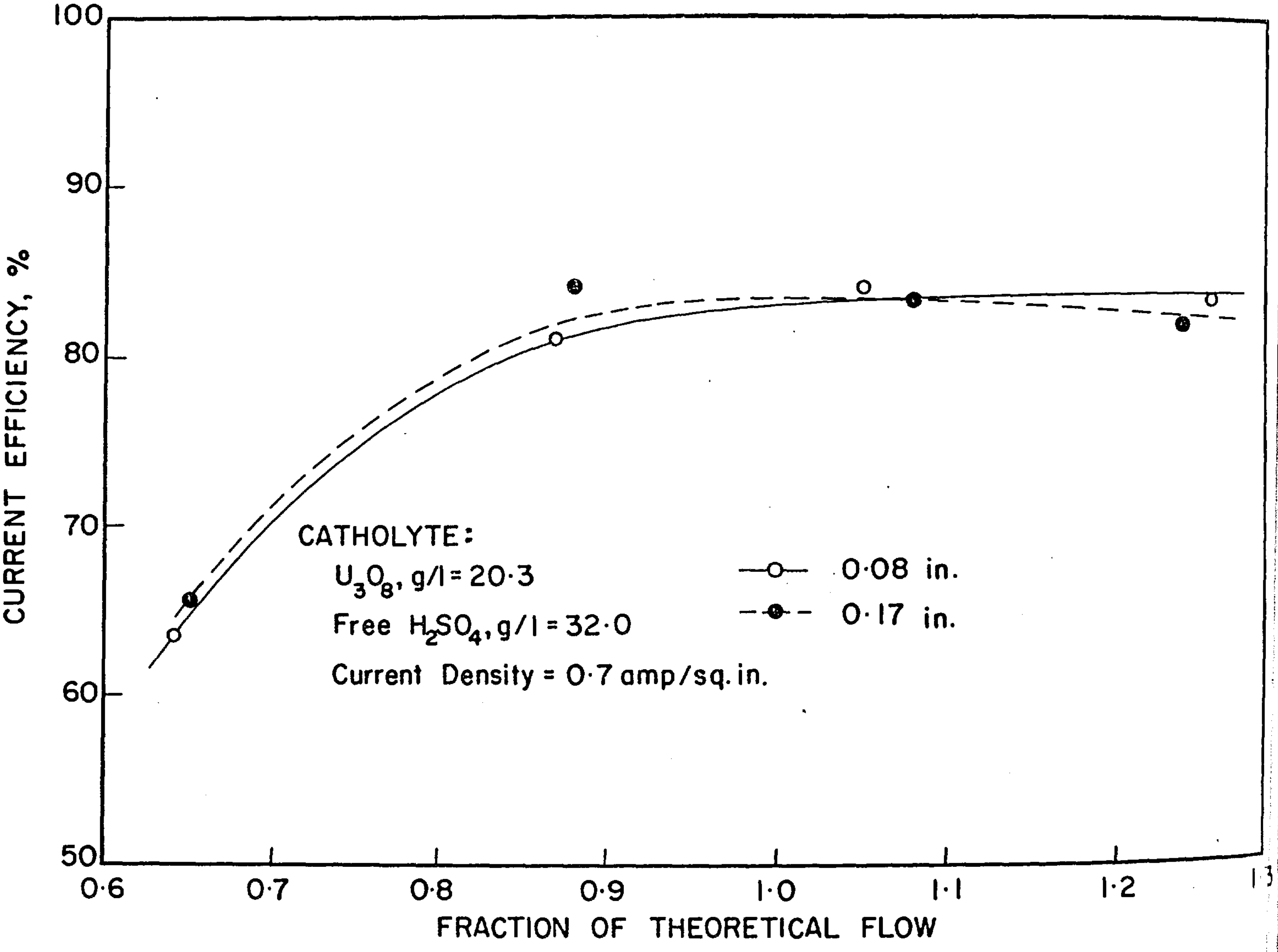


FIGURE 5

EFFECT OF DEPTH OF CATHOLYTE

Effects of Current Density and Flowrate

The results of this series of tests are presented in Table 3 and graphically in Figures 6 to 11. Figure 7 is the translation from Figure 6 of the constant flowrate intercepts expressed as % reduction. Figures 9 and 11 are similarly derived from 8 and 10.

TABLE 3

Effect of Uranyl Sulphate Concentration and Current Density

Cell: 1/2 in. x 10 in.
Anolyte: 1 M H_2SO_4
Temperature: Anolyte : 30° C
Catholyte: 30-45° C

Catholyte		Current Density (amp/sq.in.)	Fraction of Theoretical Flow	Current Efficiency (%)	Reduction (%)	Cell Voltage (volts)
U_3O_8 (g/l)	Free H_2SO_4 (g/l)					
20.3	32.0	0.4	1.31	83	63	4.0
"	"	"	0.90	79	86.5	4.1
"	"	"	0.72	69.5	96	4.2
"	"	0.7	1.26	83.5	52	4.3
"	"	"	1.05	84	80	4.4
"	"	"	0.87	81	92.5	4.5
"	"	"	0.64	63.5	99	4.6
"	"	1.0	1.14	80.5	70	4.3
"	"	"	0.88	80.5	91	4.3
"	"	"	0.79	77.0	97.5	4.4
"	"	"	0.74	73.5	99	4.4
"	"	1.6	1.14	73.0	64	4.7
"	"	"	0.90	72.0	79.5	4.8
"	"	"	0.77	67.5	86.5	4.9
"	"	"	0.66	64.5	98.5	5.0
"	"	2.0	1.23	67.5	53.5	5.2
"	"	"	1.00	66	65	5.3
"	"	"	0.83	65	78.5	5.4
"	"	"	0.65	61	94	5.5
40.7	34.0	0.7	1.19	84	70	3.9
"	"	"	1.01	84	84	3.9
"	"	"	0.88	82	93.5	4.0
"	"	"	0.75	74	99.5	4.0
"	"	1.0	1.34	87	64	4.2
"	"	"	1.22	86	69.5	4.2
"	"	"	0.88	83	95	4.2
"	"	"	0.69	70	99	4.3
"	"	1.6	1.21	83	69.5	4.7
"	"	"	1.01	83	82	4.8
"	"	"	0.86	80.5	93.5	4.8
"	"	"	0.77	76	99	4.9
"	"	2.0	1.20	80.5	65.5	5.1
"	"	"	0.96	79.5	83.5	5.2
"	"	"	0.84	78	94	5.3
"	"	"	0.74	74	99	5.4
92.9	52.0	1.2	1.41	90	59	4.8
"	"	"	1.04	88.5	84.5	4.9
"	"	"	0.84	84	98	5.0
"	"	"	0.71	76	99	5.1
"	"	2.0	1.39	94	71.5	5.0
"	"	"	1.08	93	86.5	5.1
"	"	"	0.87	86.5	99	5.3
"	"	"	0.69	77	100	5.4
"	"	2.4	1.31	95.5	72.5	5.2
"	"	"	1.02	94	94	5.3
"	"	"	0.92	91.5	99	5.4
"	"	"	0.81	87	99.5	5.5
"	"	2.8	1.33	94.5	70.5	5.4
"	"	"	1.09	92	84	5.5
"	"	"	0.89	88	98.5	5.6
"	"	"	0.78	83	99	5.7

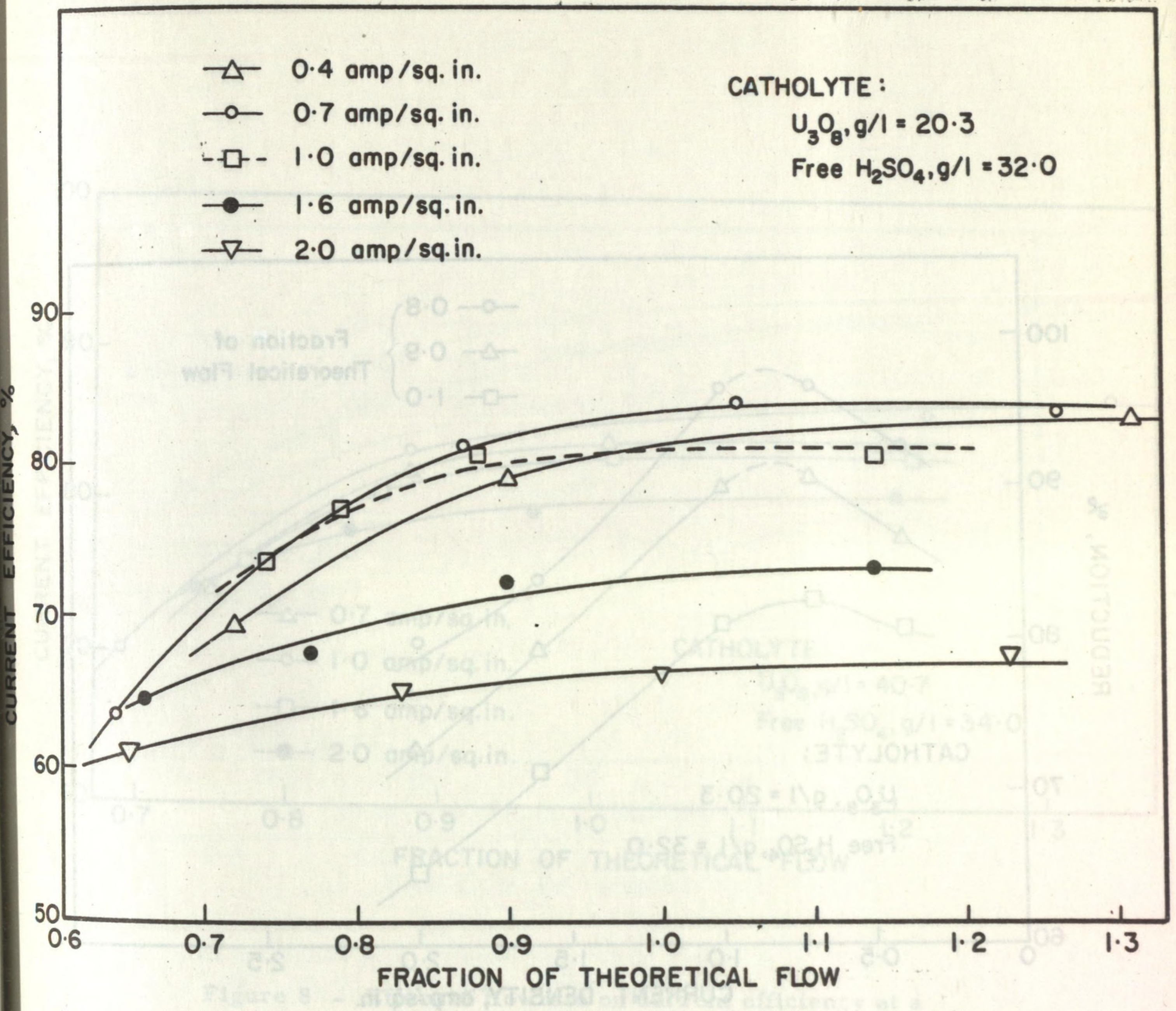


Figure 6 - Effect of flowrate on current efficiency at a given current density. Catholyte: U_3O_8, 20.3 g/l.

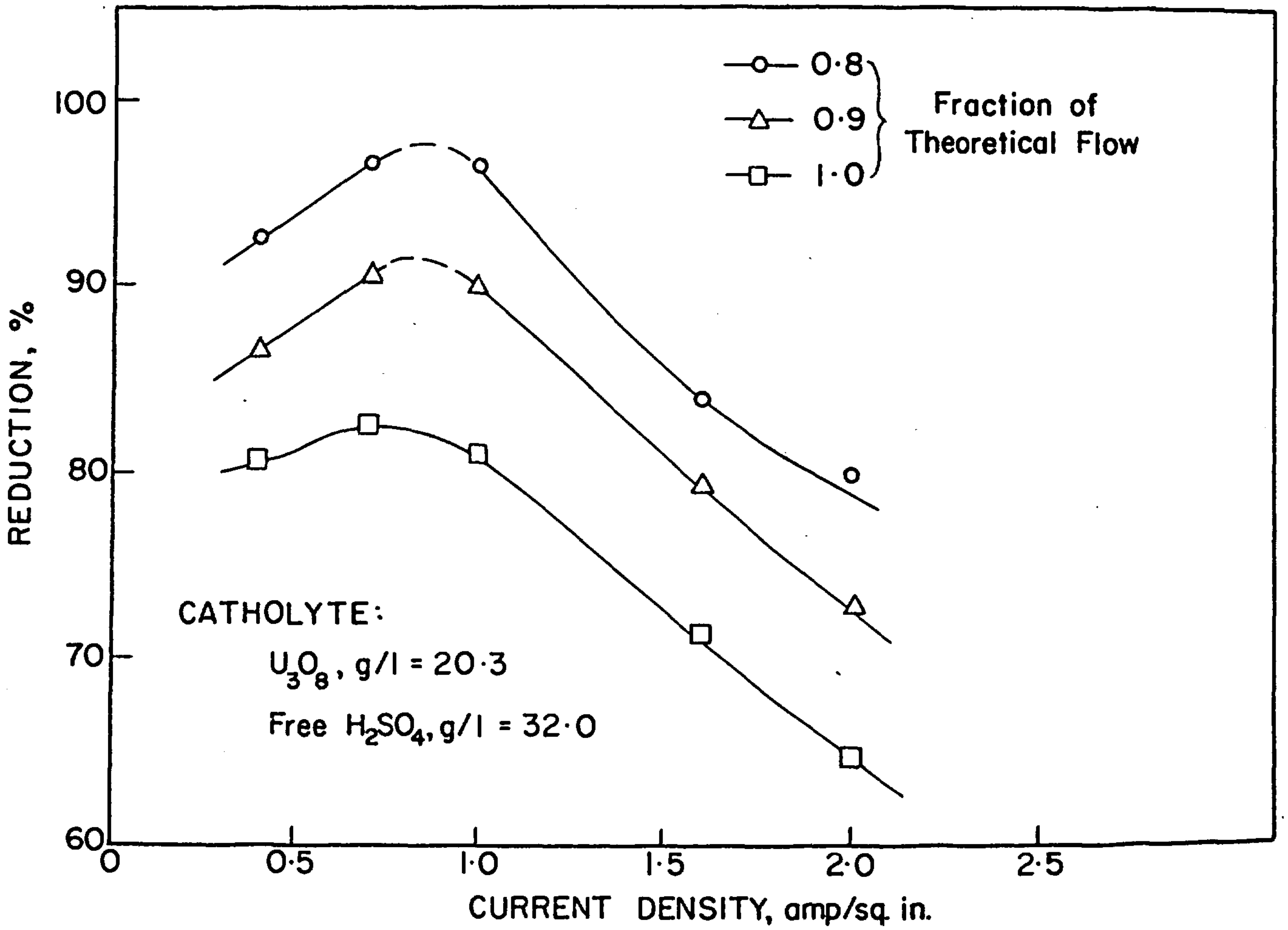


Figure 7 - Effect of current density on % reduction at a given flowrate. Catholyte: U_3O_8, 20.3 g/l.

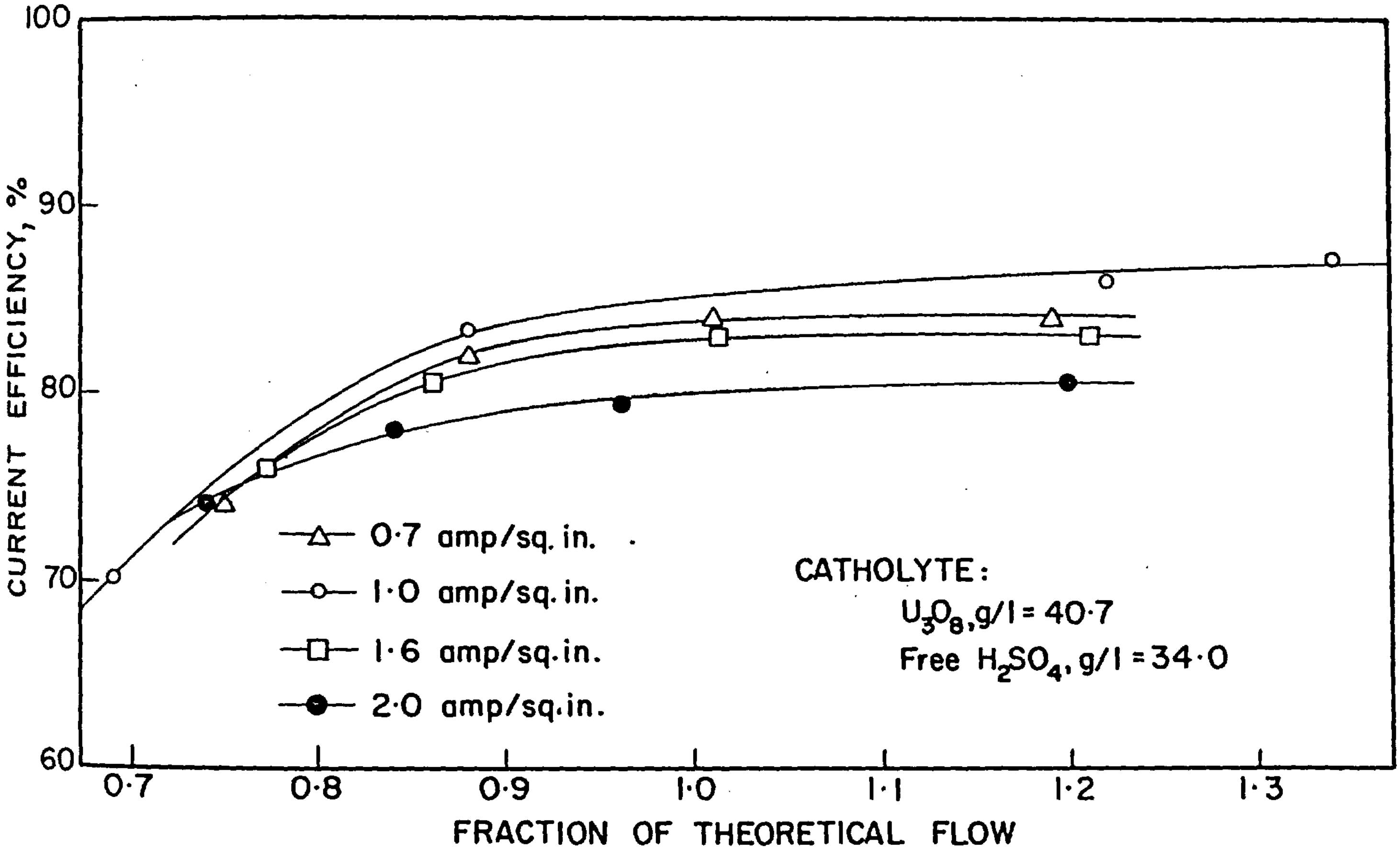


Figure 8 - Effect of flowrate on current efficiency at a given current density. Catholyte: U_3O_8, 40.7 g/l.

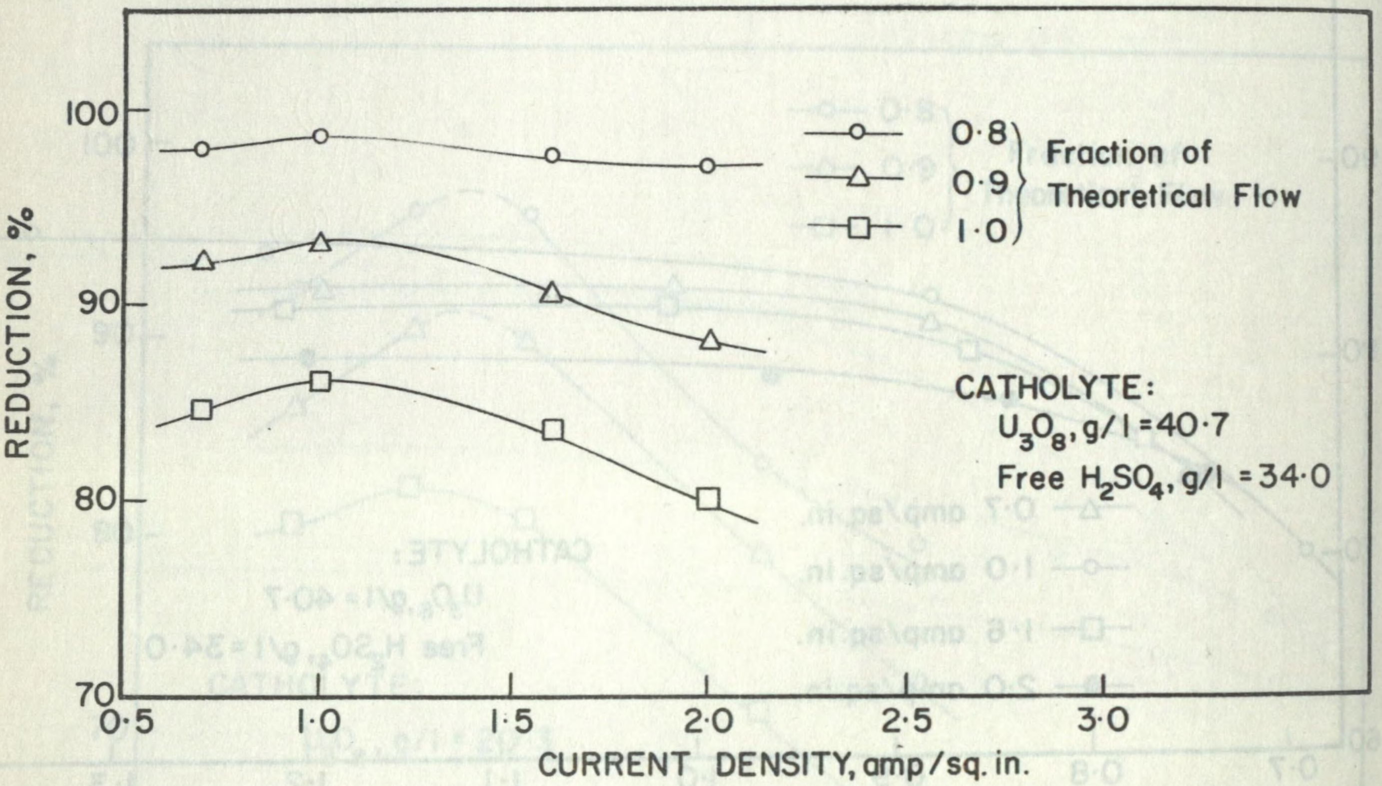


Figure 9 - Effect of current density on % reduction at a given flowrate. Catholyte: U_3O_8, 40.7 g/l.

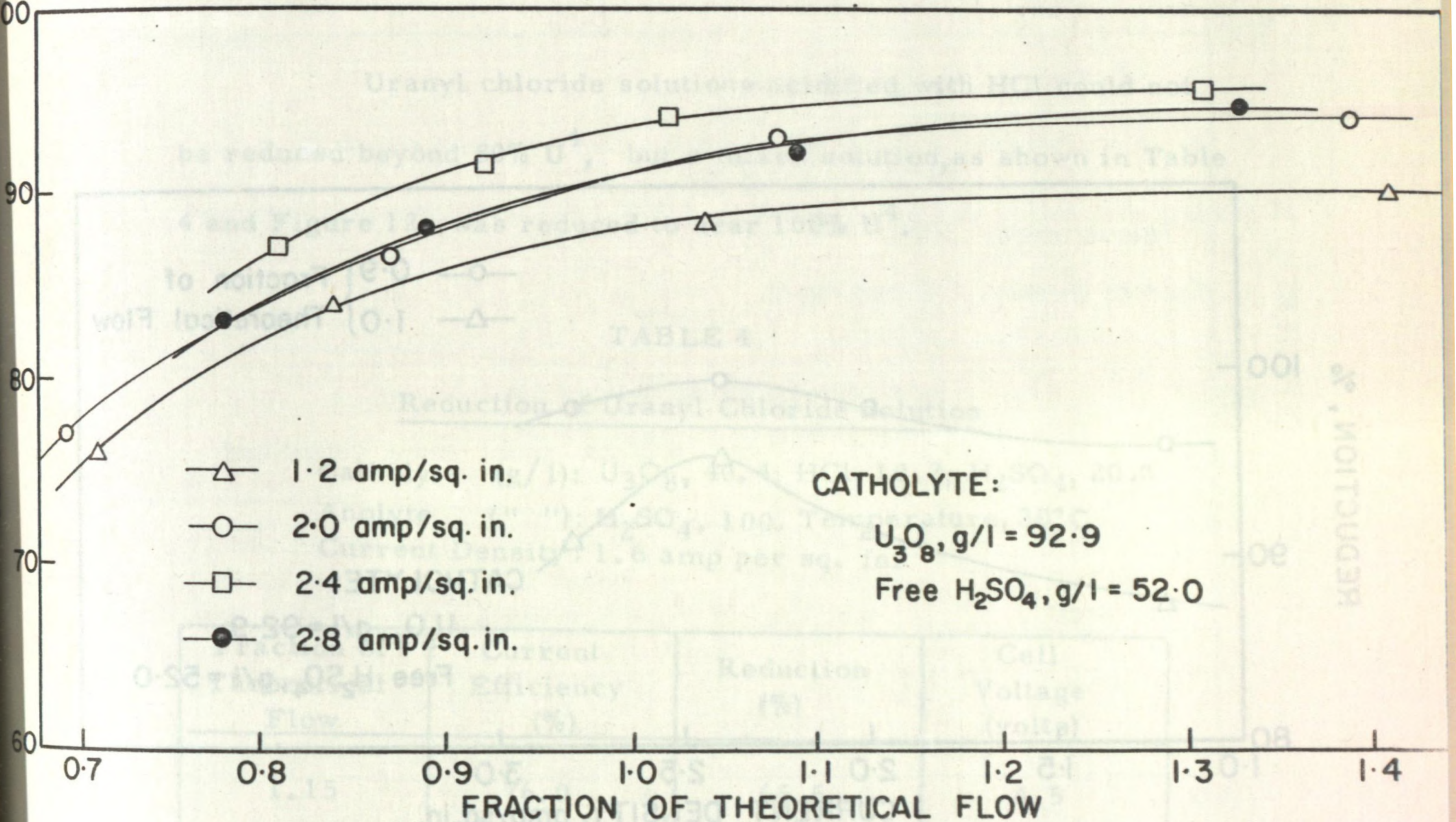


Figure 10 - Effect of flowrate on current efficiency at a given current density. Catholyte: U_3O_8, 92.9 g/l.

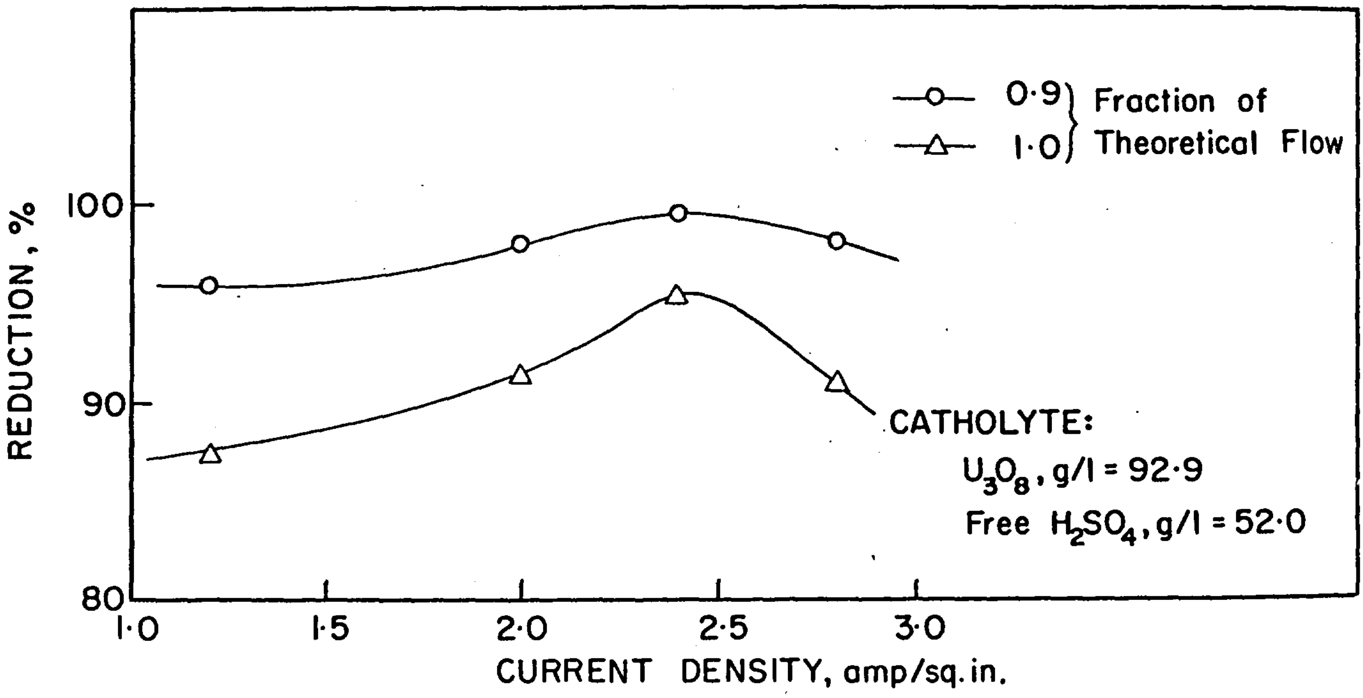


Figure 11 - Effect of current density on % reduction at a given flowrate. Catholyte: U_3O_8, 92.9 g/l.

Reduction of Chloride and Nitrate Solutions

Since chloride or nitrate salts can also be used in ion exchange or solvent extraction processes for the production of concentrated uranyl solutions, a brief examination was made of the effect of these ions on the efficiency of reduction.

Uranyl chloride solutions acidified with HCl could not be reduced beyond 80% U^4, but a mixed solution, as shown in Table 4 and Figure 12, was reduced to near 100% U^4.

TABLE 4

Reduction of Uranyl Chloride Solution

Catholyte (g/l): U_3O_8, 40.4; HCl, 10.2; H_2SO_4, 20.0
Anolyte (" "): H_2SO_4, 100. Temperature, 30°C
Current Density: 1.6 amp per sq. in.

Fraction of Theoretical Flow	Current Efficiency (%)	Reduction (%)	Cell Voltage (volts)
1.15	76.0	65.5	4.5
1.05	74.0	74.5	4.6
0.81	73	90.5	4.7
0.68	68.5	99.5	4.8

Solutions containing 20 to 100 g U_3O_8/l as uranyl sulphate acidified with nitric acid were reduced only slightly, due to the preferential reduction of the nitrate ion.

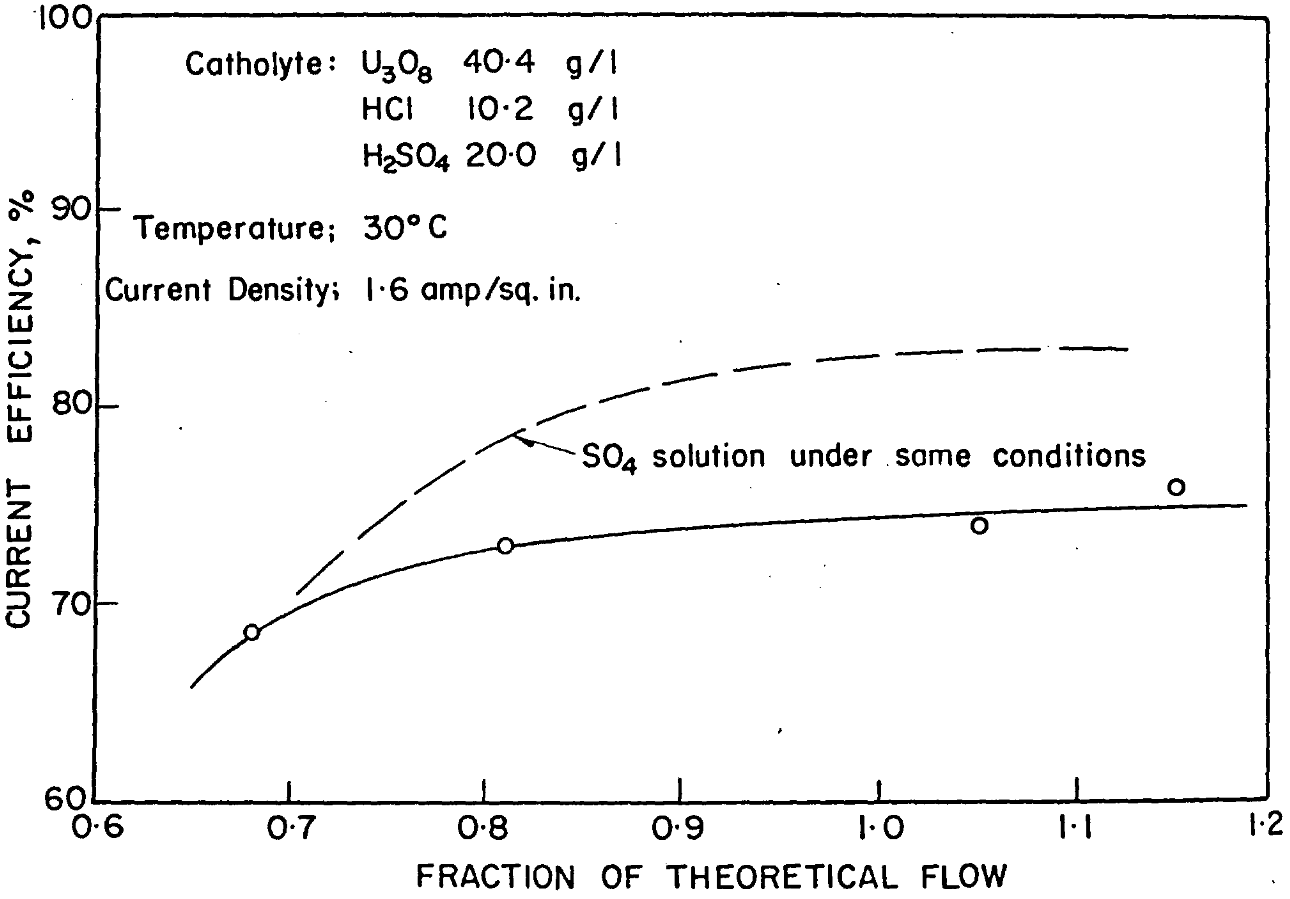


Figure 12. Reduction of chloride solution. Effect of flowrate on current efficiency at a fixed current density.

Cell Voltage

This was in part a function of acidity, current density, temperature, and uranium concentration. Other factors were held constant by using a thin ion exchange membrane of 0.025 in. thickness for all tests and setting the anode directly on the membrane.

Table 5 shows cell voltages required to maintain current density that will give near 95% reduction under the above conditions.

TABLE 5

Cell Voltage at 95% Reduction

Temperature of Anolyte: 30°C

Concentration of Catholyte (g U_3O_8/l)	Current Density (amp/ sq. in.)	Fraction of Theoretical Flow	Cell Voltage (volts)
20.3	0.8	0.8	4.6
40.7	1.0	0.8	4.3
92.9	2.4	0.9	4.5

Cell Temperature

This was maintained at 30 to 35°C in the anolyte but should higher uranium concentrations be used, which would require higher current densities for optimum results, better cooling of the cell would be required to maintain the temperature within the limits set by the materials of construction.

Cell Performance

Within the conditions of the present tests, the cell performed satisfactorily.

A slight corrosion of the lead was noticed but this would not affect the purity of the catholyte. A flat tube with cooling water is suggested, in order to increase the life of the lead anode.

The membrane showed no signs of wear or cracking and was kept at all times under weak sulphuric acid to avoid drying and shrinkage. In practice, where larger dimensions would be used a heavier Fiberglas or Teflon reinforcement is suggested.

There was no noticeable drop of the hydrogen overvoltage at the mercury surface over the period it was used. Where small quantities of uranous sulphate were formed, these were entrained in the catholyte overflow.

DISCUSSION

The reactions which occur in the electrolysis of uranyl sulphate-sulphuric acid solutions, due to the passage of two faradays, are as follows:

Cathode: $UO_2SO_4 + 4\,(H)^+ + (SO_4)^{--} + 2e$ .....1)

$\longrightarrow U(SO_4)_2 + 2\,H_2O$

Anode: $(SO_4)^{--} + H_2O \longrightarrow H_2SO_4 + 1/2\ O_2 + 2e^-$ .....2)

Sum: $UO_2SO_4 + H_2SO_4 \longrightarrow U(SO_4)_2 + H_2O + 1/2O_2$.....3)

However, because of the depletion of uranyl ions at the mercury surface. a small amount of hydrogen is evolved. In the cation-permeable membrane cell, uranium migration to the anode as the UO_2 cation is prevented by the cell voltage. while any uranyl sulphate anion is stopped by the membrane. In the anode compartment, the reaction is essentially as in 2). Any variation in current efficiency and degree of reduction will be caused by the conditions in the cathode compartment, and attention has therefore been directed to the conditions in this part of the cell.

Effect of Uranyl Sulphate Concentration and Current Density

The limits of concentration were set by the solutions obtained from ion exchange or solvent extraction processes in use or proposed for the uranium industry. Generally, the higher the concentration the more efficient is the reduction process.

Looking back to Figures 7, 9 and 11, which express the relation between current density and per cent reduction, it will be seen that for a given flowrate a specific current density exists which will give the maximum per cent reduction, and that the maximum depends on the uranium concentration in the catholyte. These conditions are summarized in Table 6.

TABLE 6

Current Density for Maximum Efficiency at Theoretical Flow

Concentrations in Catholyte ($g\ U_3O_8/l$)	Optimum Current Density (amp/ sq. in.)	Current Efficiency (%)
20.3	0.7	82
40.7	1.0	85.5
92.9	2.4	93.5

These maxima can be explained from the the effect of two conflicting trends. For a given fraction of theoretical flow, increased current density will require a higher absolute flowrate, which will favor turbulence and ion diffusion. This will increase reduction efficiency to a point where diffusion becomes limiting. A further increase in current density will then cause a drop in the overall efficiency. The maxima are more noticeable for lower uranium concentrations, which confirms the previous explanation. The maxima are also displaced towards higher current densities with increase in uranium concentration.

In order to achieve a high degree of reduction (95%) of the uranyl ion for the subsequent precipitation of near stoichiometric UO_2, the conditions set forth in Table 5 can then be used for this purpose.

Effect of Temperature

Higher temperature in electrolytic processes will reduce hydrogen overvoltage slightly (2 mv per degree C). On the other hand, overall cell resistance is reduced and ion diffusion is improved. It would therefore have been advantageous to operate at higher temperatures, but, because of the limit set by the materials of construction in the present study, and in order to control the corrosion of the lead anode, the tests were carried out near room temperature. It is felt that in practice, if the extra cost of anodes of greater resistance can be justified, cell temperature would be limited mainly by the materials of construction.

CONCLUSION

Efficient reduction of uranyl sulphate and chloride solutions has been achieved in a horizontal-membrane, mercury-cathode cell designed for this purpose. In a single-stage operation, 90% reduction of U^6 to U^4, or better, at 80 to 95% current efficiency was obtained for a catholyte solution containing from 20 to 100 g $U_3O_8/1$. Excess acid is necessary to prevent hydrolysis, and cooling devices are suggested for higher capacities.

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APPENDIX 1

Determination of U^6, U^4 and U^3 in Catholyte Solutions

1. Total uranium is determined by the standard Jones reductor-ferric iron-dichromate titration method.

2. Total $U^4 + U^3$ is determined as U^4 by aerating the sample before a ferric iron-dichromate titration.

3. Total $U^4 + U^3$ is determined by dichromate titration without prior aeration, using deaerated ferric and sulphuric acid solutions.

The difference between Titrations 1 and 2 is reported as U^6. The difference between Titrations 2 and 3, after taking into account the equivalent, is reported as U^{+3}. The U^4 is then calculated by difference.

APPENDIX 2

Calculation of Theoretical Flowrate in the 1/2 in. x 10 in. Cell

(5 sq. in.)

Catholyte U_3O_8 (g/l)	Current Density (amp/sq. in.)	Total Current (amp)	Theoretical Flowrate (ml/min)
20.3	0.4	2.0	8.6
"	1.7	3.5	15.0
"	1.0	5.0	21.5
"	1.6	8.0	34.4
40.7	0.7	3.5	7.5
"	1.0	5.0	10.7
"	1.6	8.0	17.1
"	2.0	10.0	21.4
92.9	1.2	6.0	5.6
"	2.0	10.0	9.4
"	2.4	12.0	11.2
"	2.8	14.0	13.1

$$\text{Theoretical flowrate l/m} = \frac{(\text{current, amp})\ (.0872\ \text{g}\ U_3O_8/\text{amp min})}{\text{catholyte g}\ U_3O_8/\text{l}}$$

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