

# A Study of Mercury-Cathode Membrane Cells for the Electrolytic Reduction of Uranyl Solutions\*

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## 隔膜電解槽와 水銀陰極에 의한 Uranyl 溶液의 電解還元

金 在 元 · R. Simard

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### 要 約

高純度の  $UO_2$  pellets 나 或은  $UF_4$  를 얻는 것을 目標로 하여 그 計劃의 一部로서 純粹한  $UO_2^{++}$  溶液을  $U^{++}$  溶液으로 電解還元하는 方法을 實驗하였다.

現在 實施되고 있는 方法으로서의 純粹한  $UO_3$  粉末을 水素 或은 ADU(Ammonium diuranate)를 熱分解하여 生成되는 分解된 암모니아로서 600 내지 900°C 에서還元하거나 혹은 복잡한 構造를 가진 Excer cell 로서 濕式電解하는 方法들이 있다.

이 報告는 從來의 Excer cell 을 改造하여 水銀陰極과 陽이온 交換樹脂의 隔膜及 鉛陽極으로 구성되는 간 단한 電解裝置로서  $UO_2^{++}$  溶液을 連續적으로 電解시켰을 때 가장 適合한 電解槽의 構造, 電解液의 溫度, 電解液의 種類와 濃度 또 各 流量과 電流密度에 따르는 電流效率, 電解槽電壓 등을 測定한 結果를 記錄하고 電解反應을 說明한 것이다.

實驗結果에 依하면 電解槽는 水平式으로 하여 길이와 폭의 比가 20 對 1 이고 電解液은 還元에 所要할 理論量 以上의 遊離黃酸이 共存하는 可及의 高濃度の  $UO_2SO_4$  溶液과 그에 比例하는 電流密度를 使用하여 電解함으로써 單一過程의 電解에 依하여  $UO_2^{++}$  를  $U^{++}$  로 80 내지 95%의 電流效率로서 還元시킬 수 있다는 것을 알았다.

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.

### 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

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arranging 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,<sup>(1)</sup> where purified uranium solutions are treated in Excer cells<sup>(2,3)</sup> 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<sup>(4)</sup> to produce the double salt  $\text{NaUF}_6$ , and by the cupric sulphate-sulphur dioxide couple<sup>(5)</sup> 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.<sup>(6)</sup>

While most of the above studies were directed towards the precipitation of the tetrafluoride salt for metal production, the current interest in  $\text{UO}_2$  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  $\text{UO}_2$  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  $\text{UO}_2$  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.<sup>(2)</sup> 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 compartment. 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<sup>2</sup>). 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 Sarani 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 coarse rheostat control at the rectifier or battery was supplemented by a high capacity Ni-chrome wire with sliding contact. The flowrate of catholyte was measured with a suitable Fischer-Porter rotameter.

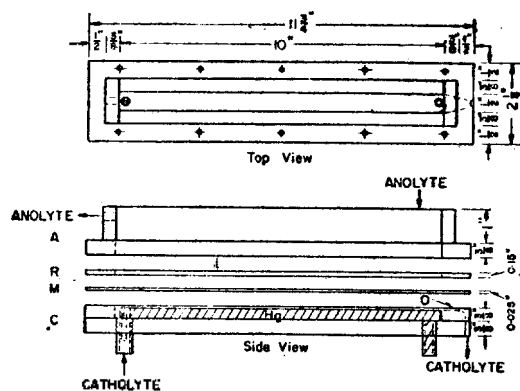


Fig. 1 - Electrolytic reduction cell.

- A - Anode compartment
- R - Rubber gasket
- M - Cation exchange membrane
- C - Cathode compartment
- O - Overflow trough

#### Procedure

##### Electrolytes

The catholyte was prepared from refined  $\text{UO}_2$  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 M  $\text{H}_2\text{SO}_4$ , 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  $\text{U}^6$  to  $\text{U}^4$ . The fraction of theoretical flow is calculated by the formula:

$$\frac{(\text{g } \text{U}_3\text{O}_8 / \text{l catholyte}) \times (\text{flowrate, l/min})}{0.0872 \times (\text{current, amp})}$$

The electrochemical equivalent for reduction of  $\text{U}^6$  to  $\text{U}^4$  is 0.0872 g  $\text{U}_3\text{O}_8$  per amp min (See Appendix 2 for calculations).

##### Cell Operation (see Fig. 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  $\text{H}_2\text{SO}_4$ . 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  $\text{U}^6$ ,  $\text{U}^4$

and  $U^3$ . The analytical procedure is briefly described in Appendix 1.

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

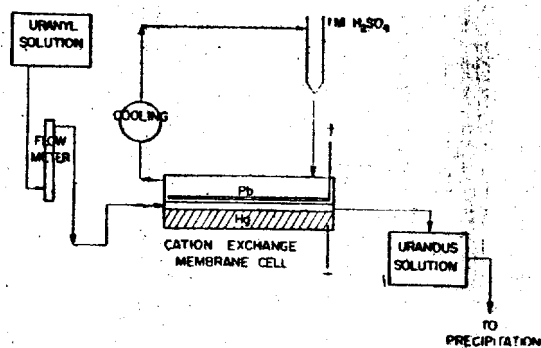


Fig. 2 - Flow diagram of electrolytic circuit.

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 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  $U_2O_5/l$  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 I 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  $4\%$ .

TABLE I.  
Effect of Cell Dimensions

Catholyte:  $98$  g  $U_2O_5/l$ ,  $51.7$  g free  $H_2SO_4/l$   
 Anolyte:  $1$  M  $H_2SO_4$   
 Current Density:  $2$  amp per sq. in.  
 Temperature:  $30^\circ - 45^\circ C$  in catholyte  
 $30^\circ C$  in anolyte

Cell Type W x L (inches)	Fraction of Theoretical Flow	Current Efficiency (%)	Reduction (%)	Cell Voltage (volts)
$1/2 \times 20$	1.35	97.5	72	4.9
$1/2 \times 20$	1.20	96.5	80	5.0
$1/2 \times 20$	0.97	95.5	98	5.1
$1/2 \times 20$	0.74	82.5	98.5	5.2
$1/2 \times 10$	1.37	94	67	5.4
$1/2 \times 10$	1.20	92.5	77	5.6
$1/2 \times 10$	0.99	94	94.5	5.8
$1/2 \times 10$	0.87	86.5	99	6.0
$3/4 \times 15$	1.35	90.5	68.5	5.8
$3/4 \times 15$	1.65	90.5	86	5.9
$3/4 \times 15$	0.89	88	98.5	5.9
$3/4 \times 15$	0.78	79.5	99	6.0
$1 \times 10$	1.31	83	62	5.8
$1 \times 10$	1.15	84	72	5.9
$1 \times 10$	0.94	79	84	6.0
$1 \times 10$	0.79	71.5	91	6.0

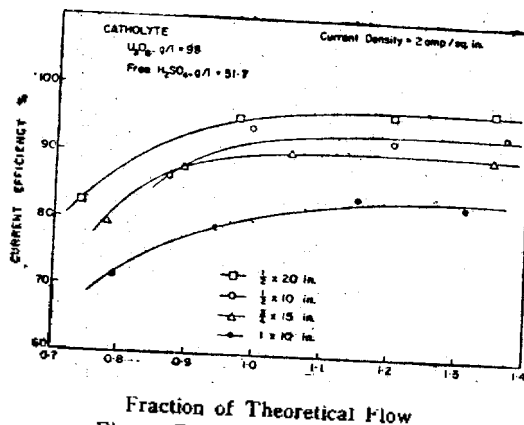


Fig. 3 - Effect of cell dimensions

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

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

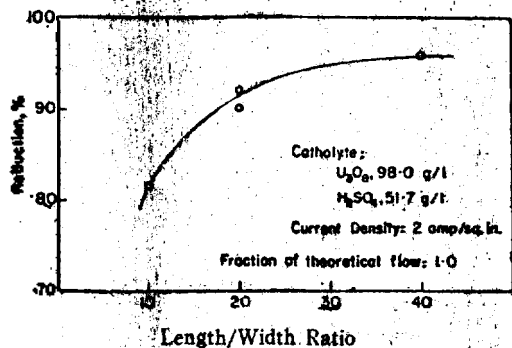


Fig. 4 - Effect of cell dimensions at maximum current efficiency.

Effect of Depth of Catholyte

A third dimension, the depth of catholyte, was also varied in a series of tests reported in Table I 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 I  
Effect of Depth of Catholyte

Catholyte: 20.3 g U<sub>3</sub>O<sub>8</sub>/l, 32 g free H<sub>2</sub>SO<sub>4</sub>/l  
 Anolyte: 1 M H<sub>2</sub>SO<sub>4</sub>  
 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
0.08	1.05	84.0	80	4.4
0.08	0.87	81	92.5	4.5
0.08	0.6	63.5	99	4.6
0.17	1.24	82	65.5	4.5
0.17	0.08	83.5	77	4.6
0.17	0.88	84	95	4.7
0.17	0.65	65.5	99	4.8

Effects of Current Density and Flowrate

The results of this series of tests are presented in Table II and graphically in Figures 6 to 11.

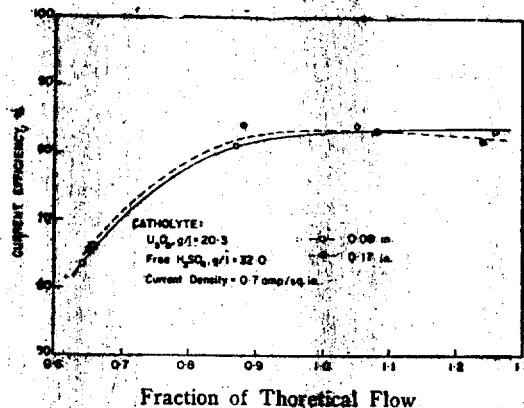


Fig. 5 - Effect of depth of catholyte.

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 II  
Effect of Uranyl Sulphate Concentration and Current Density

Cell: 1/2 in. x 10 in.  
 Anolyte: 1 M H<sub>2</sub>SO<sub>4</sub>  
 Temperature: Anolyte: 30°C  
 Catholyte: 30-45°C

Catholyte U <sub>3</sub> O <sub>8</sub> (g/l)	Free H <sub>2</sub> SO <sub>4</sub> (g/l)	Current Density (amp/sq. in.)	Fraction of Theoretical Flow	Current Efficiency (%)	Reduction (%)	Cell Voltage (volts)
20.3	32.0	0.4	1.31	83	63	4.0
20.3	32.0	0.4	0.90	79	86.5	4.1
20.3	32.0	0.4	0.72	69.5	96	4.2
20.3	32.0	0.7	1.26	83.5	52	4.3
20.3	32.0	0.7	1.05	84	80	4.4
20.3	32.0	0.7	0.87	81	92.5	4.5
20.3	32.0	0.7	0.64	63.5	99	4.6
20.3	32.0	1.0	1.14	80.5	70	4.3
20.3	32.0	1.0	0.88	80.5	91	4.3
20.3	32.0	1.0	0.79	77.0	97.5	4.4
20.3	32.0	1.0	0.74	73.5	99	4.4
20.3	32.0	1.6	1.14	73.0	64	4.7
20.3	32.0	1.6	0.90	72.0	79.5	4.8
20.3	32.0	1.6	0.77	67.5	86.5	4.9
20.3	32.0	1.6	0.66	64.5	98.5	5.0
20.3	32.0	2.0	1.23	67.5	53.5	5.2
20.3	32.0	2.0	1.00	66	65	5.3
20.3	32.0	2.0	0.83	65	78.5	5.4

20.3	32.0	2.0	0.65	61	94	5.5
40.7	34.0	0.7	1.19	84	70	3.9
40.7	34.0	0.7	1.01	84	84	3.9
40.7	34.0	0.7	0.88	82	93.5	4.0
40.7	34.0	0.7	0.75	74	99.5	4.0
40.7	34.0	1.0	1.34	87	64	4.2
40.7	34.0	1.0	1.22	86	69.5	4.2
40.7	34.0	1.0	0.88	83	95	4.2
40.7	34.0	1.0	0.69	70	99	4.3
40.7	34.0	1.6	1.21	83	69.5	4.7
40.7	34.0	1.6	1.01	83	82	4.8
40.7	34.0	1.6	0.86	80.5	93.5	4.8
40.7	34.0	1.6	0.77	76	99	4.9
40.7	34.0	2.0	1.20	80.5	65.5	5.1
40.7	34.0	2.0	0.96	79.5	83.5	5.2
40.7	34.0	2.0	0.84	78	94	5.3
40.7	34.0	2.0	0.74	74	99	5.4
92.9	52.0	1.2	1.41	90	59	4.8
92.9	52.0	1.2	1.04	88.5	84.5	4.9
92.9	52.0	1.2	0.84	84	98	5.0
92.9	52.0	1.2	0.71	76	99	5.1
92.9	52.0	2.0	1.39	94	71.5	5.0
92.9	52.0	2.0	1.08	93	86.5	5.1
92.9	52.0	2.0	0.87	86.5	99	5.3
92.9	52.0	2.0	0.69	77	100	5.4
92.9	52.0	2.4	1.31	95.5	72.5	5.2
92.9	52.0	2.4	1.02	94	94	5.3
92.9	52.0	2.4	0.92	91.5	99	5.4
92.9	52.0	2.4	0.81	87	99.5	5.5
92.9	52.0	2.8	1.33	94.5	70.5	5.4
92.9	52.0	2.8	1.09	92	84	5.5
92.9	52.0	2.8	0.89	88	98.5	5.6
92.9	52.0	2.8	0.78	83	99	5.7

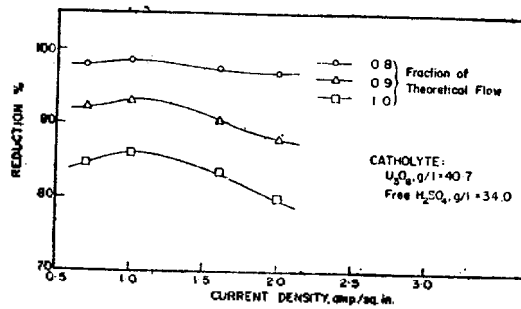


Fig. 7 - Effect of current density on % reduction at a given flowrate. Catholyte:  $U_3O_8$ , 40.7 g/l.

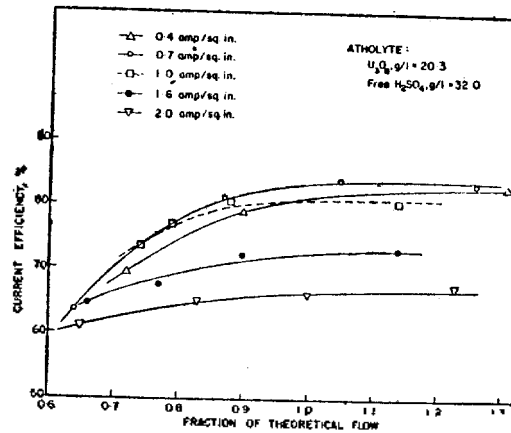


Fig. 8 - Effect of flowrate on current efficiency at a given current density. Catholyte:  $U_3O_8$ , 20.3 g/l.

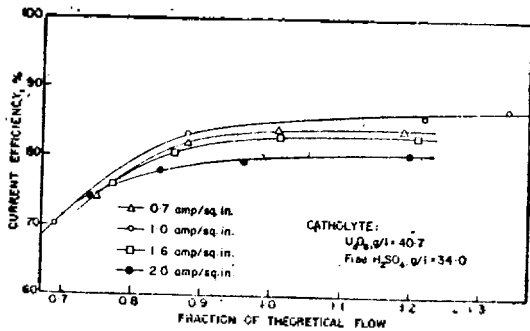


Fig. 6 - Effect of flowrate on current efficiency at a given current density. Catholyte:  $U_3O_8$ , 40.7 g/l.

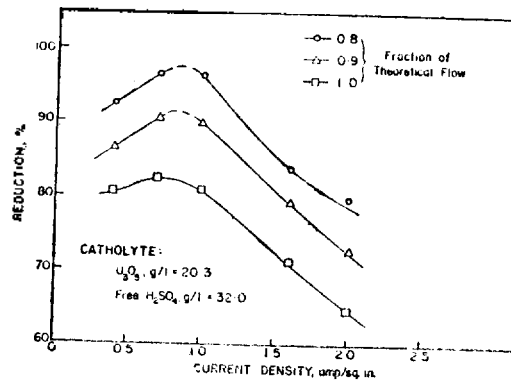


Fig. 9 Effect of current density on % reduction at a given flowrate. Catholyte:  $U_3O_8$ , 20.3 g/l.

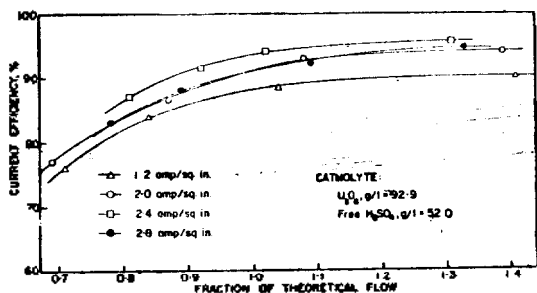


Fig. 10 - Effect of flowrate on current efficiency at a given current density. Catholyte:  $U_3O_8$ , 92.9 g/l.

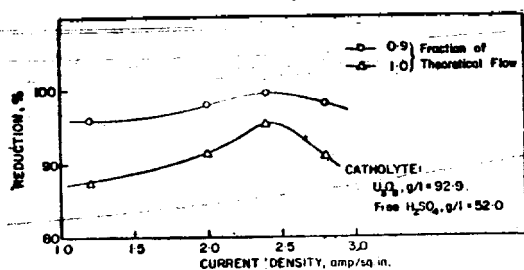


Fig. 11 - Effect of current density on % reduction at a given flowrate. Catholyte:  $U_3O_8$ , 92.9 g/l.

**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 V and Figure 12, was reduced to near 100%  $U^4$ .

TABLE V

**Reduction of Uranyl Chloride Solution**

Catholyte (g/l):  $U_3O_8$ , 40.4; HCl, 10.2;  $H_2SO_4$ , 20.0  
 Anolyte (g/l):  $H_2SO_4$ , 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.

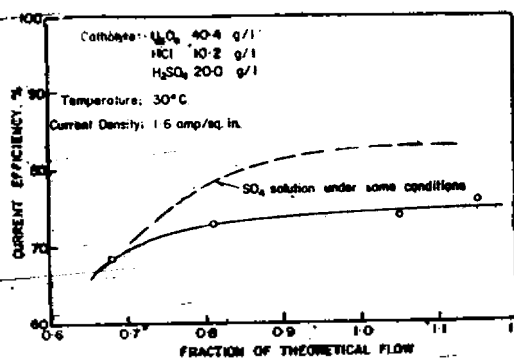


Fig. 12 - Reduction of chloride solution. Effect of flowrate on current efficiency at a fixed current density.

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

TABLE V

**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.

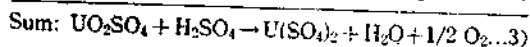
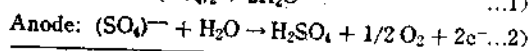
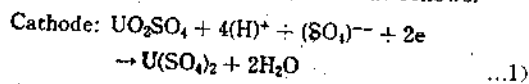
A slight corrosion of the lead was noticed but this would not affect the purity of the catholyte. A flat tube with colling water is suggested, in order to increase the life of the lead anode.

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 Fibreglas 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:



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  $\text{UO}_2$  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 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 Fig. 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 VI.

TABLE VI  
Current Density for Maximum Efficiency at Theoretical Flow

Concentrations in Catholyte (g $\text{U}_3\text{O}_8$ /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 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  $\text{UO}_2$ , 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



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  $U^{VI}$  to  $U^{IV}$ , or better, at 80 to 95% current efficiency was obtained for a catholyte solution containing from 20 to 100 g  $U_3O_8/l$ . Excess acid is necessary to prevent hydrolysis, and cooling devices are suggested for higher capacities.

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#### APPENDIX I

##### 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 I

##### Calculation of Theoretical Flowrate in the 1/2 in. $\times$ 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
20.3	1.7	3.5	15.0
20.3	1.0	5.0	21.5
20.3	1.6	8.0	34.4
40.7	0.7	3.5	7.5
40.7	1.0	5.0	10.7
40.7	1.6	8.8	17.1
40.7	2.0	10.0	21.4
92.9	1.2	6.0	5.6
92.9	2.0	10.0	9.4
92.9	2.4	12.0	11.2
92.9	2.8	14.0	13.1

Theoretical flowrate l/m

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