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60 Abstract : In Purex process, plutonium and uranium are co-extracted into organic phase and these are partitioned by reducing Pu(IV) to Pu(III) using hydrazine stabilized uranous nitrate solution. Usually, uranous nitrate is added in much higher quantity than the stoichiometric requirement to effect complete reduction of plutonium. In conventional electrolytic cells only 60 to 70% of uranyl to uranous conversion is achieved. Use of this solution results in dilution of plutonium product. In addition to this, each externally fed uranous nitrate batch increases uranium processing load and affects the plant throughput. In order to keep the additional uranium processing load to a minimum, it is necessary to increase the uranous content to near cent percent level in the externally fed uranous nitrate solution. The studies carried out at PREFRE (Power Reactor Fuel Reprocessing) laboratory have shown that it is possible to produce concentrated uranous nitrate solution, nearly free from uranyl nitrate, by using a cation exchange membrane. This paper describes the development work carried out at PREFRE plant, Tarapur for production of cent percent uranous nitrate solution. Development of electrolytic cells for uranous production, from laboratory scale to pilot plant scale, has been explained.

70 Keywords/Descriptors : URANIUM NITRATES; MEMBRANES; ION EXCHANGE MATERIALS; ELECTROLYSIS; ELECTROLYTIC CELLS; CATIONS; ANODES; CATHODES; PUREX PROCESS; HYDRAZINE; REDUCTION; TITANIUM; SUBSTRATES; PH VALUE; CURRENT DENSITY; FLOWSHEETS; TITANIUM OXIDES; RUTHENIUM OXIDES; SURFACE COATING

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99 Supplementary elements :

1) INTRODUCTION:

PUREX process is widely employed for reprocessing spent fuels in fuel reprocessing plants⁽¹⁾. In this process the feed solution containing the dissolved fuel is contacted with 30 percent tributyl phosphate(TBP) to extract uranium and plutonium leaving behind the fission products in aqueous phase. From the loaded organic, uranium and plutonium are separated from each other by the process known as partitioning and the resulting two streams are further purified separately to obtain the uranium and plutonium products. Partitioning of uranium and plutonium, extracted in organic phase, can be achieved either by adopting non-reductive or reductive stripping methods. In the former method separation is achieved by forming aqueous favouring complexes of Pu(IV) with sulphates, carboxylic acids or by saturating the organic solvent with uranium. But this method is generally not favoured for commercial application. In the latter method, separation is achieved by reducing Pu(IV) to aqueous favouring Pu(III). The reducing agents used for this purpose are ferrous sulfamate, hydroxylamine nitrate, hydrogen in presence of catalyst and uranous nitrate. Hydrazine stabilized uranous nitrate is now used in a number of reprocessing plants for partitioning of uranium and plutonium⁽²⁾. Unlike other reducing agents, uranous nitrate does not contribute ions that are chemically

corrosive and it also does not increase the salt content in the raffinate waste generated⁽³⁾. Uranous nitrate can be produced by chemical, photochemical⁽⁴⁾ or electrochemical methods. The former two methods are not yet used for large scale production. The electrochemical method is relatively simpler and suitable for large scale production. Experiments were conducted in our laboratory to study the electrochemical reduction of uranyl ions to arrive at a proper design of the membrane cell for large scale production of uranous nitrate.

2) ELECTROLYTIC CELLS:

Essentially an electrolyser consists of a container for the electrolyte, an anode, a cathode and a direct current supply. When a voltage is applied to the terminals of the electrodes, an electric current flows through the circuit and electrochemical reactions take place at the surface of the electrodes. Reduction takes place at the cathode and oxidation at the anode. Electrolytic cells are used in a variety of shapes and sizes and are classified in different ways based on the cell geometry, operational requirements, electrode types etc.⁽⁵⁾. A wide variety of materials are used in the construction of these cells. Operating at the highest possible current density is not the only criteria of a cell design. How well the cell meets the upstream and downstream requirements of the plant is an important consideration.

3) THE ELECTROLYSERS DEVELOPED AT PREFRE:

At PREFRE plant, efforts have been continued to improve the electrolytic cell designs to meet the entire uranous requirement of the plant. A brief chronological account of development in electrolyser units is given below: (6)

3.1. Mercury cathode, platinum anode electrolyser:

The first electrolyser unit in the plant used a pool of mercury as the cathode and platinum wire gauze as the anode. The formation of solid deposits on the mercury surface, loss of mercury through the out flowing streams and need for constant operator attention were some of the main drawbacks noticed. Also the risk of formation of mercury azides existed. Hence this cell was unsuitable for routine production.

3.2. Graphite cathode, platinum anode electrolyser:

Graphite cathode and platinum anode were used in this cell. Because of the fragile nature of the graphite the cathode life was observed to be limited.

3.3. Titanium cathode, platinum anode electrolyser:

The cell with Titanium cathode and platinum anode gave satisfactory results in producing uranous in sufficient quantities. But the very high cost of platinum and the special security requirements associated with the use of platinum posed certain problems.

3.4. Titanium cathode, platinum coated titanium anode

electrolyser:

In this cell the anode used was a substrate of titanium on which a thin layer of platinum was coated. The coating failed after some time in use.

3.5. Titanium cathode, TSIA anode electrolyser:

TSIA (Titanium Substrate Insoluble Anode) was prepared by coating titanium with the oxides of precious metals like ruthenium, rhodium, platinum, iridium etc. This electrolyser gave excellent results. The coated anode can be used for 8-9 lakh Ampere hours of operation before re-coating becomes necessary.

Though all these cells produced sufficient quantities of uranous to meet the plant requirements, only 60-70 % conversion of uranyl nitrate to uranous nitrate could be achieved due to undivided cell design.

4) ION EXCHANGE MEMBRANES:

In an undivided cell part of the uranous produced at the cathode gets oxidised by the oxygen generated at anode. To prevent this the catholyte should be separated from the anolyte by a suitable diaphragm. Porous plastic diaphragm does not give very satisfactory result since the catholyte and anolyte can get mixed together by diffusion. Cation exchange membranes which are impermeable to liquids but permeable to cations are excellent in providing a selective

barrier to separate catholyte from anolyte in uranous production cell.

Ion exchange membranes are ion exchange resins prepared in the form of thin flexible sheets and contain mobile counter ions in an insoluble matrix. The basic requirements of a membrane for efficient operation of the cell can be summarized as follows: (7,8,9)

a) High capacity:

This is a measure of the availability of the counter ions for exchange and high capacity will facilitate the easier flow of ions.

b) High degree of selectivity for cations:

The transference number for cations should be as high as possible (About 0.99).

c) Low electrical resistance:

This factor decides the ease with which the ions migrate through the membrane. Low electrical resistance can be achieved by using a membrane with a large water content coupled with a high concentration of fixed charges.

High electrical resistance of the membrane will result in high cell voltage for a given current density, higher Ohmic resistance in the cell and lowering of current efficiencies.

d) Good chemical stability:

The membrane should withstand the corrosive environment

of the cell.

e) Good physical strength and dimensional stability:

The membrane should be able to withstand the stresses it encounters in use. To improve its physical strength some membranes are cast over a glass or plastic woven material.

f) Low rate of electro-osmosis:

Even though the membrane is not porous, water molecules can still permeate as water of hydration of the ions. Depending on the nature of the membrane and the operating conditions, as much as 5-50 moles of water per Faraday can permeate the membrane.

g) High transfer rate for counter ion

h) Thermal stability.

i) Low cost

j) Resistance to fouling.

5) Classification of membranes:

A) Membranes are classified as cation exchange or anion exchange membranes depending on the nature of the counter ion.

B) Another classification is based on the functional group. For cation exchange membranes the functional groups generally used are acidic groups like sulphonic, phosphoric, carboxylic or hydroxyl groups.

C) Yet another classification is based on the physical structure:

a) Homogeneous membranes are ion exchanger gels and the exchange component forms one continuous phase.

b) Heterogeneous membranes are prepared by embedding colloidal ion exchanger particles in an inert binder. Many of the thermo plastics can be used as the binder.

c) Inter-polymer membranes are formed by the combination of a polyelectrolyte with a linear inert polymer. They form inter-penetrating net works of the two polymers giving a rather uniform structure and good mechanical properties.

d) Graft copolymer membranes: Polyethylene films are impregnated with styrene or styrene divinyl benzene mixtures and are exposed to gamma radiation. This results in grafting of the styrene and divinyl benzene to the polyethylene base. Strong acid cation exchange membranes are obtained by sulphonation of the graft copolymer. These membranes have outstanding mechanical and good electrochemical properties.

e) Impregnated membranes: Porous films can be impregnated with polyelectrolytes to prepare impregnated membranes.

6) CRITERIA FOR CELL DESIGN:

A wide variety of cell designs are used in industrial electrolysis, the guiding principle being that the cell should be simple in design and operation. Several important factors are to be considered in the design of an

electrolyser^(10,11,12,13). One important parameter is the electrode area required for achieving the required production rate. Often this cannot be arrived at by theoretical considerations alone. Experimental data giving current efficiency and dependence of current efficiency on the current density is required. Detailed investigations have been carried out by several authors about the production of uranous nitrate using different materials like porous plastic sheet, glass frit and ion exchange membrane as the separator^(14,15,16,17). For achieving near cent percent uranyl to uranous conversion, the electrolyser should be of the divided cell type, where the catholyte and anolyte are separated by a barrier. Apart from the choice of a divided cell configuration, several other factors are pertinent in the design of an electrolyser for uranous production. These factors are shape and size of the cell, material and geometry of the electrodes, current density to be used, the electrode area required, concentration of uranyl nitrate, nitric acid and hydrazine in the feed etc. Since uranous nitrate is unstable, hydrazine nitrate is added as a stabilizer. Since nitric acid is consumed during the electrolysis sufficient nitric acid concentration is maintained in the feed at all times.

In choosing the parameters for the cell design often a compromise is made, since some of the factors are contradictory. For example, for a given cell, operating at

maximum possible current density is desirable but often the relationship between the current density and the current efficiency is such that at high current densities the current efficiency is reduced drastically. Hence the need for choosing the optimum current density.

Uranous reduction is a first order reaction with the rate dependent on the uranyl concentration. If a cell is operated with very high concentration of uranyl, say 400-500 g/l., then due to acid consumption at the electrodes the acidity will be reduced drastically resulting in the precipitation of UO_3 . Hence the concentration of uranyl to be used is not solely based on the desired production rate.

In a chemical reactor the reaction takes place throughout the volume of the reactor. But in an electrolyser the electrochemical reaction takes place only at the surface of the electrodes. Hence the species taking part in the reaction gets depleted rapidly in the solution layer adjacent to the electrodes. If this layer is not replenished quickly, undesirable side reactions take place at the electrode. Fast flow rates prevent this. Fast flow rates will also help in replenishing the diffusion layers adjacent to the membranes with the species of interest and ensuring high production rates.

In summary the cell requirements can be listed as follows:

- a) Use of electrodes with high selectivity for the

reactions of interest

- b) Minimum inter electrode gap
- c) Maximum specific electrode area.
- d) Optimum current density
- e) Fast flow rates.
- f) Efficient cooling of the streams.
- g) Cation exchange membrane with high capacity and low electrical resistance.

7) DETAILS OF CELLS FABRICATED AT PREFRE:

Electrolytic cells with cation exchange membrane, to separate catholyte from anolyte, were fabricated. In all the cells TSIA (Titanium Substrate Insoluble Anode) as anode have been used. TSIA electrode was prepared in the laboratory by coating the expanded titanium metal sheet with ruthenium and titanium double oxide. (17,18,19) In this coating process a solution of ruthenium trichloride and titanium tetra chloride in propanol is applied to a clean titanium expanded metal sheet. After drying, the electrode is heated to a temperature of 400°C . This process is repeated several times till the required thickness is obtained. Triple oxide coating is done by using a solution of chlorides of palladium, titanium and ruthenium. Expanded titanium metal sheet was used as cathode in all the cells except the large sized cell for pilot plant operation. In the latter cell coated expanded titanium metal sheet was

used as cathode.

CELL NO.1 - About 0.1 mm thick cation exchange membrane "Neosepta" was used. About 50 cm² area of the membrane was screwed tight over an opening in the central perspex plate, used to separate anode and cathode chambers in a cell made of perspex. Titanium cathode area of about 90 cm² in the catholyte volume of 3 lts. was used. Circulation of catholyte through side tubes was maintained at 20 lph. [Fig.1]

CELL NO.2 - Two compartment perspex cell was designed using 92 cm² of the cation exchange membrane supplied by the Central Salt and Marine Chemical Research Institute of Bhavnagar. This membrane was of the inter-polymer type made from polyethylene and polystyrene divinyl benzene and with sulphonic acid as the ionogenic group. The membrane was fitted on the opening of the central perspex plate with the help of perspex mesh structures and nuts and bolts. Titanium cathode of about 150 cm² area was used in the catholyte volume of about 0.6 lts. [Fig.1]

CELL NO.3 - In this cell cation exchange membrane (supplied by M/S.Thermax, Chemicals Division, Pune) of about 172 cm² area was fitted on the central separating frame with the help of plastic wire mesh supports. Cell was made of perspex sheets and high density polyethylene frames. Catholyte was recirculated at 20 lph from a 2 litres external reservoir. Water cooled coils were used to cool the

catholyte. Cathode area used was 150 cm^2 . [Fig-1]

CELL NO.4 - FILTER PRESS CELL:

After completing several experiments with the previously described cells, it was decided to produce several kilograms of uranous by continuous operation. A filter press type cell was fabricated for this purpose [Fig. 2]. The details of this cell are as follows:

Cell details:

| | | |
|-----------------------------------|---|---------------------|
| Electrode dimension | : | 20 cm (L)x10 cm (W) |
| No. of catholyte chambers | : | 3 |
| No. of anolyte chambers | : | 2 |
| Total cathode area | : | 800 cm^2 |
| Total anode area | : | 800 cm^2 |
| Overall dimension of each chamber | : | 26.5 x 18 x 1 cms. |
| Volume of catholyte chamber | : | 250 ml |

Operating parameters:

| | | |
|--------------------|---|-------------------------------|
| Cell voltage | : | 2.75 to 3.0 Volts |
| Total current | : | 30 Amperes |
| Recirculation rate | : | 35 l/hr. |
| Cathode | : | Expanded titanium metal sheet |
| Anode | : | TSIA |

This cell was made from perspex sheets and the chamber to chamber flow channels were cut on the frame of the cell itself, resulting in a compact cell. The membranes were installed in between the chambers in a leak tight manner and

were supported by plastic mesh. The cation exchange membrane used was of the inter polymer type with sulphonic acid ionogenic group.

CELL NO.5 - LARGE SIZED CELL FOR PILOT PLANT OPERATION:

After successful production of uranous with filter press cell, a larger sized cell with about 4 times more cathode area was fabricated to increase net uranous production rate. Design details for this pilot plant cell are given below :

Cell details:

| | | |
|-----------------------------------|---|----------------------|
| Electrode dimension | : | 63 cm (L)x24 cm (W) |
| No. of catholyte chambers | : | 2 |
| No. of anolyte chambers | : | 1 |
| Total cathode area | : | 3000 cm ² |
| Total anode area | : | 3000 cm ² |
| Overall dimension of each chamber | : | 73 X 24 X 2.5 cms |
| Volume of catholyte chamber | : | 3 litres. |

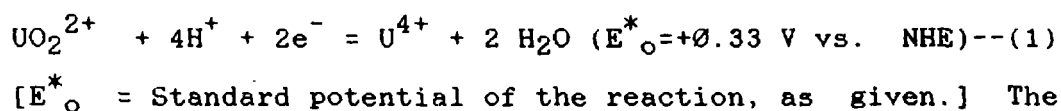
Operating parameters:

| | | |
|--------------------|---|--------------------------------|
| Cell voltage | : | 2.75 to 3.0 Volts |
| Total current | : | 100 Amperes |
| Recirculation rate | : | 200 lph. |
| Cathode | : | Coated titanium expanded sheet |
| Anode | : | TSIA |

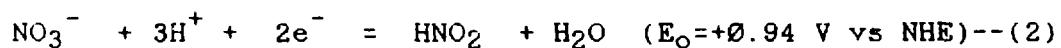
The cell was fabricated from 1 inch thick PVC sheets. Cell consisted of two catholyte chambers and one central anolyte chamber. Each catholyte chamber was separated from

anolyte chamber by cation exchange membrane sheet of about 1500 cm² area, supported by plastic mesh on either side and inter-pressed between PVC frames. The whole unit was assembled using stainless steel frames and made leak tight by tightening with nuts and bolts. Inlet and outlet nozzles were provided in each chamber. Coated expanded titanium sheets as cathode (2 Nos.) and TSIA as anode (1 No.), were used in this cell. Electrical connections were given from top. Care was taken to tighten the contacts properly. Fig.3 (a) and 3 (b) show sectional view and exploded view, respectively, of the large sized cell used for pilot plant operation. Fig. No.4 shows the flow diagram of the pilot plant unit.

8) **ELECTROCHEMICAL PRINCIPLES:** At cathode: The net reaction for the formation of uranous at cathode is,



other two side reactions which need to be controlled are nitrous acid formation and hydrogen evolution.



At anode:

For 1-2 M nitric acid as anolyte the only reaction at anode of the divided cell is oxygen evolution.



9) EXPERIMENTAL:

Experiments were carried out using cell No.1 to check the performance of cation exchange membrane in the production of uranous. Cathode potential corresponding to 55 mA/cm^2 current density, was in the range of -0.22 V to -0.55 V vs SCE throughout the electrolysis. Catholyte temperature was in the range of $36-46^\circ\text{C}$.

Uranous concentration was determined by titrating against standard potassium dichromate. Cell performance results in terms of percentage of uranous formed, are given in Table-1.

Cell No.2 was used to study the effect of parameters like uranyl concentration and cathode current density. In one case, for a constant current density of 100 mA/cm^2 , uranyl concentration in the range 186 g/l to 340 g/l was studied [Table-2]. In the second case cathode current density was varied keeping initial uranyl nitrate concentration nearly same. The operation was continued upto $\sim 99\%$ conversion of uranyl to uranous nitrate. [Table-3].

Cell No.3 was used to study electrolytic reduction of different concentrations of uranyl nitrate at different cathode current densities [Table-4]. In this experiment catholyte was recirculated through an external reservoir to simulate the conditions for large scale production of uranous. Residence time of about 6 minutes was maintained.

Filter press type cell was used for producing about 14 kgs of uranous in continuous operation. In this cell the anodes used were coated with oxides of palladium, ruthenium and titanium. Cooling was provided for both the catholyte and anolyte streams. Feed uranium concentration was 225 g/l, acidity was about 2 M and hydrazine concentration was 0.5-0.6 M.

Large sized cell for pilot plant operation was installed with proper exhaust arrangement. One 100 litres capacity tank with immersed cooling coils was used to circulate and cool catholyte. Anolyte was circulated without cooling. Catholyte and anolyte were circulated using magnetically coupled centrifugal pumps at the rate of 200 lph. Provision was made to avoid the flooding of cell. Feed taken for uranous nitrate production ranged from 30 to 100 liters for batch operation. In the feed solution, uranyl nitrate concentration, acidity and hydrazine concentration were in the range of 185-190 g/l, 2.4-2.8 M and 0.6-0.9 M respectively. Current passed was 100 amperes. Samples were removed every hour for the analysis of uranous, acidity and hydrazine concentrations. Cell was tested for continuous operation of 30 hours. Use of coated expanded titanium metal sheet in place of expanded titanium metal sheet cathode showed very little consumption of hydrazine. In all the experiments with cation membranes, an increase in catholyte volume of about 10-15% was observed.

10) RESULTS AND DISCUSSION:

Initial experiment using cell No.1 confirmed the near cent percent conversion of uranyl nitrate to uranous nitrate, with the overall current efficiency of 80% [Table.1] Net conversion rate of uranyl nitrate to uranous nitrate was observed to be 3.6 g/amp.hr.

The encouraging results led to the fabrication of cell No.2. Optimum uranyl concentration and optimum cathode current density were determined using this cell [Tables 2 & 3, Figs. 5 & 6]. The best suited initial uranyl nitrate concentration for the production of uranous at 100 mA/cm² cathode current density was found to be about 250 g/l, as indicated by the net higher rate of uranous formation (3.4 g/amp.hr.). For the uranyl concentration range of 186 to 194 g/l., cathode current density of 30 to 45 mA/cm² was found to be giving relatively higher current efficiency. The experiment for the large scale production of uranous under simulated condition of continuous recirculation through an external reservoir was found to be successful. An attempt was made to gradually decrease the cathode current density to maintain highest current efficiency condition [Table-4 & Fig.7]. This was done because, as the electrolysis proceeds, the net uranyl concentration available for reduction decreases. Hence it is necessary to apply optimum cathode current densities corresponding to maximum attainable current efficiencies, for different

uranyl concentrations as revealed in Table-5 & Fig. 8.

Filter press type cell was meant to simulate the industrial scale production of uranous. The same current density was maintained through out the experiment. The operation of this cell was trouble free. 14 kgs of uranous was produced at the rate of 100 g/hr, and corresponding to about 40 mA/cm² cathode current density. Fig. 2 shows the details of the cell and Table 6 gives the results of experimental runs.

Large size cell was used for the production of about 28 Kg. of near cent percent uranous nitrate in four batches. Table No.7 gives the results of all the 4 runs. The overall uranous production rate achieved was in the range of 500-550 g/hr., corresponding to the cathode current density of 33 mA/cm² (Table No.8). Catholyte and anolyte temperatures were always less than 40°C during the cell operation involving passage of 100 Amperes current. Diffusion of uranium from catholyte to anolyte was observed on putting off the D.C. supply.

11) CONCLUSION:

In an electrolytic cell, separating the catholyte from anolyte by a cation exchange membrane makes it possible to produce cent percent uranous nitrate. Pilot plant operation has confirmed the production of 12 Kg. of uranous per day in a continuous run corresponding to cathode area of about 3000

cm^2 and 33 mA/cm^2 cathode current density. Higher rate of uranous production, to meet the plant requirement, can be achieved by increasing the current density or having multiple array of such cells.

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TABLE - 1

Uranous Production using Cation Exchange Membrane

Total uranium concentration: 232 g/l
 Acidity : 2.2 M HNO₃
 Hydrazine concentration : 1.4 M
 Cathode current density : 55 mA/cm²
 Permselective membrane : Cation exchange membrane
 (NEOSEPTA)

| Sr. No. | Electrolysis duration hrs. | Percentage U ⁴⁺ conversion | Overall Current Efficiency in % | Overall rate g/Amp.hr. |
|---------|----------------------------|---------------------------------------|---------------------------------|------------------------|
| 1 | 4 | 13.9 | | |
| 2 | 10 | 33.8 | | |
| 3 | 14 | 42.3 | | |
| 4 | 18 | 54.6 | | |
| 5 | 24 | 71.8 | 80.0 | 3.57 |
| 6 | 27 | 77.6 | | |
| 7 | 33 | 84.2 | | |
| 8 | 39 | 100.0 | | |

TABLE - 2

Effect of Change in Uranyl Concentration on the Rate of Uranous Production at Constant Cathode Current Density

Cathode C.D : 100 mA/cm^2
 Acidity : 1.5-1.9 M HNO_3
 Hydrazine : 0.4-0.45 M

| Expt. No. | Uranyl Conc. g/l | Duration of electrolysis hrs. | % of uranous formed | Overall rate U^{4+} g/Amp.hr |
|-----------|------------------|-------------------------------|---------------------|---------------------------------------|
| 1 | 186.2 | 1 | 56.6 | 2.75 |
| | | 2 | 91.1 | |
| | | 3 | 99.9 | |
| 2 | 256.0 | 1 | 45.2 | 3.42 |
| | | 2 | 80.5 | |
| | | 3 | 100.0 | |
| 3 | 301.0 | 1 | 25.0 | 3.09 |
| | | 2 | 71.0 | |
| | | 3 | 98.2 | |
| | | 4 | 100.0 | |
| 4 | 339.8 | 1 | 33.8 | 2.69 |
| | | 2 | 63.0 | |
| | | 3 | 91.5 | |
| | | 4 | 98.4 | |
| | | 5 | 99.2 | |

TABLE - 3

Effect of Variation of Current Density on the Rate of Uranous Production at nearly same Initial Uranyl Concentration

Acidity : 2.1 M Hydrazine : 0.5 M

| Ex. No. | Uranyl Conc. g/l | Cathode C.D mA/cm ² | Ele. hrs. | % of U ⁴⁺ formed | Overall current effi. % | Overall rate of U ⁴⁺ produced | |
|---------|---------------------|-----------------------------------|-----------|-----------------------------|-------------------------|--|-------|
| | | | | | | g/Amp.hr | g/hr. |
| 1 | 195.8 | 33.3 | 1 | 20.0 | 65.6 | 2.91 | 14.6 |
| | | | 2 | 45.3 | | | |
| | | | 3 | 60.2 | | | |
| | | | 4 | 77.3 | | | |
| | | | 5 | 88.6 | | | |
| | | | 6 | 96.5 | | | |
| | | | 7 | 98.9 | | | |
| | | | 8 | 99.1 | | | |
| 2 | 194.6 | 46.7 | 1 | 28.2 | 68.6 | 3.04 | 21.3 |
| | | | 2 | 53.2 | | | |
| | | | 3 | 74.8 | | | |
| | | | 4 | 92.3 | | | |
| | | | 5 | 98.8 | | | |
| | | | 6 | 99.3 | | | |
| 3 | 194.4 | 66.7 | 1 | 34.0 | 57.8 | 2.57 | 25.7 |
| | | | 2 | 70.0 | | | |
| | | | 3 | 92.4 | | | |
| | | | 4 | 97.1 | | | |
| | | | 5 | 99.3 | | | |
| 4 | 196.0 | 83.3 | 1 | 51.8 | 55.2 | 2.45 | 30.1 |
| | | | 2 | 74.9 | | | |
| | | | 3 | 94.0 | | | |
| | | | 4 | 96.2 | | | |
| 5 | 186.2 | 100.0 | 1 | 56.6 | 61.9 | 2.75 | 41.2 |
| | | | 2 | 91.1 | | | |
| | | | 3 | 99.9 | | | |

TABLE - 4

Large Scale Production of Uranous Under Different Current Densities

Uranyl concentration : 335.5 g/l
 Acidity : 2.2 M HNO₃
 Hydrazine : 0.5 M
 Cathode C.D. : 150 - 80 mA/cm²

| Sr. No. | Duration of Electrolysis Hrs. | % of U ⁴⁺ formed | Current Efficiency in % | Cathode C.D. mA/cm ² |
|---------|-------------------------------|-----------------------------|-------------------------|---------------------------------|
| 1 | 1 | 15.4 | 100.6 | 150 |
| 2 | 2 | 28.5 | 88.4 | 150 |
| 3 | 3 | 42.4 | 85.2 | 150 |
| 4 | 4 | 54.6 | 74.2 | 150 |
| 5 | 5 | 63.1 | 63.7 | 115 |
| 6 | 6 | 73.5 | 71.5 | 115 |
| 7 | 7 | 80.9 | 85.9 | 80 |
| 8 | 8 | 85.6 | 61.6 | 80 |
| 9 | 9 | 88.5 | 30.7 | 80 |
| 10 | 10 | 93.1 | 48.9 | 80 |
| 11 | 11 | 95.5 | 27.3 | 80 |
| 12 | 12 | 97.0 | 18.1 | 80 |
| 13 | 13 | 97.2 | 10.4 | 80 |
| 14 | 14 | 99.2 | 13.6 | 80 |

TABLE - 5

Selection of Suitable Cathode Current Density for
Different Ranges of Uranyl Concentration

| Sr. No. | Uranyl Conc. range g/l | Cathode C.D. mA/cm ² | Corresponding maximum current efficiency in % |
|---------|------------------------|---------------------------------|---|
| 1 | 6-7 | 20 | ~ 15 |
| 2 | 15-20 | 33 | ~ 40 |
| 3 | 45-55 | 47 | ~ 63 |
| 4 | 90-108 | 67 | ~ 90 |
| 5 | 186-195 | 100 | ~ 100 |

TABLE-6

Uranous Production in Filter Press Cell

Concentration of uranyl : 215.6 g/l
 Acidity : 2.05 M
 Hydrazine concentration : 0.76 M
 Cell current : 30 Amps.
 Cell voltage : 3 Volts
 Volume of the feed : 28.5 l
 Current Density : 40 mA/cm²

| Sr. No. | Ele. hrs. | Gms. of U ⁺⁴ Produced | Uranous Conc. g/l | U ⁺⁴ g/Amp.hr. | |
|---------|-----------|----------------------------------|-------------------|---------------------------|--------------|
| | | | | Cumulative | Differential |
| 1 | 19.5 | 2722 | 89.25 | 4.7 | 2.2 |
| 2 | 31.5 | 4368 | 130.40 | 4.6 | 2.3 |
| 3 | 39.5 | 5083 | 151.72 | 4.29 | 2.5 |
| 4 | 51.5 | 5980 | 178.50 | 3.9 | 1.7 |
| 5 | 59.0 | 6378 | 190.40 | 3.6 | 1.9 |

TABLE-7

Pilot Scale Uranous Nitrate Production using Coated Electrodes

Acidity : 2.4 - 2.8 M

Concentration of Hydrazine : 0.6 - 0.9 M

| Run No. | Uranyl Conc. g/l | Net conversion of U(VI) to U(IV) in % | Total Uranous nitrate gms | Cathode C.D. mA/cm ² | Overall current effi. % | Av. consumption in moles / mole of U ⁺⁴ produced | |
|---------|------------------|---------------------------------------|---------------------------|---------------------------------|-------------------------|---|-----------|
| | | | | | | Acid | Hydrazine |
| 1 | 110.07 | 99.98 | 728.0 | 8 | 69.12 | --- | 0.3184 |
| 2 | 181.05 | 94.26 | 5680.4 | 30 | 106.00 | 1.560 | 0.3116 |
| 3 | 184.45 | 99.28 | 6196.9 | 30 | 128.00 | 1.449 | 0.2630 |
| 4 | 188.91 | 97.81 | 14265.0 | 30 | 124.00 | 1.430 | 0.0515 |

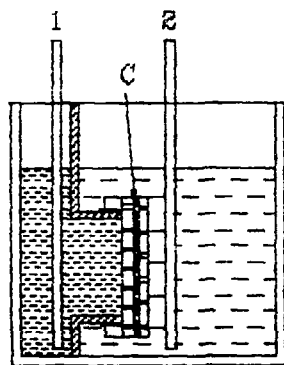
TABLE-8

Uranous Production Rate at Different Percentage Conversion

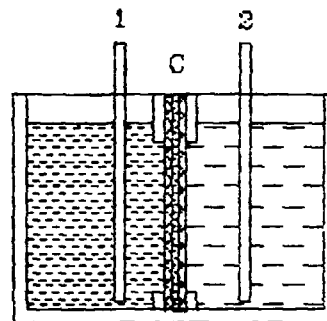
Feed uranyl concentration : ~ 200 g/l

Total current : 100 Amps.

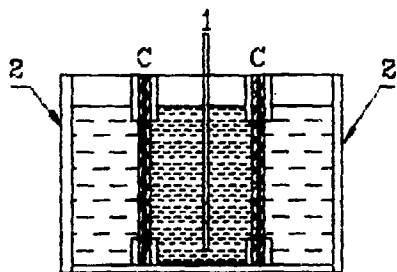
| % Conversion of uranyl nitrate to uranous nitrate. | Corresponding rate in gms. of U ⁺⁴ /hr. | | |
|--|--|-----|-----|
| | Experiment No. | | |
| | 1 | 2 | 3 |
| 50 | 800 | 691 | 695 |
| 70 | 783 | 632 | 668 |
| 100 | 563 | 473 | 510 |



CELL No. 1.



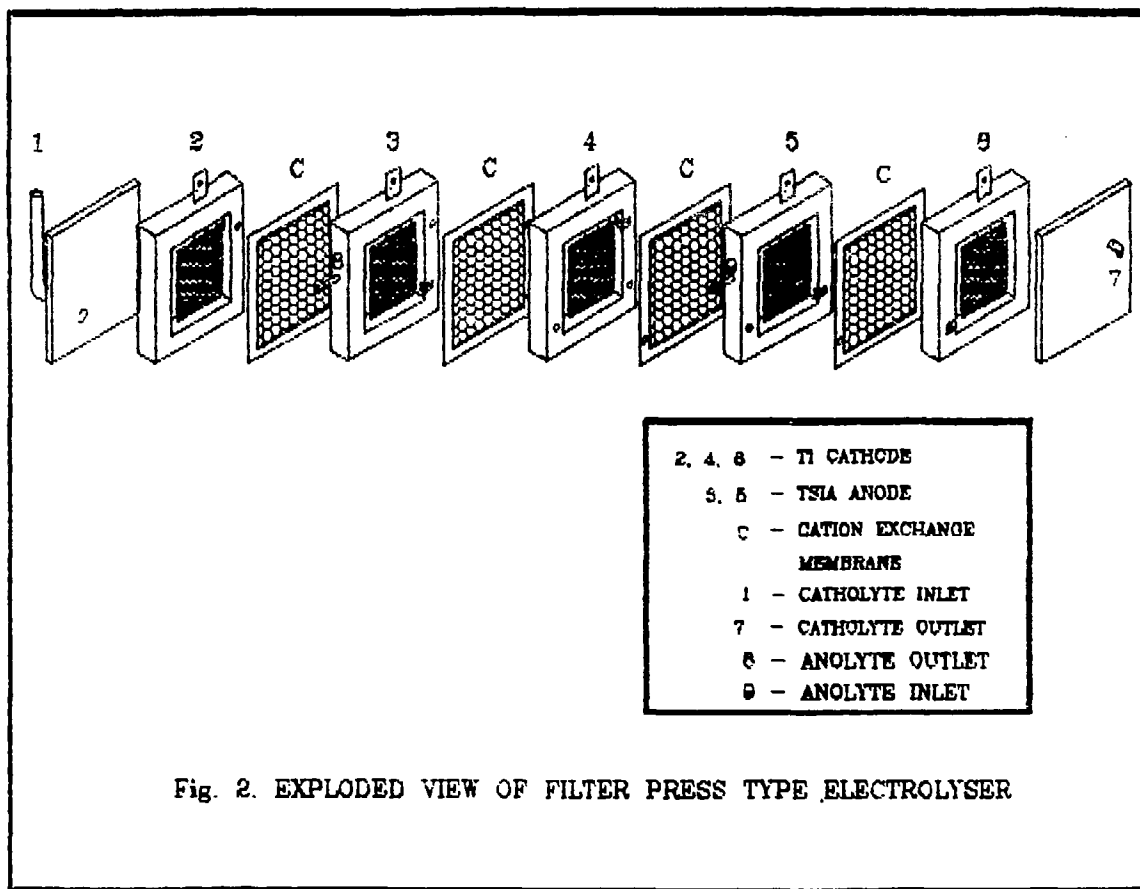
CELL NO. 2.

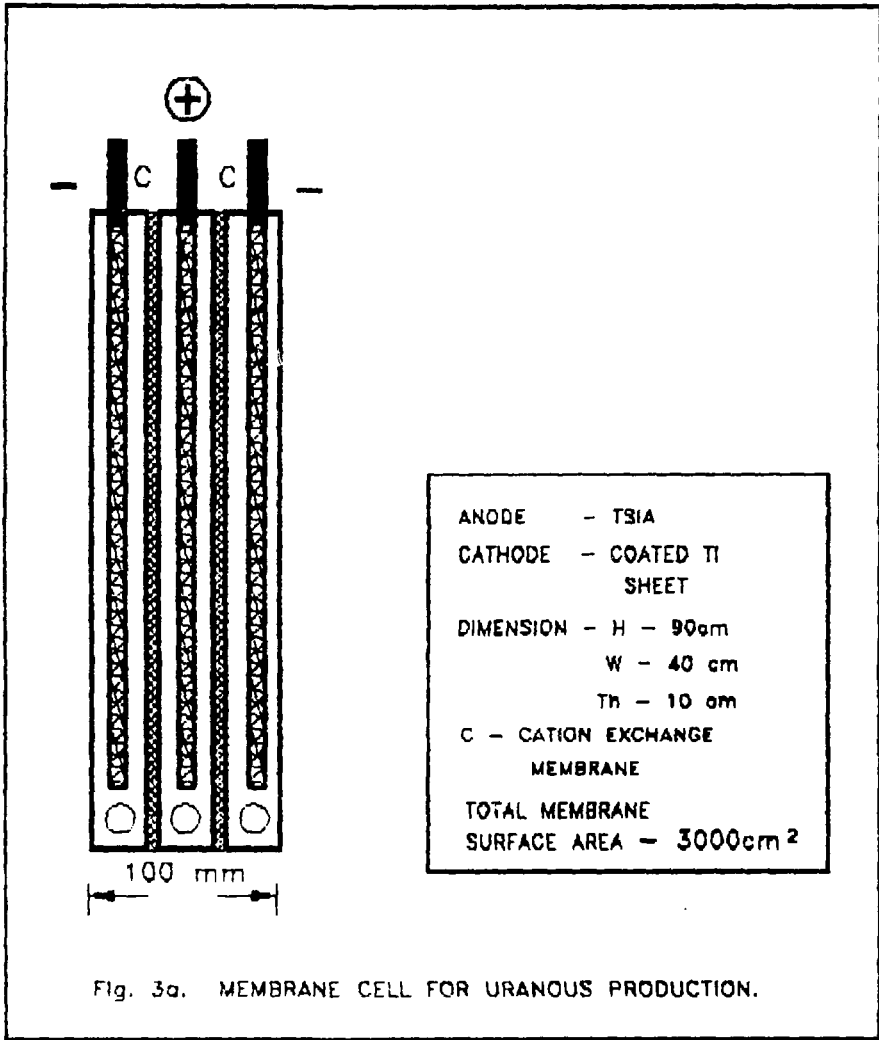


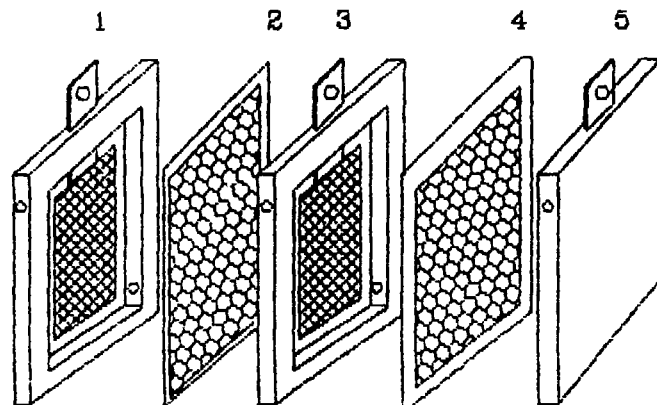
CELL No. 3.

1 - ANODE
 2 - CATHODE
 C - CATION EXCHANGE
 MEMBRANE

Fig. 1. DIFFERENT CELL DESIGNS.







- 1, 3 - CATHODE
- 2 - ANODE
- 4 - CATION MEMBRANE
SUPPORTED WITH
PLASTIC NET

Fig. 3b) EXPLODED VIEW OF MEMBRANE CELL

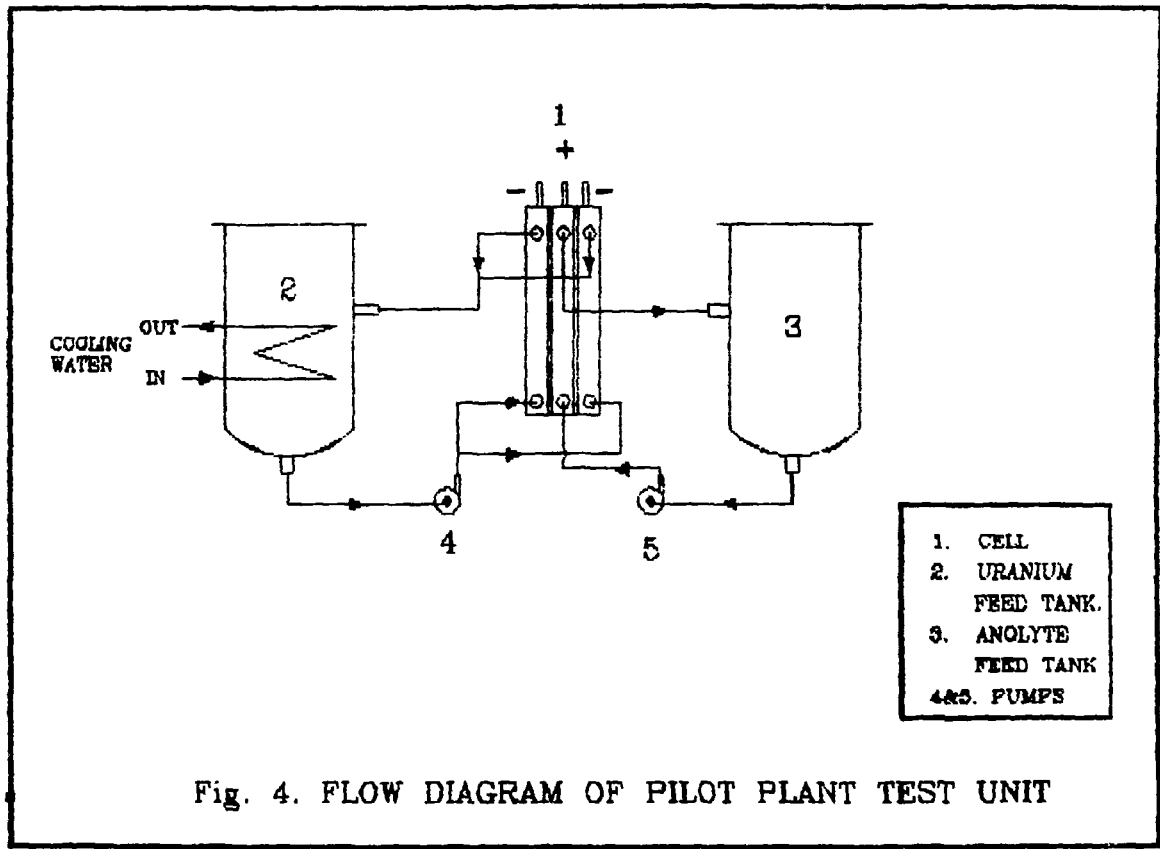
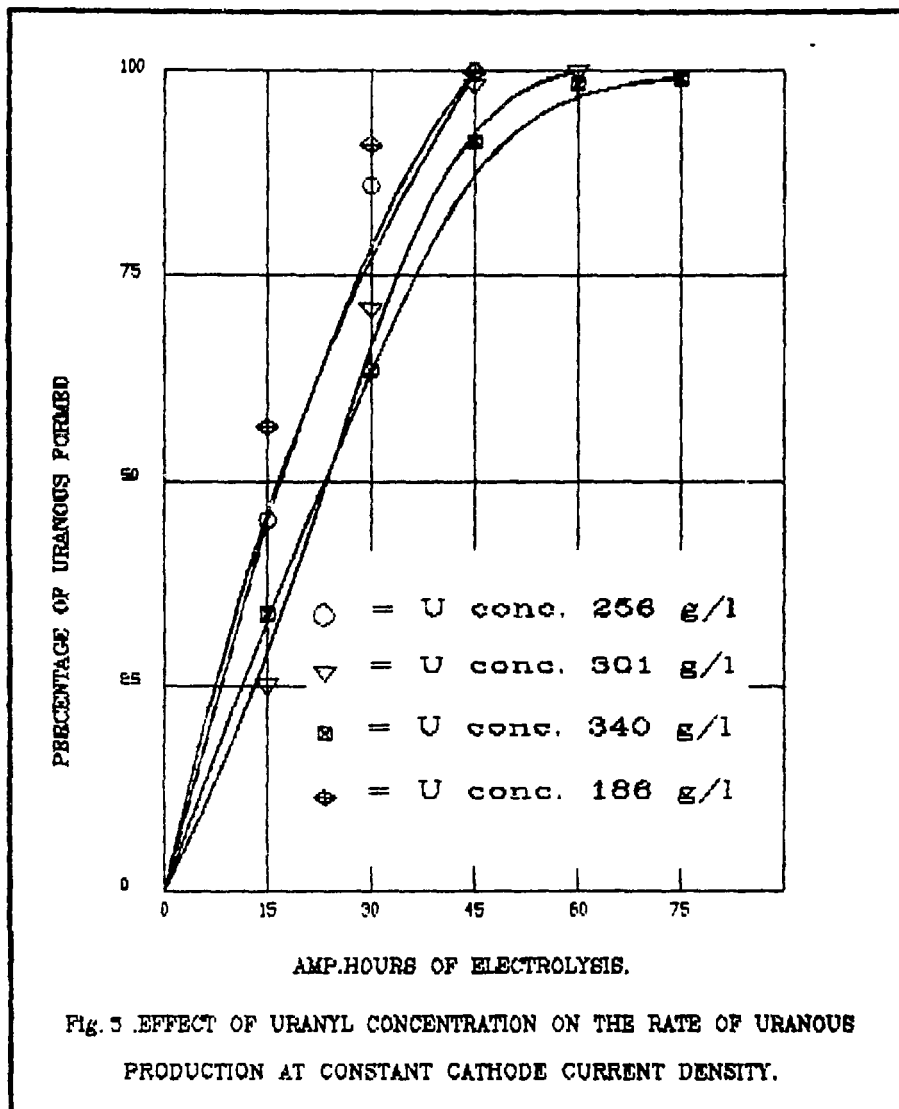


Fig. 4. FLOW DIAGRAM OF PILOT PLANT TEST UNIT



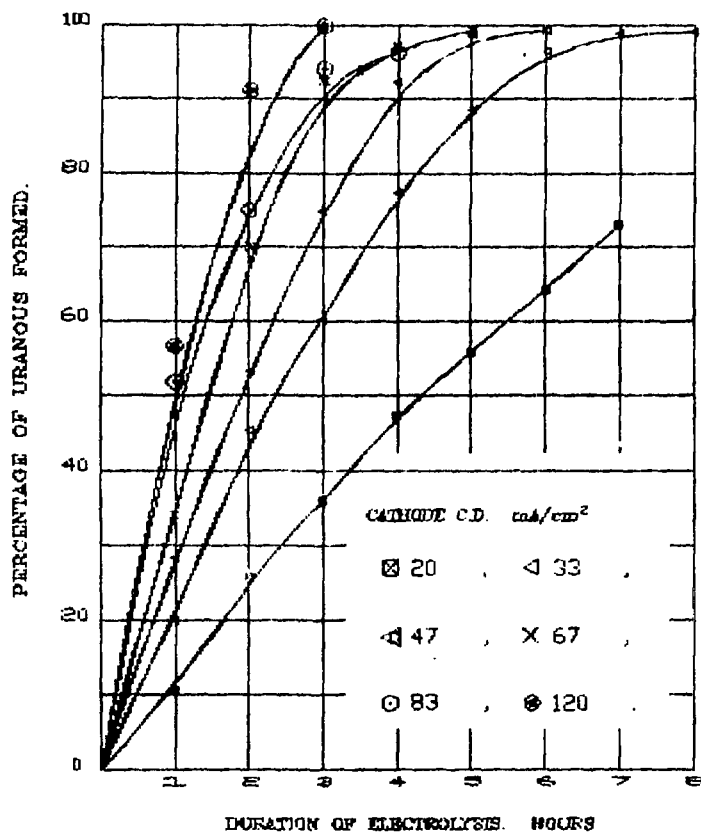


Fig. 6. EFFECT OF CATHODE CURRENT DENSITY ON URANOUS PRODUCTION.

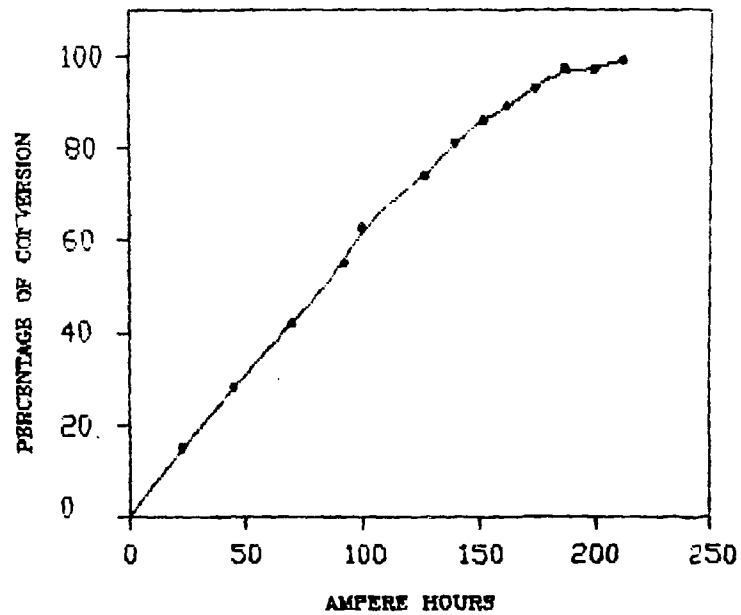


Fig. 7. PRODUCTION OF URANOUS UNDER DECREASING CATHODE CURRENT DENSITY.

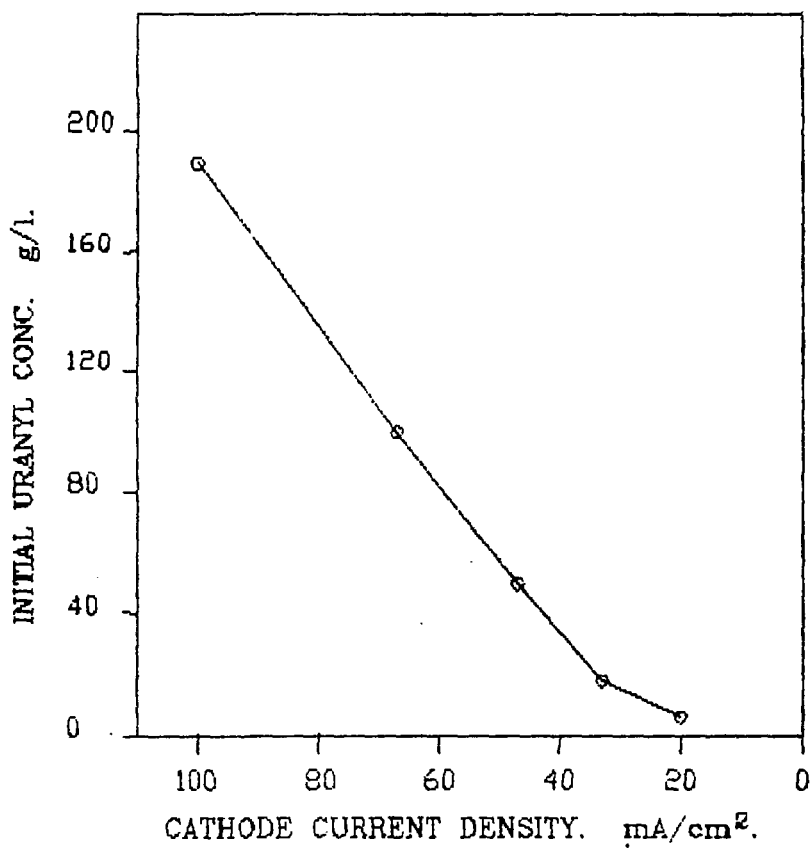


Fig. 8. OPTIMUM CATHODE CURRENT DENSITY FOR DIFFERENT URANYL NITRATE CONCENTRATION

