URANOUS NITRATE PRODUCTION FOR PUREX PROCESS APPLICATIONS USING PtO2 CATALYST AND H2/H2 - GAS MIXTURES

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60	Abstract :	In the Purex process of spent fuel reprocessing, the twin objectives- decontamination and partitioning are achieved by extracting uranium (VI) and plutonium (IV) together in the solvent 30% TBP-dodecane and then selectively reducing Pu (IV) to Pu (III) in which valency it is least extractable in the solvent. Uranous nitrate stabilized with hydrazine nitrate is the widely employed partitioning agent. The conventional method of producing U(IV) is by the electrolytic reduction of uranyl nitrate with hydrazine nitrate as uranous ion stabilizer. The percentage conversion of U(VI) to U(IV) obtained in this method is 50 -60 %. The use of this solution as partitioning agent leads not only to the dilution of the plutonium product but also to increase in uranium processing load by each externally fed uranous nitrate batch. Also the oxide coating of the anode, TSIA (Titanium Substrate Insoluble Anode) wears out after a certain period of operation. This necessitates recoating which is quite cumbersome considering the amount of the decontamination involved. An alternative to the conventional electrolytic method of reduction of uranyl nitrate to uranous nitrate was explored at FRD laboratory. The studies have revealed that near 100% uranous nitrate can be produced by reducing uranyl nitrate with H_2 gas or H_2(8%)-Ar/N_2 gas mixture in presence of PtO_2 catalyst. This report describes the laboratory scale studies carried out to optimize the various parameters. Based on these studies reduction of uranyl nitrate on a pilot plant scale was carried out. The design and operation of the reductor column and the various studies carried out in the pilot plant studies are discussed. Near 100% conversion of uranyl nitrate to uranous nitrate and also the redundancy of supply of electrical energy make this process a viable alternative to the existing electrolytic method.
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Pt O$_2$ उत्प्रेरक और H$_2$ गैस का प्रयोग करते हुए प्यूरेक्स प्रक्रिया अनुप्रयोगों के लिए यूरेनस नाइट्रेट का उत्पादन

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सारांश

भुक्तशेष ईंधन पुनर्संसाधन की प्यूरेक्स प्रक्रिया में, ये लक्ष्य -विसंदूषण एवं विभाजन दोनों प्राप्त किये जाते हैं । यह प्रक्रिया 30% TBP– डोडेकेन विलायक में यूरेनियम (VI) और प्लूटोनियम (IV) दोनों का एक साथ निष्कर्षण कर तत्पश्चात Pu (IV) से Pu (III) में वरणात्मक अपचायन किया जाता है जिसमें संयोजक के विलायक में यह न्यूनतम निष्कर्षणीय है । डाइहाइड्राजीन नाइट्रेट के साथ स्थिर किया हुआ यूरेनस व्यापक रूप से प्रयुक्त विभाजन एजेंट है । यूरेनस आयन स्थिरक के रूप में डाइहाइड्राजीन नाइट्रेट का इलेक्ट्रोलाइटिक अपचायन U (IV) के उत्पादन की पारंपरिक पद्धति है । इस पद्धति में U(VI) से U (IV) की प्रतिशतता परिवर्तन 50 से 60% है । इस विलयन को विभाजन एजेंट के रूप में प्रयोग करने से न केवल प्लूटोनियम उत्पाद का तनुकरण होता है बल्कि प्रत्येक बाहर से भरे जाने वाले यूरेनस नाइट्रेट बैच द्वारा यूरेनियम संसाधन भार को बढ़ाता है । ऐनोड TSIA (टाइटेनियम सबस्ट्रेट इन्सल्यूबल ऐनोड) का ऑक्साइड विलेपन भी प्रचालन के कुछ समय के पश्चात घटने लगता है । इसके कारण पुनः लेपन करने की आवश्यकता होती है जो उत्पन्न विसंदूषण को देखते हुए काफी कठिन कार्य है । अतः ईंधन पुनर्संसाधन प्रभाग की प्रयोगशाला में पारंपरिक इलेक्ट्रोलाइटिक पद्धति के विकल्प की खोज की गई है । अध्ययनों से पता चला है कि यूरेनी नाइट्रेट को Pt O$_2$ उत्प्रेरक की उपस्थिति में H$_2$ गैस या H$_2$ (8%)- Ar/N$_2$ गैस आमिश्र के साथ अपचायन करने पर 100% के निकट यूरेनस नाइट्रेट का उत्पादन किया जा सकता है । इस रिपोर्ट में विभिन्न प्रचालों को क्रियाशील करने के लिए विस्तृत प्रयोगशाला स्तर के अध्ययन पर चर्चा की गई है । अपचायक कॉलम के अभिकल्पन एवं प्रचालन तथा पायलट संयंत्र अध्ययनों में किये गये विभिन्न परीक्षणों की भी चर्चा है । यूरेनाइल नाइट्रेट से यूरेनस नाइट्रेट में लगभग 100% परिवर्तन और विद्युत ऊर्जा की आपूर्ति की आवश्यकता नहीं होने के कारण इस पद्धति को वर्तमान इलेक्ट्रोलाइटिक पद्धति का अधिक सफलतापूर्वक विकल्प माना जाता है ।

URANOUS NITRATE PRODUCTION FOR PUREX PROCESS APPLICATIONS USING PtO$_2$ CATALYST AND HYDRAZINE NITRATE AS REDUCTANT

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Abstract

In spent fuel reprocessing by Purex process uranium and plutonium are extracted together in the solvent 30% TBP-dodecane to effect decontamination from fission products and trivalent actinides. In a subsequent partition step, uranium and plutonium are separated from each other by selectively reducing Pu(IV) to Pu(III) in which valency it is least extractable in the above solvent. The reduction of Pu(IV) to Pu(III) is accomplished with the reducing agent uranous nitrate, which is produced conventionally by electrolytic reduction of U(VI) with hydrazine nitrate as uranous nitrate stabilizer. In this method of reduction the percentage conversion attainable is only 50 to 60 %. The use of this solution as partitioning agent leads not only to the dilution of the plutonium product but also to increase in uranium processing load by each externally fed uranous nitrate batch. Also the oxide coating of the anode, TSIA (Titanium Substrate Insoluble Anode) wears out after a certain period of operation. This necessitates recoating which is quite cumbersome considering the amount of the decontamination involved. So an alternative to the conventional electrolytic method has been explored in the laboratory at FRD. It is observed that quantitative reduction of uranyl nitrate to uranous nitrate can be achieved with hydrazine nitrate as reductant in presence of PtO$_2$ catalyst. Extensive laboratory scale studies were carried out to optimize the various parameters for quantitative reduction. The optimum parameters for the reduction of 4 grams of uranyl ion as a single batch (20 ml) with a catalyst amount of 320 milligrams are H$^+$ = 1 M, N$_2$H$_5^+$ = 1.0 M and temperature = 60ºC and the time for quantitative reduction under these optimized conditions was 60 minutes. These studies were then extended to pilot plant scale and the catalyst amount used in these studies was 80 grams. When the column was operated

under the optimized conditions, the uranous production per single batch (10 litres) was 1.75 kg in five hours. The amenability of the process for batch as well as continuous modes of operation was studied and the results of which are discussed in this report. The pilot plant scale studies have revealed that the developed process can produce uranous nitrate at a significant rate for Purex process requirements. The near quantitative reduction and the redundancy of the supply of electrical energy render this process a more viable alternative to the existing electrolytic method of reduction.

1) Introduction

Spent fuel reprocessing has, over the years, evolved concomitantly with the technological development owing to the thrust laid on high separation efficiency and minimization of waste volumes. Extensive studies with model simulation techniques revealed the potential of the process for achieving high separation efficiencies and even the feasibility of one cycle process provided some key areas of the process are paid more attention. One of the key areas outlined is the partition step of the Purex process. The partition step involves the separation from each other of the co-extracted U(VI) and Pu(IV) in 30% TBP-Dodecane. The partitioning of Pu(IV) from U(VI) in the solvent is achieved by selectively reducing Pu(IV) to Pu(III) in which state it is least extractable in the solvent. Among the various reductants tried for this purpose, ferrous sulphamate and uranous nitrate stand out to be the best as far as kinetics of reduction are concerned. Ferrous sulphamate introduces iron and sulphate impurities in the process streams and these impurities not only are corrosive to the process equipment but also lead to salt formation related problems in the subsequent evaporation of process streams. Whereas uranous nitrate introduces no impurity as uranium is within the system. Hence the reprocessing plants world over which adopted Purex process switched over to uranous nitrate from sulphamate once the feasibility of Pu(IV) reduction with uranous was established.

The reprocessing plants' requirement of uranous nitrate is mostly met by the electrolytic reduction of uranyl nitrate. This reduction process since its inception has undergone many changes with respect to electrode materials, design of the electrolytic cell etc., with a view to improve the kinetics of reduction, percentage conversion and safety. Though the kinetics of reduction and safety aspects of this process could be improved

significantly, the percentage conversion aspect still remained as a major drawback. Better conversion rates necessitate the separation of cathodic and anodic compartments by an ion exchange membrane, otherwise uranous ions produced at the cathode get re-oxidised at the anode and thus the reaction never proceeds to completion (1) and as a result the net load of uranium to be processed increases and this also leads to the dilution of plutonium product. But membrane separation of the electrode compartments on a plant scale is not only quite cumbersome but also beset with many practical difficulties like choking up of the membrane. So the electrolytic reduction of uranyl ion on a plant scale is generally carried out without any separation of the electrode compartments resulting in lesser conversion rates (the conversion rates obtained are generally about 50% under the operating conditions). Thus the total uranium throughput for uranous generation is twice the amount of plant uranous requirement. The other problem concerns the anode, which is titanium coated with oxides of Ti, Ru and Pd (TSIA). The drawback with this electrode is that the coating of the oxides wears out on continuous operation of the electrolytic cell resulting in decreased conversion rates. So the electrode needs to be re-coated after certain period of operation which is a cumbersome process considering the amount of decontamination involved before it is sent for re-coating. Considering all the difficulties associated with the electrolytic reduction method, need was felt for an alternative route for uranous generation. Few workers have studied the reduction of uranyl nitrate with formic acid as uranous ion stabilizer, hydrogen gas as reductant and platinum oxide as catalyst in the context of Sol gel process (2). The feasibility of reducing uranyl nitrate under the Purex process conditions with hydrogen gas as reductant, hydrazine nitrate as uranous ion stabilizer and platinum oxide as catalyst was initially studied by the authors (3). During the course of these studies on uranyl nitrate reduction with hydrogen gas the authors found that hydrazine nitrate even in the absence of H_2 gas could reduce uranyl nitrate to uranous nitrate in presence of PtO_2 (Adam's catalyst). Swanson et.al., too observed the reduction of uranyl nitrate with hydrazine in presence of Pt coated on alumina (4). But the uranous nitrate thus produced from uranyl nitrate solutions of Purex origin got re-oxidized rapidly. They attributed it to some unknown poison present in the process uranyl nitrate solutions. The other drawback with their method was that the catalyst coated on the substrate got dislodged on continuous use. These drawbacks

disabled them to use this method as an alternative to the electrolytic method of reduction. The authors of this report used PtO_2 powder (Adam's catalyst) and carried out extensive studies on the reduction of uranyl nitrate with hydrazine. The effect of various parameters like feed acidity, feed hydrazine concentration, amount of the catalyst, elevated temperatures etc., on the reduction of uranyl ion was studied and the optimum parameters for quantitative reduction were established. Then the reduction of uranyl nitrate of Purex origin was carried out under the established optimum conditions. The time for quantitative reduction and reduction pattern were found to be more or less same as those obtained with the uranyl nitrate solutions of oxide origin. The uranous solutions produced were also quite stable even on standing for few months. Encouraged by this, the method was extended to pilot plant scale and the reductions of uranyl nitrate solutions of Purex origin were carried out. The uranous nitrate solutions thus obtained were quite stable even after several months. In a batch wise operation of the column with Purex process uranyl nitrate solutions at ambient temperatures, fouling of the catalyst was observed. The source of fouling of the catalyst was traced to the dissolved organic present in the process uranyl nitrate solutions and as a preceding step to the reduction process the uranyl nitrate solutions were passed through a column of Duolite S-861 resin (5). This coupled with the operation of the column at elevated temperatures minimizes fouling of the catalyst, thus enabling the batchwise as well as continuous operation of the column. A simple method of reactivating the fouled catalyst was established. The results and experience with the pilot plant operations of this method revealed the potential of this method as an alternative to the existing electrolytic method of reduction of uranyl nitrate solutions. The catalytic method of reduction of uranyl nitrate with hydrazine as a process for uranous nitrate generation has some distinct advantages over the electrolytic method. As quantitative reduction of uranyl nitrate can be achieved in a relatively simple and rapid way, the uranium throughput for uranous generation can be cut down to almost half and also more concentrated plutonium product can be obtained. Unlike the electrolytic method the redundancy of the supply of electrical energy renders this process a viable alternative to the existing electrolytic method.

The studies carried out are divided into two parts for convenience as follows.

Part 1: Laboratory Scale Studies

Part 2: Pilot Plant Scale Studies

The Part 1 deals exclusively with the laboratory scale studies on the reduction of uranyl nitrate with hydrazine while Part 2 deals with the design and operation details of the pilot plant column and also the various studies carried out on uranyl nitrate reduction with hydrazine nitrate in this column.

2) Electrochemical principles

Metal ion reductions with hydrazine are well reported (6) and some of the reductions, which do not take place under normal conditions would readily occur in presence of a heterogeneous catalyst like Pt, Ni etc. In fact hydrazine itself decomposes in presence of a heterogeneous catalyst though the products of decomposition depend on the nature of the solution (6). Very little work has been reported as regards the uranyl nitrate reduction with hydrazine. Swanson et al., reported the reduction of uranyl nitrate with hydrazine in presence of Pt coated on alumina catalyst (4). They supposed the decomposition of hydrazine to yield hydrogen, which upon adsorption on the catalyst reduces uranyl ion to uranous ion. Latimer et. al. (7), however, reported that the decomposition of hydrazine in acidic medium to take place as follows.
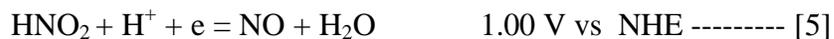
$$N_2 + 5H^+ + 4e = N_2H_5^+ \qquad \text{-0.23 V vs NHE} \quad \text{----------[1]}$$

The uranyl ion half reaction is

$$UO_2^{2+} + 4H^+ + 2e = U^{4+} + 2H_2O \qquad \text{0.33 V vs NHE} \quad \text{-----------[2]}$$

The overall reaction in the reduction of uranyl ion being

$$2UO_2^{2+} + 3H^+ + N_2H_5^+ = 2U^{4+} + N_2 + 4H_2O \qquad \text{-------------- [3]}$$
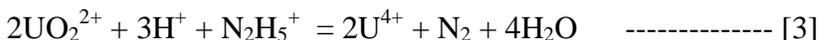
Though high acidities seem to favour the forward reaction of the above equilibrium, the associated nitrate ions, however, tend to play a detrimental role in the reduction process of uranyl ion which can be understood from the following equilibria.

$$NO_3^- + 3H^+ + 2e = HNO_2 + H_2O \qquad 0.94 \text{ V vs NHE} \text{ ------ [4]}$$

$$HNO_2 + H^+ + e = NO + H_2O \qquad 1.00 \text{ V vs NHE} \text{ --------- [5]}$$

Since standard redox potential of NO_3^-/HNO_2 is cathodic to that of UO_2^{2+}/U^{4+}, nitrate ion can be reduced to HNO_2, which in turn can oxidize U^{4+} to UO_2^{2+} very rapidly. And also high nitrate ion concentrations tend to deactivate the platinum catalyst (8). So injudicious use of high nitrate concentrations should be avoided in the reduction of uranyl nitrate. The generation of nitrous acid, in the undesired parallel reaction cannot, however, be avoided altogether. Thus a nitrous acid scavenger is imperative to destroy HNO_2 as soon as it is formed. In the reduction of uranyl nitrate with hydrazine, the latter has the dual role of being reductant for uranyl ion and stabilizer for uranous ion.

3) Experimental details

3.1 Reductor for laboratory scale studies

In the laboratory scale studies of uranyl nitrate with hydrazine, a glass cell of 60 ml capacity containing a porous fritted filter disc (G-4) at the bottom was used. A sketch of the reductor cell is shown in Fig 1. A glass stirrer driven by a motor for agitation of the solution during reduction and a thermocouple in a thermowell for temperature monitoring were provided from top. Sampling and solution withdrawal can be achieved by opening the valve at the bottom. In order to carry out reduction studies at elevated temperatures, a thermal tape was wound around the cell.

3.2 Reduction procedure in laboratory scale studies

Initially 320 mg of PtO_2 catalyst was transferred into the cell along with 1 M HNO_3 + 1 M $N_2H_5 NO_3$. Once the gas bubbling was over a fresh 20 ml of 1 M HNO_3 + 1 M $N_2H_5 NO_3$ was taken into the cell for 12 hours during which period all the hydrazine was consumed. Then the catalyst was thoroughly washed with 1 M HNO_3. Then the procedure adopted for reduction was to transfer 20 ml of feed uranyl nitrate solution of required composition into the cell and then to start stirrer as well as temperature monitor. In the case of the studies at elevated temperatures, the power to the thermal tape was then switched on. Sampling and withdrawal of solution were done by opening the valve at the bottom of the reductor.

3.3 Reagents

Stock solution of uranyl nitrate of 300 g/l was prepared by dissolving U_3O_8 (from UMP, BARC) in HNO_3. Lower concentrations of uranyl nitrate were obtained by suitable dilution of the above stock solution. Hydrazine carbonate was neutralized with HNO_3 and a stock solution of 5.0 M was prepared and this solution was used for hydrazine requirements of the feed. All the reagents used were of AR grade. The catalyst used was

PtO$_2$ (Adams' catalyst, particle size- 20μ), which was supplied by Arora Matthey Ltd., Kolkatta.

3.4 Analytical Methods

The solution was sampled at regular intervals and the samples were analysed for total uranium concentration, uranous nitrate concentration, free acidity and hydrazine concentration by the following analytical procedures.

1. Modified Davis-Gray method was employed to obtain total uranium content (9).

2. A redox titration with standard potassium dichromate was employed to obtain uranous concentration (10).

3. Free acidity determination was done in oxalate medium at 5.6 pH by titrating with standard alkali.

4. After the free acidity determination by the above method, addition of formaldehyde would liberate HNO$_3$ associated with hydrazine. Titration with standard alkali would give an estimate of the hydrazine (11).

4) Results and discussion

Hydrazine is known to be a good reducing agent but many of the metal ion reductions are brought about by this reductant only in presence of heterogeneous catalysts. The authors, during their studies on uranyl ion reduction with H$_2$ gas in presence of Adams' catalyst, found that hydrazine even in the absence of H$_2$ gas could reduce uranyl ion to uranous ion. Extensive studies were carried out on laboratory scale to see the practical significance of uranyl ion reduction with hydrazine and also to see the effect of various parameters on the reduction and to optimize the conditions for quantitative reduction. While studying the effect of each parameter, the percentage conversion of uranyl ion to uranous ion, decrease in acidity and decrease in hydrazine concentration were monitored during reduction and these were plotted against time and are discussed below under the subheadings variation of uranyl ion concentration, variation of acidity and variation of hydrazine concentration respectively.

4.1 Effect of feed acidity

The reduction of uranyl nitrate solution of composition U = 100 g/l and $N_2H_5^+$ = 1.0 M was studied at feed acidities of 0.47 M, 0.975 M, 1.56 M and 1.975 M. The variations of uranyl nitrate concentration, acidity and hydrazine concentration during reduction were monitored and the results are discussed below.

4.11 Variation of uranyl ion concentration

As can be seen from Fig 2, the time for quantitative reduction was less at a feed acidity of 0.47 M and it increased with the increase in feed acidity. The time for quantitative reduction was only 100 minutes at a feed acidity of 0.47 M whereas at a feed acidity of 1.975 M the conversion was only 88% even after 400 minutes. The curves, as can be seen from Fig 2, tend to bend more and more towards the abscissa with the increase in feed acidity indicating the lowering of the uranyl ion reduction kinetics with the increase in HNO_3 concentration. The lowering of the kinetics with the increased HNO_3 concentrations must, as discussed in the **Electrochemical Principles,** be due to the increased nitrate ion concentrations as the increased H^+ concentrations can only enhance the kinetics as can be seen from equilibrium [3].

4.12 Variation of acidity

Acidity during reduction, as can be seen from Fig.3 was decreasing more or less linearly with time at all feed acidities. The total acid consumptions at feed acidities 0.47 M and 0.975 M were 0.47 M and 0.625 M while the ones at feed acidities 1.56 M and 1.975 M were 0.26 M and 0.275 M respectively. At a feed acidity of 0.47 M the entire feed acid, which was less than the stoichiometric amount (0.6 M) as demanded by the equilibrium [3], was consumed. Despite the feed acidity being substoichiometric, near quantitative reduction of uranyl ion to uranous ion could be obtained. At a feed acidity 0.975 M the total acid consumption was more or less same as the one expected from equilibrium [3]. While at still higher feed acidities the acid consumptions were quite less than the one demanded by the stoichiometry. This shows the complex nature of the dependence of the reduction reaction on feed acidity.

4.13 Variation of hydrazine concentration

As can be seen from Fig 4 the curves for hydrazine consumption tend to become linear with the increase in feed acidity. The hydrazine consumption at feed acidities 0.47 M, 0.975 M, 1.56 M, 1.975 M were 0.19 M, 0.33 M, 0.53 M, and 0.43 M respectively (the first three correspond to near quantitative reduction of uranyl ion while the last corresponds to only about 88 % conversion). As can be seen from above, the hydrazine consumption at 0.47 M feed acidity was close to the amount demanded by the stoichiometry in the reduction of uranyl ion as suggested by equilibrium [3]. Whereas as the feed acidity was increased the amount of hydrazine consumption also increased indicating a parallel reaction of hydrazine decomposition becoming significant at the increased feed acidities.

4.2 Effect of feed hydrazine concentration

The reduction of uranyl nitrate solution of composition U = 100 g/l and H^+ = 1.0 M was studied at feed hydrazine concentrations of 0.54 M, 0.7 M & 1.1 M. The variations of uranyl ion concentration, the acidity and the hydrazine concentration were monitored during reduction and the results are discussed below.

4.21 Variation of uranyl ion concentration

As can be seen from Fig 5, the reduction kinetics improved significantly as the feed hydrazine concentration was increased. At a feed hydrazine concentration of 1.1 M near quantitative reduction could be observed in about 3 hours while at feed hydrazine concentrations of 0.54 M and 0.7 M the conversions were 90% and 92% in 6 hours and 5 hours respectively.

4.22 Variation of acidity

As can be seen from Fig 6, the acidity at a feed hydrazine concentration of 1.1 M, decreased rather sharply up to 60 minutes and thereafter the consumption was more or less linear. However, the consumption of acid at feed hydrazine concentrations of 0.54 M & 0.7 M was linear through out. The total acid consumptions at feed hydrazine concentrations of 0.54 M, 0.7 M & 1.1 M were 0.435 M, 0.5 M and 0.625 M respectively.

4.23 Variation of hydrazine concentration

As can be seen from the curves of Fig 7 the hydrazine consumption followed more or less a linear path at all feed hydrazine concentrations. The total hydrazine consumptions decreased as the feed hydrazine concentrations were increased. The total hydrazine consumptions at feed hydrazine concentrations 0.54 M, 0.7 M & 1.1 M were 0.49 M, 0.405 M and 0.32 M respectively.

4.3 Effect of temperature

The reduction of uranyl nitrate solution of composition U = 200 g/l, H^+ = 0.9 M and $N_2H_5^+$ = 1.1 M was studied at a catalyst amount of 320 mg, at temperatures room temperature, 42°C, 50°C and 60°C. The variations of uranyl ion concentration, acidity and hydrazine concentration were monitored during reduction and the results are discussed below.

4.31 Variation of uranyl ion concentration

Temperature by far seems to have the maximum impact on the rate of reduction of uranyl ion. The slopes of the curves of Fig 8 increased appreciably with the increase in temperature indicating the enhancement of kinetics of reduction as the temperature was varied from room temperature to 60°C. The time for quantitative reduction also decreased significantly as the temperature was increased from ambient to 60°C. The time for quantitative reduction was about one hour at 60°C whereas the time for near about 80 % conversion at room temperature was about 6 hours.

4.32 Variation of acidity

The rate of acid consumption as indicated by the curves of Fig 9 was increasing with the increase in temperature. The rate of acid consumption was in accordance with the uranyl ion reduction rate and the total acid consumed was more or less the same at all the temperatures.

4.33 Variation of hydrazine concentration

As the slopes of the curves of the Fig 10 indicate the rate of hydrazine consumption increased as the temperature was increased. And also the total hydrazine consumption increased with the increased temperatures. The total hydrazine consumption was 0.35 M at room temperature where about 80 % reduction of uranyl ion was observed. At other temperatures where near quantitative reductions were observed, the total hydrazine consumptions were 0.525 M at 42° C, 0.65 M at 50° C and 0.78 M at 60° C. As the stoichiometric amount demands a far lesser consumption of hydrazine for the quantity of uranyl ion reduced, the higher consumption of hydrazine can be attributed to its thermal decomposition at higher temperatures.

4.4 Effect of feed uranyl nitrate concentration

The reduction of uranyl nitrate solution of composition $H^+ = 1.0$ M and $N_2H_5^+ = 1.0$ M was studied at feed uranium concentrations of 53 g/l, 108 g/l, and 200.5 g/l. The amount of the catalyst used in this study was 300 mg and its catalytic activity is different from the lot used in all other studies. The variations of uranyl ion concentration, acidity and hydrazine concentration were monitored during reduction and the results are discussed below.

4.41 Variation of uranyl ion concentration

As can be seen from the curves of Fig 11, the rate of reduction increased with the feed uranyl nitrate concentration. The time taken for the same % conversion was found not to vary any significantly with the feed uranyl nitrate concentration at the given feed acidity and hydrazine concentrations.

4.42 Variation of acidity

The rate of acid consumption increased with the increased feed uranyl nitrate concentrations (Fig 12). The total acid consumed also increased with the increased feed uranyl nitrate concentrations. At a feed uranium concentration of 53 g/l the acid consumed was 0.1 M, which was less than the stoichiometric amount 0.37 M. The acidity consumed at a uranyl nitrate concentration of 108.4 g/l was 0.47 M whereas the

stoichiometric consumption should be around 0.675 M. Again at a feed uranyl nitrate concentration of 200.5 g/l the acid consumption was 1.05 M whereas as per the stoichiometry the consumption should be around 1.26 M.

4.43 Variation of hydrazine concentration

The rate of hydrazine consumption decreased as the feed uranyl nitrate concentration increased (Fig 13). Also the total amount of hydrazine consumed also decreased as the feed uranyl nitrate concentration increased. The hydrazine consumed at 53 g/l of feed uranyl nitrate concentration was 0.75 M which was quite more than the stoichiometric amount i.e. 0.11 M. At 108.4 g/l of feed uranyl nitrate concentration, the hydrazine consumption was 0.52 M whereas the stoichiometry demands a consumption of only 0.225 M. And at 200.5 g/l feed uranyl nitrate concentration, the hydrazine consumed was 0.51 M and as per the stoichiometry the consumption should be 0.42 M. So as the feed uranyl nitrate concentration increased the hydrazine consumption was closely approaching the stoichiometric amount. The higher hydrazine consumption at lower feed uranyl nitrate concentration must be due to the parallel reaction of hydrazine decomposition.

4.5 Effect of the pretreatment of the catalyst

4.51 Effect on the decomposition of hydrazine

These experiments were carried out with a view to see the effect of the pretreatment of the catalyst with 1 M HNO_3. The amount of the catalyst used was 320 mg. Initially the catalyst was treated with 1.0 M HNO_3 for 20 hours and then after removing this solution 20 ml of 1 M HNO_3 + 1 M $N_2H_5NO_3$ (1st experiment) was taken into the cell and the variations of temperature, acidity and hydrazine concentration with time were followed. After removing this solution, another 20 ml of 1 M HNO_3 + 1 M $N_2H_5NO_3$ (2nd experiment) was taken into the cell and again the variations of temperature, acidity and hydrazine concentration with time were followed. As can be seen from Fig 14 the curves for 'Hydrazine-HNO_3 Treated' (1st experiment) and 'Hydrazine-Hydrazine Treated' (2nd experiment) followed more or less the same course and reached a maximum temperature of 34.6°C at about the same time. As there was temperature rise in the first experiment

the initial temperature for the second curve was more. Acidity as shown by the curves "Hydrazine-HNO$_3$ Treated" and "Hydrazine-Hydrazine Treated" of Fig 15 remained more or less constant. The hydrazine consumption as can be seen from Fig 16 was about 0.5 M in the case of HNO$_3$ pretreatment while in the case of hydrazine pretreatment it was about 0.3 M. The results of this experiment show that the maximum temperature attained during decomposition of hydrazine was irrespective of the pretreatment of the catalyst. Acidity remained more or less constant i.e. there was hardly any consumption of acid during hydrazine decomposition. The hydrazine decomposition was, however, more in the case of HNO$_3$ pretreatment than in the case of hydrazine pretreatment.

4.52 Effect of pretreatment on the reduction of uranyl nitrate

The reduction of uranyl nitrate of composition U = 100 g/l, H$^+$ = 1.0 M & N$_2$H$_5^+$ = 1.0 M was carried out after pre-treating the catalyst (catalyst amount 320 mg) with 1 M HNO$_3$ and 1 M HNO$_3$ + 1 M N$_2$H$_5$NO$_3$ in two separate experiments. The pre-treatment of the catalyst either with 1 M HNO$_3$ or with 1 M HNO$_3$ + 1 M N$_2$H$_5$NO$_3$ did not alter the time for quantitative reduction of uranyl nitrate (Fig17). The total consumptions of acid and hydrazine as shown by the curves "uranium - HNO$_3$ Treated" and "uranium – Hydrazine Treated" were also not altered much (Fig.15 & Fig. 16).

4.6 Fouling and reactivation of the catalyst

4.61 Batch experiments

Batch reduction of uranyl nitrate solution of composition U = 208 g/l, H$^+$ = 1.0 M & N$_2$H$_5^+$ = 1.0 M was carried out to see the effect of continuous reduction on the catalyst. The reduction was carried out at a temperature of 50°C under stirred conditions. Reduction of six batches was carried out and the results were presented in Table 1. From the above Table 1, it can be seen that there was a gradual increase in time for quantitative reduction but near quantitative reductions could be observed in all the cases. While the acid consumption was the same in all the cases the hydrazine consumption was decreasing marginally. After removing the last batch the catalyst was washed with acid and then 1 M HNO$_3$ + 1 M N$_2$H$_5$NO$_3$ solution was taken into the cell. The bubbling normally associated with the hydrazine decomposition was found to be very less. The

physical observation of the catalyst revealed that the catalyst was in small clusters, which was originally in a fine powdery form.

4.62 Acid treatment of the fouled catalyst

The catalyst was then washed with 1 M HNO_3 and then 1M HNO_3 was taken into the cell and a temperature of 50°C was maintained for one hour. Then it was observed that the catalyst was turned to its original fine powdery form and was settling at the bottom very nicely. After this treatment, reduction of uranyl nitrate solution of same composition as used in the batch reduction was carried out and as it can be seen from the last row of the table the time for quantitative reduction was again as that obtained in the first batch. This revealed that the continuous reduction of uranyl nitrate solution lead to the cluster formation of the catalyst (fouling of the catalyst) thus affecting the active catalytic surface of the catalyst. The fouling of the catalyst might be due to the dissolved organic present in the uranyl nitrate solution. Subsequent studies on dissolved organic in plant uranyl nitrate solutions revealed the presence of dissolved organic mostly DBP. Acid treatment of the catalyst at higher temperature removed the cluster formation thus restoring the active catalytic surface though it was not removing dissolved organic completely.

4.63 Na_2CO_3 treatment of the fouled catalyst

The above acid treatment though it removes the clustering of the catalyst, was not completely dissolving the organic precipitate (which was mainly due to DBP). However, it was observed that this precipitate was dissolving completely in 2% Na_2CO_3. So a method was developed to dissolve the organic precipitate with 2% Na_2CO_3 and thus to reactivate the fouled catalyst. The reduction of plant uranyl nitrate solution was carried out repeatedly till the clusters of the catalyst as observed earlier were formed. Then the catalyst was washed with 20 ml of 1 M HNO_3 and then thoroughly washed with H_2O till the washings contain no traces of acid. Then the catalyst was treated with 20 ml of 2% Na_2CO_3 solution for one hour at room temperature under stirred condition. The solution was then removed and the catalyst was thoroughly washed with H_2O till the washings contain no traces of Na_2CO_3. The physical observation revealed that the original fine

powdery form of the catalyst was restored and the catalyst was nicely settling at the bottom. The sodium carbonate washings contain significant amounts of the DBP as the gas chromatographic analysis revealed. Then the catalyst was washed with 1 M HNO_3 and then the reduction of uranyl nitrate solution of composition U = 208 g/l, H^+ = 1.0 M & $N_2H_5^+$ = 1.0 M was carried out at a temperature of 60°C. The time for quantitative reduction was found to be 60 minutes, which was the time required for the reduction of uranyl nitrate solution with an unfouled catalyst in the earlier experiments.

5) Summary

From the above laboratory scale studies it is obvious that lower feed acidities and higher feed hydrazine concentrations favoured uranyl ion reduction kinetics. Also the time for the same percentage of conversion in the range of feed uranyl ion concentrations studied was independent of the feed uranyl ion concentration. When the effect of a parameter on the reduction of uranyl nitrate was studied it was observed that whenever the total hydrazine consumption increased the total acid consumption decreased and vice versa except in the study at elevated temperatures. The total acid consumption was more or less same at all temperatures while the total hydrazine consumption increased with the increase in temperature. The increase in total hydrazine consumption with the increase in temperature can be attributed to the fact that the thermal decomposition of hydrazine increases with the increase in temperature. The optimum parameters for the reduction of 4 grams of uranyl ion at a catalyst amount of 320 mgs were H^+= 1.0 M, $N_2H_5^+$ = 1.0 M, Temperature = 60 °C. The time for quantitative reduction under these conditions was about 60 minutes.

The pretreatment of the catalyst either with 1 M HNO_3 or 1 M $N_2H_5NO_3$ hardly affected the time for quantitative reduction, the total acid consumption and the total hydrazine consumption. Fouling of the catalyst was observed when plant uranyl nitrate solution contained dissolved organic and the fouling of the catalyst adversely affected the rate of reduction of uranyl nitrate. So it is necessary to remove dissolved organic before taking it for reduction. The fouled catalyst could be regenerated easily with 2% Na_2CO_3.

About 4 grams of uranyl nitrate of Purex origin could be quantitatively reduced to uranous nitrate with 320 mgs of catalyst in about 60 minutes. Thus the laboratory scale

studies revealed the feasibility of producing uranous nitrate by reducing uranyl nitrate with hydrazine nitrate in presence of PtO_2 catalyst.

PART 2: PILOT PLANT SCALE STUDIES

6) Reductor for pilot plant operation

A tubular glass with 163 mm of OD, 153 mm of ID and 1180 mm of height was used as a reductor column. Both ends of this column were tightly closed by thick HDPE flanges held in position by four fastening rods (Fig18). Teflon soft gaskets were used as sealants between the glass ends and the HDPE flanges. The inner surface of the bottom flange was conical shaped and at the central opening of the bottom flange a threaded SS conical cup was tightly fitted into the flange along with a sintered filter disc of G-4 rating (with teflon gasket). This sintered filter disc served the purposes of both retaining the catalyst powder as well as diffusing the Ar/N_2 gas into the solution of the reductor to agitate it. A side limb, the top of which can be connected to a gas cylinder through flow meter, was connected through a valve to the conical cup at the bottom so that the gas can be passed through the filter disc into the solution. An SS crown was fitted over the top HDPE flange and various lines were provided through it. One of the lines was connected to an air ejector so that the Ar/N_2 gas, which was used for agitating the solution and also the reaction product gases could be evacuated. Through another line a thermowell containing a thermocouple was introduced to monitor temperature. Through the central line a specially designed and fabricated filter system, which will be discussed in a separate section, was introduced for product withdrawal and sampling. The product line was connected to a conical flask of 10 litres capacity with the help of a cork. When suction was applied in the conical filter flask the solution in the reductor column passed through the cartridge filter and got collected in the conical flask. A line was provided from conical filter flask to the column through a peristaltic pump so that solution if needed can be transferred back to the column. Yet another line was used for pumping feed solution into the column. The entire glass column was enveloped with an SS mesh. The entire unit was enclosed in a perspex enclosure so that plant uranyl nitrate solutions can be operated safely. An exhaust fan was provided to one of the side panels of the enclosure so that negative pressure with respect to outside can be maintained in the enclosure. The exhaust of the enclosure was connected to a fumehood through a duct. In case of reduction studies at elevated temperatures, the heating of the column solution was done with a thermal tape

which was wound around the glass column and the thermal tape was connected to power point through a Dimmerstat so that by applying suitable voltage required temperatures could be attained.

7) Filter system

A filter system was designed in Laboratory, FRD, Trombay and fabricated in the workshop, FRD, Trombay specially for filtering out product uranous nitrate solutions. This system, as shown in Fig 19, consists essentially of an SS cartridge filter of diameter 80 mm and height 248 mm. This was then enveloped with an SS sheet, the diameter of the envelope being 107 mm and was connected to an SS stem of length 1130 mm. Without this envelope, when the solution level in the column fell below the top level of the cartridge the flow rate was affected due to the competition of air. When the cartridge was enveloped the solution out side this envelope had to flow downwards and then enter into the annular space between the cartridge and the envelope and then into the cartridge. This system was useful especially in the continuous operation of the column. The filtration rate without the envelope was about 45 minutes for the withdrawal of 5 liters of solution and the same with the envelope was about 10 minutes under similar withdrawal conditions.

8) Introduction of catalyst into the column

Twenty grams each of PtO_2 catalyst was taken in four one litre glass beakers and about 250 ml of 1M HNO_3 + 0.5 M hydrazine nitrate solution was taken into them. The reaction started instantaneously as indicated by the gas bubbling. After the reaction subsided the catalyst from each of the beakers was filtered through an SS sintered filter disc of G-4 rating, which was then thoroughly washed with 1 M HNO_3. Then the catalyst was transferred into the reductor column with 1 M HNO_3. Thus the total amount of PtO_2 taken into the reductor column was 80 grams. After transferring the catalyst into the column the HNO_3 solution was withdrawn from bottom by opening the bottom valve and then 1M HNO_3 + 1M $N_2H_5NO_3$ solution was taken into the reductor. The gas bubbling started instantaneously. After the gas bubbling stopped which was an indication that the decomposition of hydrazine nitrate was completed, the solution was withdrawn and three

litres of 1 M HNO_3 solution was taken into the solution. The catalyst was always immersed in about 3 litres of 1 M HNO_3 when the column was not operated.

9) Operational procedure and feed preparation

The sequence of operations followed in operating the column in the reduction studies was that the exhaust fan was first started and negative pressure was ensured and then ejector to evacuate gases was started. The feed uranyl nitrate solution was then transferred into the column. In the studies at elevated temperatures the heating of the column solution was started till it attained the required temperature. Bubbling of the solution was done by purging Ar/N_2 gas from bottom. While sampling, the gas was first stopped and then by applying suction, solution was withdrawn into the conical flask. After withdrawing about two litres of solution sampling was done and then the solution withdrawn was transferred back into the column with the help of a peristaltic pump and the gas purging was started again. In the case of the withdrawal of the solution gas purging was, first stopped and then the solution was withdrawn by applying suction in the conical flask. The column was then thoroughly washed with 1 M HNO_3 solution and then about 3 litres of 1 M HNO_3 solution was taken into the column and the exhaust fan was then switched off. The uranyl nitrate solutions used in all these studies were of Purex origin and these solutions which were passed through a column of Duolite S-861 resin in order to remove dissolved organic were only used in the feed preparation for various studies in the pilot plant reductor. The reduction was always carried out with Ar/N_2 gas purging (2 litres/min). A stock 5 M hydrazine nitrate solution was prepared by neutralizing commercially available hydrazine carbonate and this solution was used for the feed requirements of hydrazine nitrate. Commercially available nitric acid was used for acid requirements of the feed.

10) Reduction of uranyl nitrate solution at room temperature

This study was carried out to see the feasibility of reduction of uranyl nitrate solution of Purex origin at pilot plant scale level. Five litres of feed uranyl nitrate solution of composition U = 113.9 g/l, HNO_3 = 1.125 M and $N_2H_5NO_3$ = 0.99 M was taken into the

column and sampling was done at regular time intervals and the results obtained were as presented in Table 2. About 95% conversion could be obtained in about 5 hours. The time for this percentage conversion when compared to the one obtained in laboratory scale study (98% in 3 hours in laboratory scale study) revealed slower kinetics of reduction in the pilot plant column. The acid consumption and hydrazine consumptions were 0.5 M and 0.39 M respectively. The acid consumption was slightly less than that in the laboratory scale study (0.625 M) while the hydrazine consumption was more or less same in both the cases. This study revealed that about 540 grams of uranous nitrate could be produced in five hours.

11) Batch operation of the column at room temperature

As conversion of 95% could be obtained at a significant rate in the earlier study, batch experiments were carried out at room temperature in order to see the amenability of the process for batch operation. The feed of composition U = 115.5 g/l, HNO_3 = 1.125 M and $N_2H_5NO_3$ = 0.99 M was prepared and reduction of five batches of this solution was carried out one after the other. As can be seen from Table 3 the percentage conversions were in the range 94% to 95% and the time taken for each batch was about 5 hours. The uranyl nitrate concentrations given in the table were as determined in the samples and these concentrations varied slightly from the initial concentration of the feed as prior to the introduction of the first batch there was a backlog solution (HNO_3 in which the catalyst was immersed) in the column. The total amount of uranous produced in the batch operation of the column was 2.7 kg at 94.7% conversion in about 27 hours of operation (the time includes feed transfer and product withdrawal).

12) Reduction of uranyl nitrate solution in pilot plant column at 60° C

The feasibility of enhancing the kinetics of reduction at elevated temperatures with the same catalyst inventory as that used in the earlier experiment was studied initially with a ten litre batch of uranyl nitrate solution. The composition of the feed solution was uranium = 176 g/l, HNO_3 = 0.99 M and $N_2H_5NO_3$ = 0.99 M and the temperature at which the reduction was carried out was 60° C. As can be seen from Table 4 about 99% conversion could be achieved in five hours. However, in the laboratory scale studies with

more or less the same composition of the solution the time taken for the same percentage conversion was two hours. The reasons for this are the time taken for heating the solution to $60°C$ and also the method of agitation of the solution. In the pilot plant scale studies the time taken for heating the solution to $60°C$ was about one hour whereas in the laboratory scale studies the time taken for heating the solution to the same temperature was about 5 minutes. In pilot plant scale studies only a moderate agitation of the solution could be done by purging Ar/N_2 gas from bottom (2 ltrs/ min at 2 kg/cm^2). This agitation was not as good as the one in laboratory scale studies in which case the solution could be thoroughly agitated with a mechanical stirrer. So if an efficient heating system and a better agitation of the solution can be provided to the pilot plant column the time for quantitative reduction can be further cut down. The total acid and hydrazine consumptions were 0.935 M and 0.45 M. About 1.74 kg of uranous at a conversion of 99% could be produced in five hours. So the reduction at $60°C$ increased the production rate by more than three times the one obtained at room temperature.

13) Batch operation of the column at 60° C

By carrying out the reduction at $60°C$ uranous production rate could be enhanced by more than three times for the same catalyst inventory as that used in the reduction at room temperature. So the study of operating the column in batch mode at $60°C$ was undertaken. The feed of composition U = 195 g/l, HNO_3 = 1.58 M and $N_2H_5NO_3$ = 1.12 M was prepared and reduction of 10 litres of solution as a single batch was studied. Like this the reduction of four batches of solution was carried out one after the other. As can be seen from Table 5 the percentage conversions were in the range 90% to 91% and the times for these conversions varied from five to six hours. In the experiment carried out earlier at $60°C$, the acidity of the product solution was only 0.055 M. So in the batch experiments a feed acidity of 1.58 M was employed so that the final product solution would be sufficiently acidic. However, this increased the time for quantitative conversion. The total amount of uranous produced in these batch experiments was about 7.1 kg at a conversion of 91% in about 25 hours.

14) Continuous operation of the column at 60° C

This study was carried out to see the feasibility of operating the column on a continuous basis. The feed of composition U = 200 g/l, HNO_3 = 0.85 M, $N_2H_5NO_3$ = 0.9 M was prepared and initially reduction of five litres of the solution was carried out in the column at $60°$ C. After about 150 minutes, feed was introduced at a rate of 5 litres/hour and product was withdrawn at the same rate. Sampling was done at regular intervals and the results were presented in Table 6. The conversion after about 200 minutes of operation was found to be only about 66%. So after 230 minutes of operation the flow rates of both feed and product were reduced to 4 litres/hour. Then the conversion after 275 minutes of operation was 75% and this remained more or less constant even after 305 minutes of operation. So the flow rates of both the feed and the product were again reduced to 3 litres/minute. The conversion rate then improved and reached a maximum of 98.5% after 560 minutes of operation and this remained more or less constant for the next 120 minutes of operation. The uranous yield per hour was 700 grams at a conversion of 69% and at a flow rate of 5 litre /hour, 608 grams at a conversion of 75% and flow rate of 4 litres/hour and 600 grams/hour at a conversion of 98.5% and at a flow rate of 3 litres/hour. Thus the optimum flow rate for a conversion of 98 to 99% is 3 litres/hour. The column was operated in the continuous mode for about 12 hours. This study revealed that the catalytic reduction process is amenable to continuous operation.

15) Summary

Pilot plant scale studies were carried out with a catalyst (PtO_2) inventory of 80 grams and with uranyl nitrate solutions of Purex origin, which were passed through Duolite S-861 resin to remove dissolved organic. With a single batch of five litres, about 540 grams of uranous could be produced in about five hours at room temperature. In the batch operation of the column at room temperature total five batches were processed (each batch constituting five litres) and about 2.7 Kg of uranous could be produced in about 27 hours (the time includes the feed transfer and the product withdrawal). When the column was operated at 60°C the production per single batch (here the batch constitutes 10 litres) increased to about 1.75 kg in about five hours with the same catalyst inventory as that

used in the earlier studies. In the batch operation of the column at 60°C four batches were processed (each batch constituting about 10 litres) and about 7.1 kg of uranous could be produced in about 25 hours (the time includes the feed transfer and the product withdrawal). In the continuous operation of the column, for a conversion of 99%, the optimum flow rates for feed transfer and product withdrawal were found to be 3 litres/hour each. At these flow rates of feed transfer and product withdrawal uranous could be produced at a rate of about 600 grams per hour. About 25 kg of uranous produced in various pilot plant scale studies were supplied for Purex process applications. The pilot plant scale studies thus revealed that the developed process could produce uranous nitrate at a rate significant for Purex process requirements and also revealed that the developed process is amenable to batch mode as well as continuous mode of operation. The near quantitative reduction of uranyl nitrate to uranous nitrate and also the redundancy of supply of electrical energy render this process a more viable alternative to the existing electrolytic method of reduction.

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Table 1

Batch reduction of uranyl nitrate on laboratory scale

Acidity = 1.0 M, Hydrazine = 1.0 M, Uranium = 208 g/l.
Amount of Catalyst = 320 mgs, Operating temperature = 50 C.

Batch No.	Time for Quantitative Reduction (Min)	Final Acidity (M)	Final Hydrazine Conc.(M)
1	90	Pr. Nil	0.50
2	90	Pr. Nil	0.50
3	135	Pr. Nil	0.49
4	135	Pr. Nil	0.495
5	180	Pr. Nil	0.485
6	185	Pr. Nil	0.485
7*	90	Pr. Nil	0.60

* After the acid treatment of the catalyst at 50º C.

Table 2

Reduction of uranyl nitrate solution in pilot plant column at room temperature

Feed : Acidity 1.125 M, Hydrazine = 0.99 M, Uranium = 113.3 g/l.
Volume of feed = 5 litres.

Time (Min)	U(IV) (g/l)	% Reduction	Acidity (M)	Hydrazine (M)
60	20.80	18.3	1.10	0.98
120	36.06	31.7	1.05	0.92
180	66.64	58.5	0.87	0.83
240	99.64	87.4	0.69	0.66
300	107.80	94.7	0.62	0.60

Table 3

Batch operation of the column at room temperature

Feed : Acidity 1.125 M, Hydrazine = 0.99 M, Volume of each batch = 5 litres.

Batch No.	U(IV) (g/l)	U(IV) (g/l)	% Reduction	Time (Min)
1	113.3	108.89	95.22	300
2	113.9	107.81	94.65	300
3	114.4	108.4	94.76	300
4	115.2	109.01	94.46	300
5	115.3	108.58	94.17	300

Table 4

Reduction of uranyl nitrate solution in pilot plant column at 60º C

Feed : Acidity 0.99 M, Hydrazine = 0.99 M, Uranium = 176.0 g/l.
Volume of feed = 10 litres.

Time (Min)	U(IV) (g/l)	% Reduction	Acidity (M)	Hydrazine (M)
135	100.61	57.16	0.45	0.83
180	135.78	77.15	0.35	0.68
240	161.42	91.71	0.13	0.58
300	174.30	99.03	0.06	0.54

Table 5

Batch operation of the column at 60º C

Feed : Acidity 1.58 M, Hydrazine = 1.12 M, Volume of each batch = 10 litres.

Batch No.	U(VI) (g/l)	U(IV) (g/l)	% Reduction	Time (Min)
1	180.30	165.23	91.64	320
2	188.02	169.03	90.17	320
3	193.00	175.04	90.69	374
4	193.16	176.7	91.47	380

Table 6

Continuous operation of the column at 60º C

Feed : Acidity 0.85 M, Hydrazine = 0.9 M, Solution level in the column = 5 litres.

Time (Min)	Flow rate (ltrs/hr)	U(IV) (g/l)	% Reduction	Acidity (M)	Hydrazine (M)
122		176.5	87.8	Pr. Neutral	0.01
147	5				
202	5	134.3	66.5	0.2	0.4
230	4	139.6	69.1	Pr. Neutral	
275	4	151.7	75.1		
305	3	151.5	75.0		
335	3	169.6	84.0		
395	3	180.8	89.5		0.6
425	3	180.4	89.3		
455	3	181.0	89.6		
500	3	185.5	91.8	Pr. Neutral	0.7
560	3	199.1	98.6		
620	3	199.0	98.5		
680	3	199.1	98.5	Pr. Neutral	0.7

Fig 1 : Reductor for laboratory scale studies
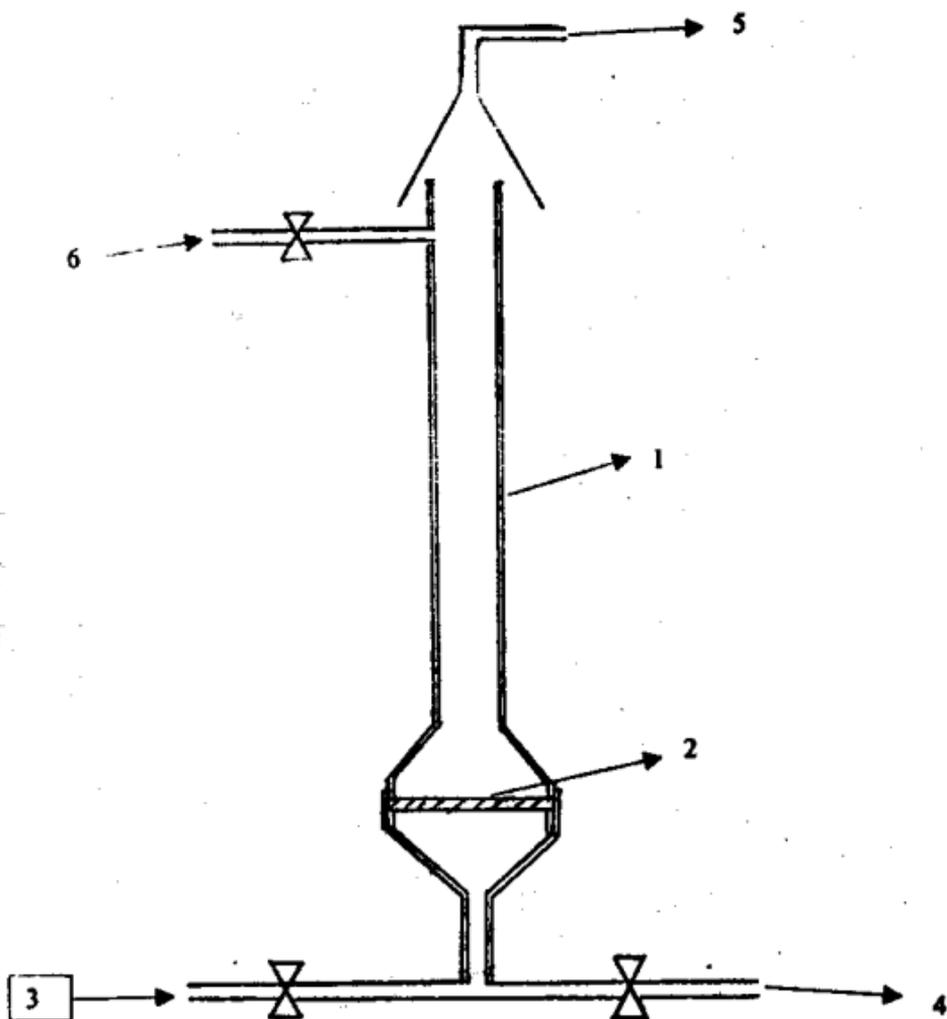
1.SS column, 2.SS sintered filter disc, 3. H_2 gas inlet, 4. Solution outlet,

5. To ejector, 6. Ar gas inlet

Fig 2 : Effect of feed acidity on uranyl ion reduction
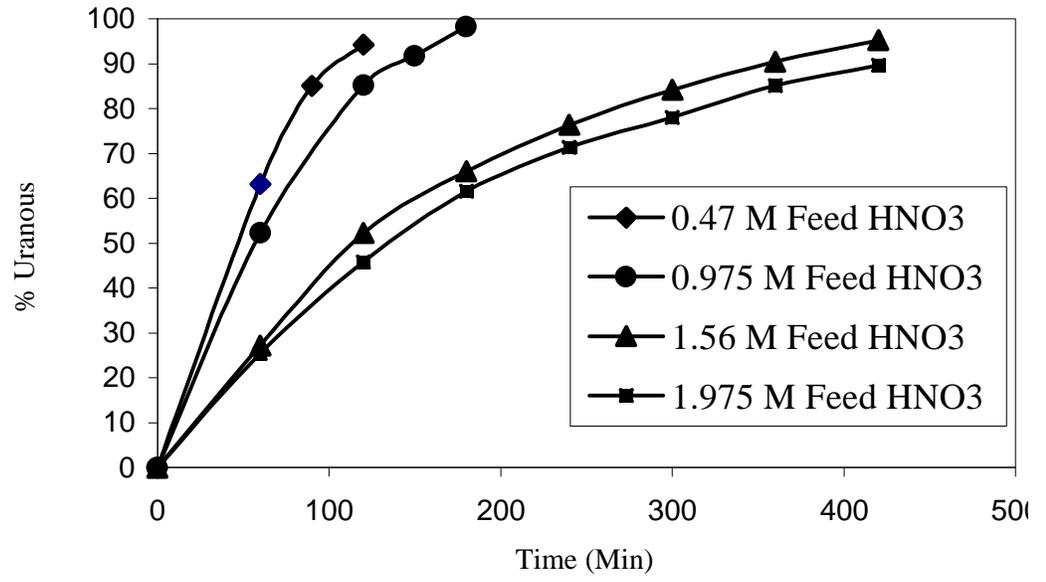
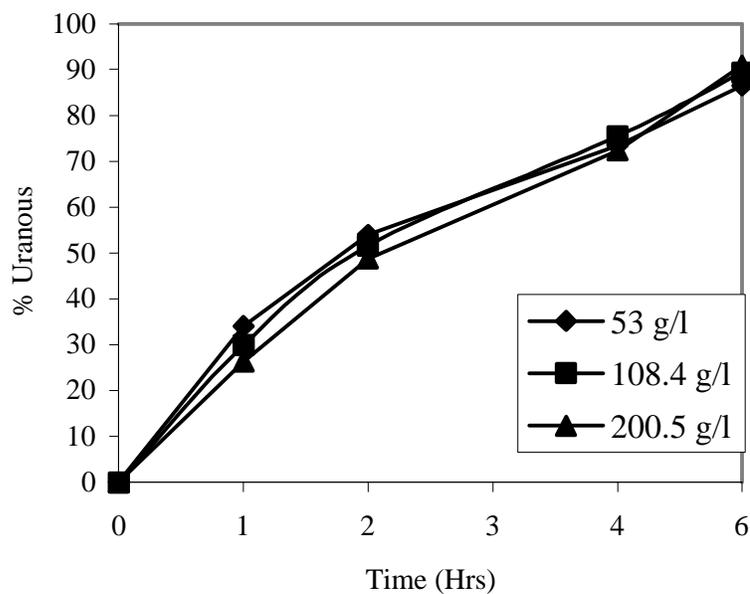**Fig 3 : Variation of acidity during the reduction of uranyl ion at different fee acidities**
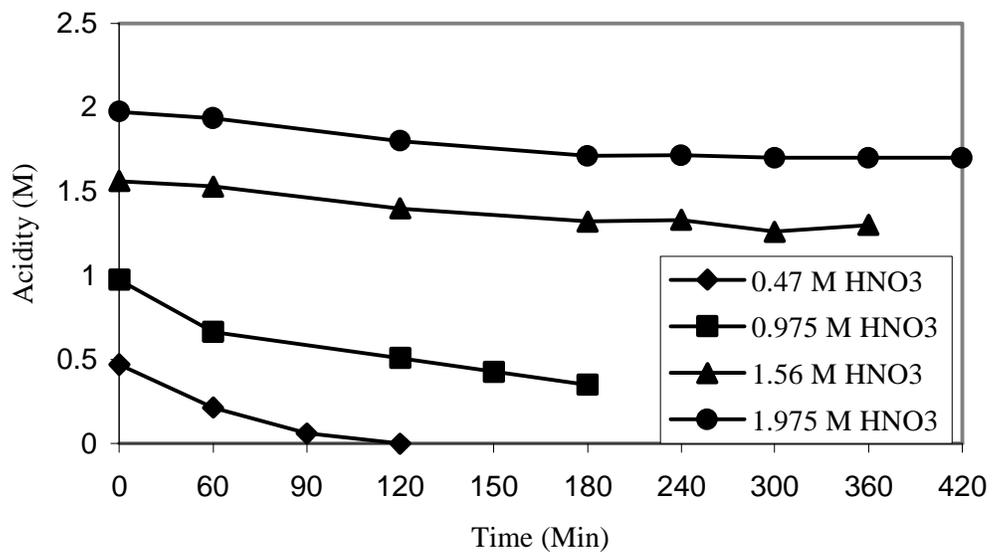
Fig 4 : Variation of hydrazine concentration on the reduction of uranyl nitrate at different H_2 gas flow rates
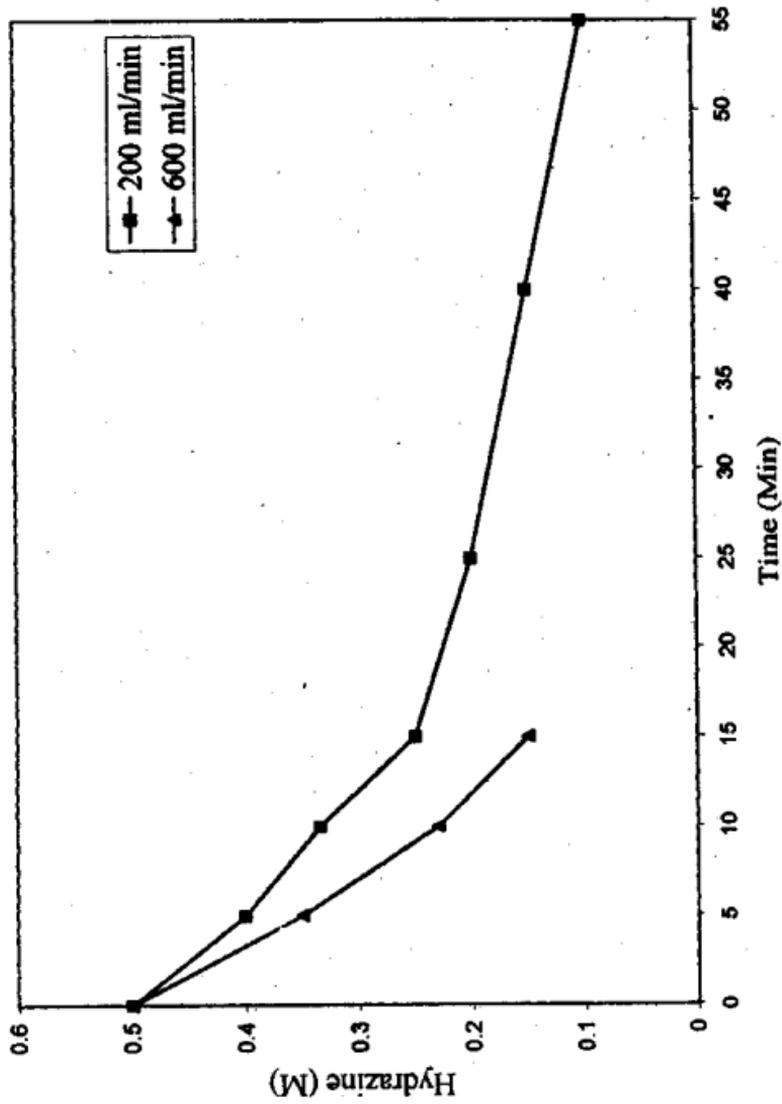
Fig 5 : Effect of hydrazine concentration on uranyl ion reduction
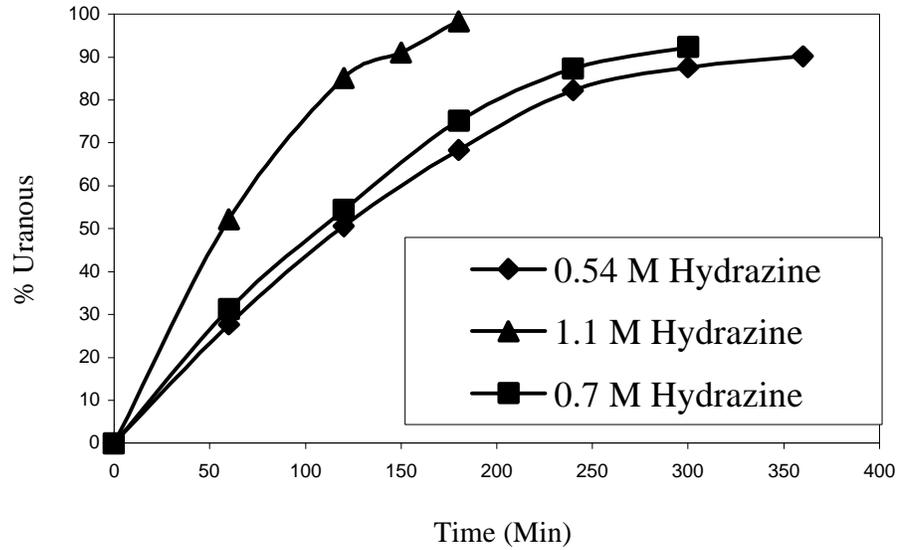
Fig 6 : Variation of acidity in the reduction of uranyl ion at different feed hydraz concentrations
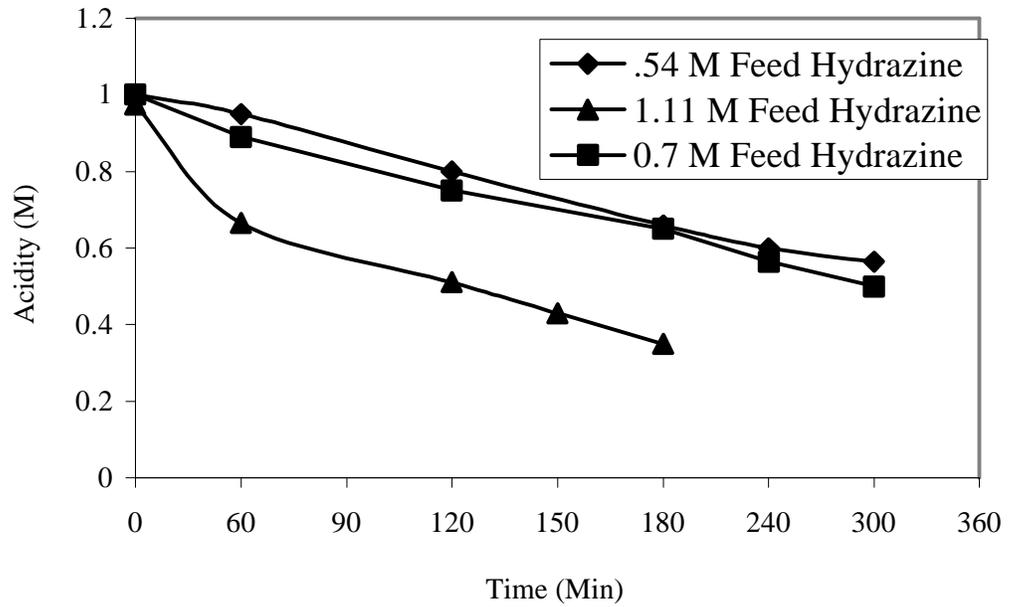
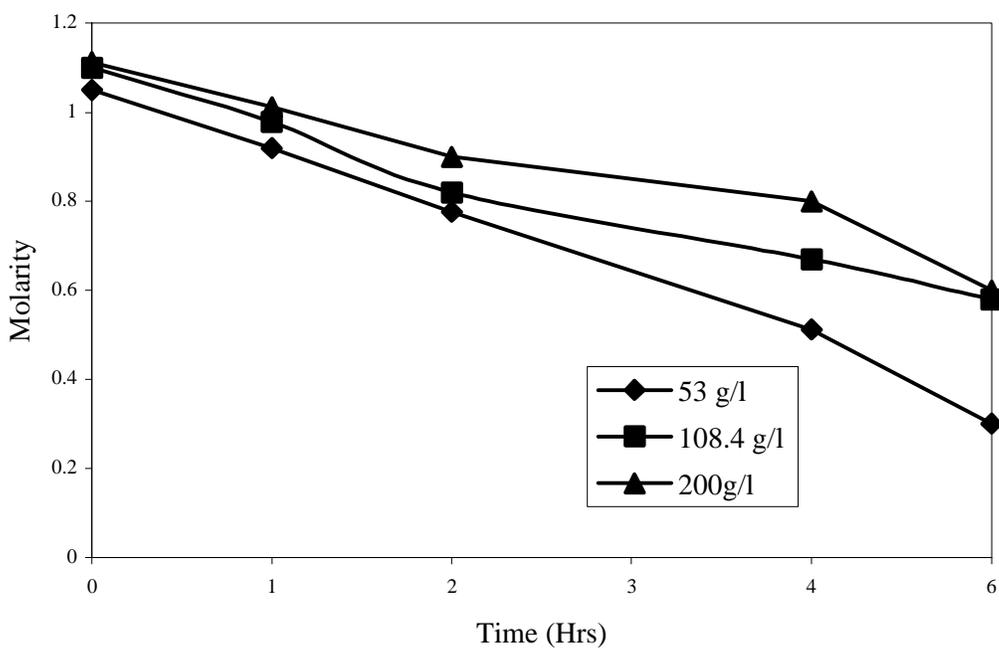**Fig 7 : Variation of hydrazine concentration in the reduction of uranyl ion at different feed hydrazine concentrations**
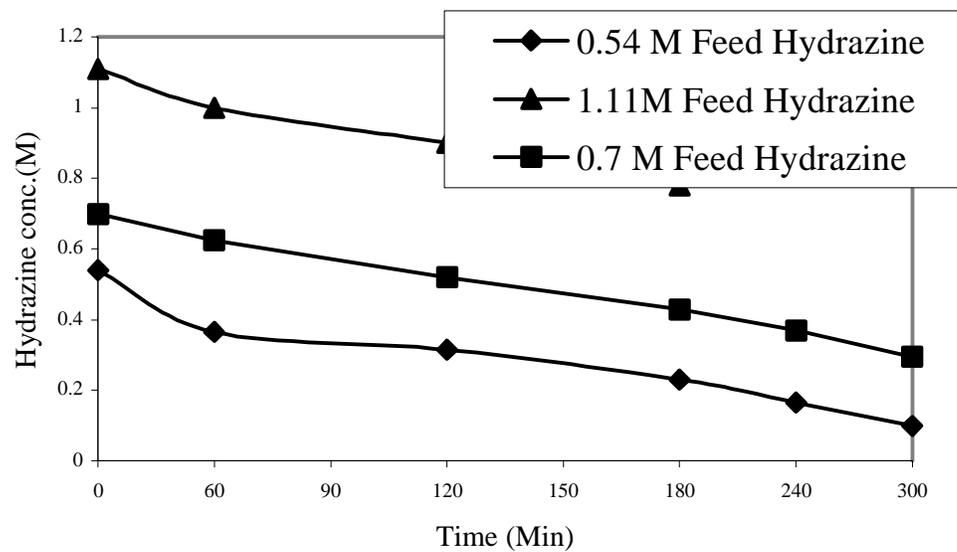
Fig 8 : Effect of temperature on the reduction of uranyl ion
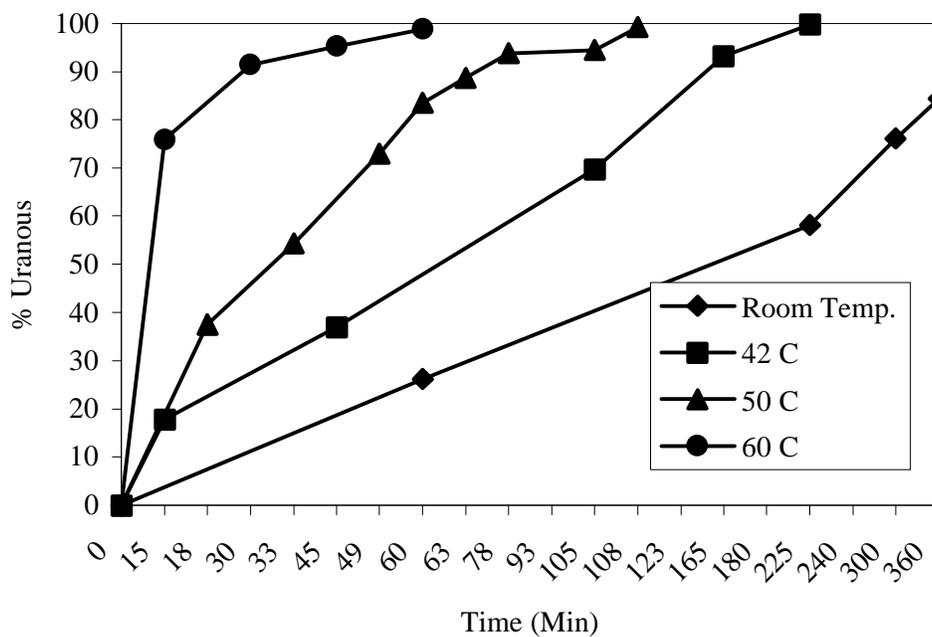
Fig 9 : Variation of acidity during the reduction of uranyl ion at different temperatures
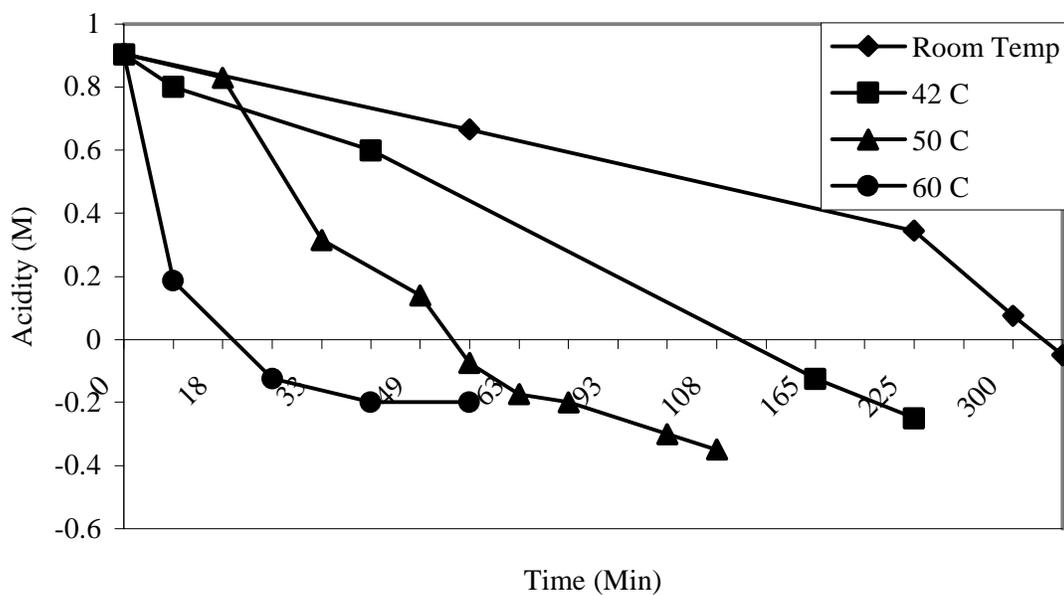
Fig 10 : Variation of hydrazine concentration during the reduction of uranyl nit at different temperatures
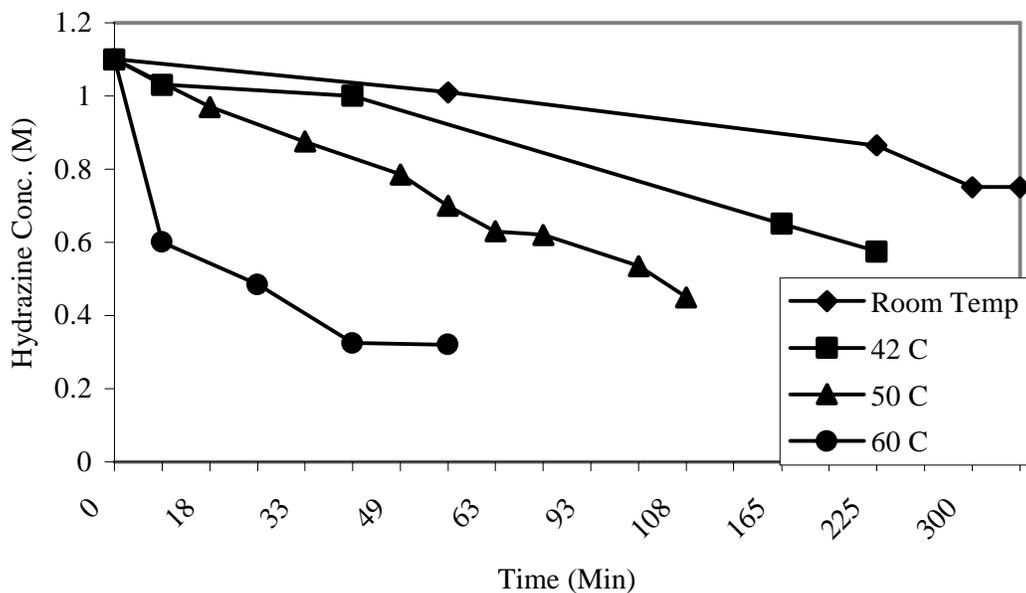
Fig 11 : Effect of feed uranyl nitrate concentration on uranyl ion reduction

**Fig 12 : Variation of acidity during the reduction of uranyl ion at different fee
uranyl nitrate concentrations**

**Fig 13: Variation of hydrazine concentration during the reduction of uranyl nit
at different feed uranyl nitrate concentrations**

Fig 14 : Effect of the amount of the catalyst on the reduction of uranyl nitrate
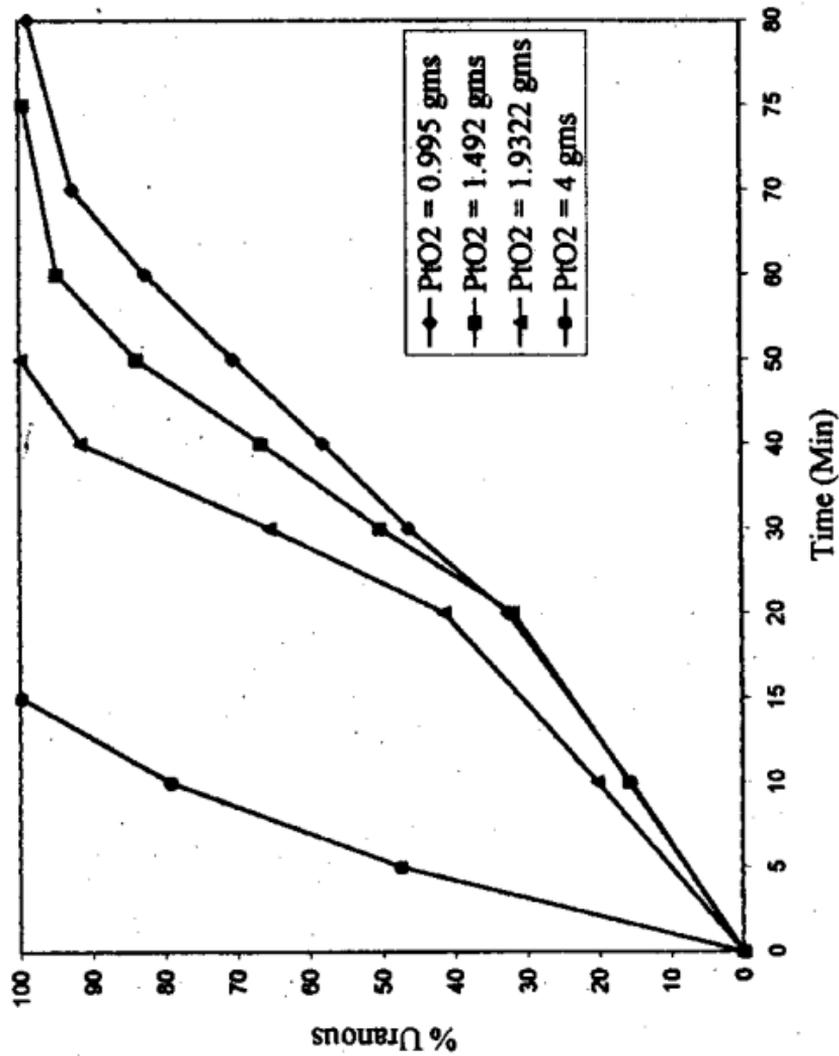
Fig 15 : Variation of acidity during the reduction of uranyl nitrate with H_2 gas at different catalyst amounts

Legend:
- PtO_2 = 0.995 gms
- PtO_2 = 1.492 gms
- PtO_2 = 1.9322 gms
- 4.0 gms

X-axis: Time (Min)
Y-axis: Molarity
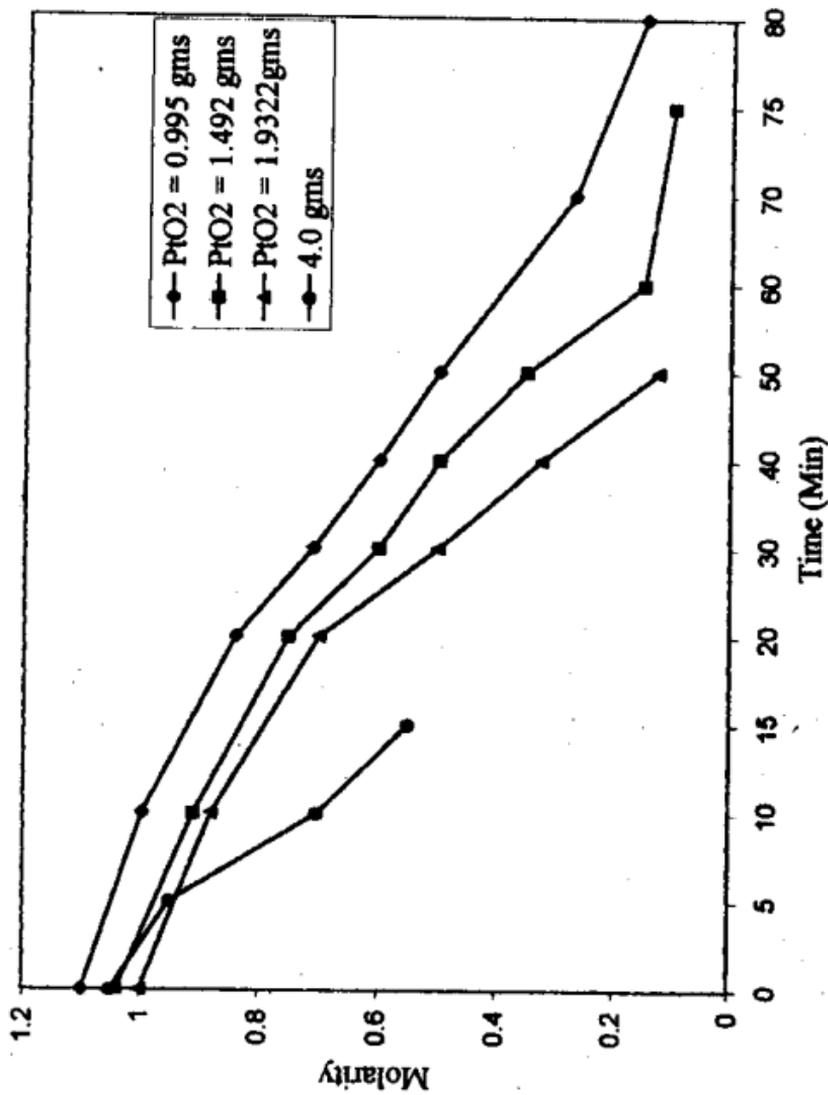
Fig 16 : Variation of hydrazine concentration during reduction of uranyl nitrate with H_2 gas at different amounts of catalyst
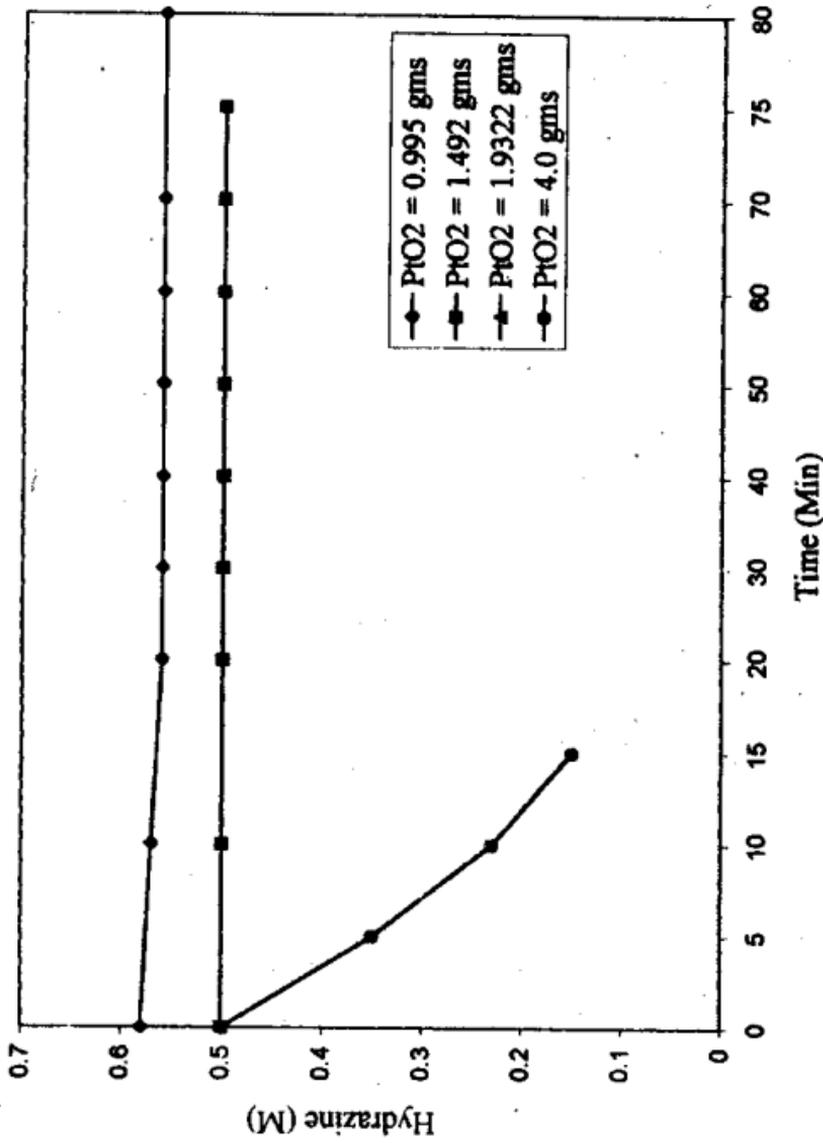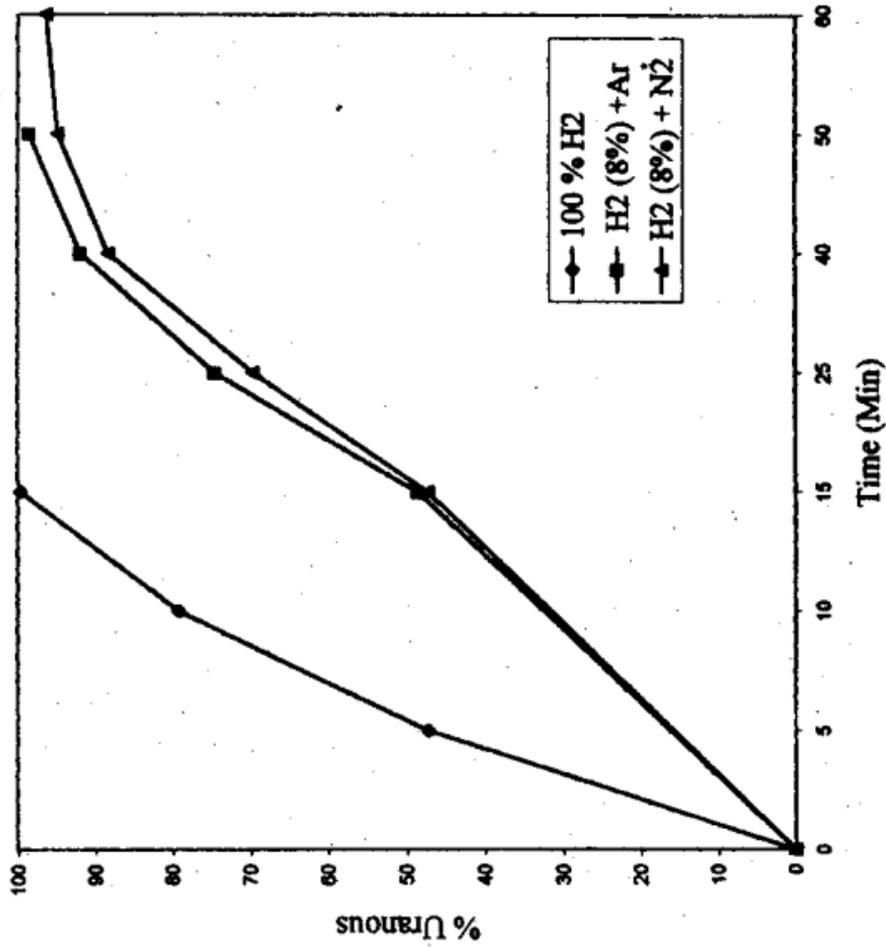
Legend:
- PtO2 = 0.995 gms
- PtO2 = 1.492 gms
- PtO2 = 1.9322 gms
- PtO2 = 4.0 gms

Y-axis: Hydrazine (M)
X-axis: Time (Min)

Fig 17 : Reduction with H₂ gas mixtures

Legend:
- 100 % H2
- H2 (8%) + Ar
- H2 (8%) + N2

X-axis: Time (Min)
Y-axis: % Uranous

Fig 18 : Variation of acidity during the reduction of uranyl nitrate with H₂ gas mixtures
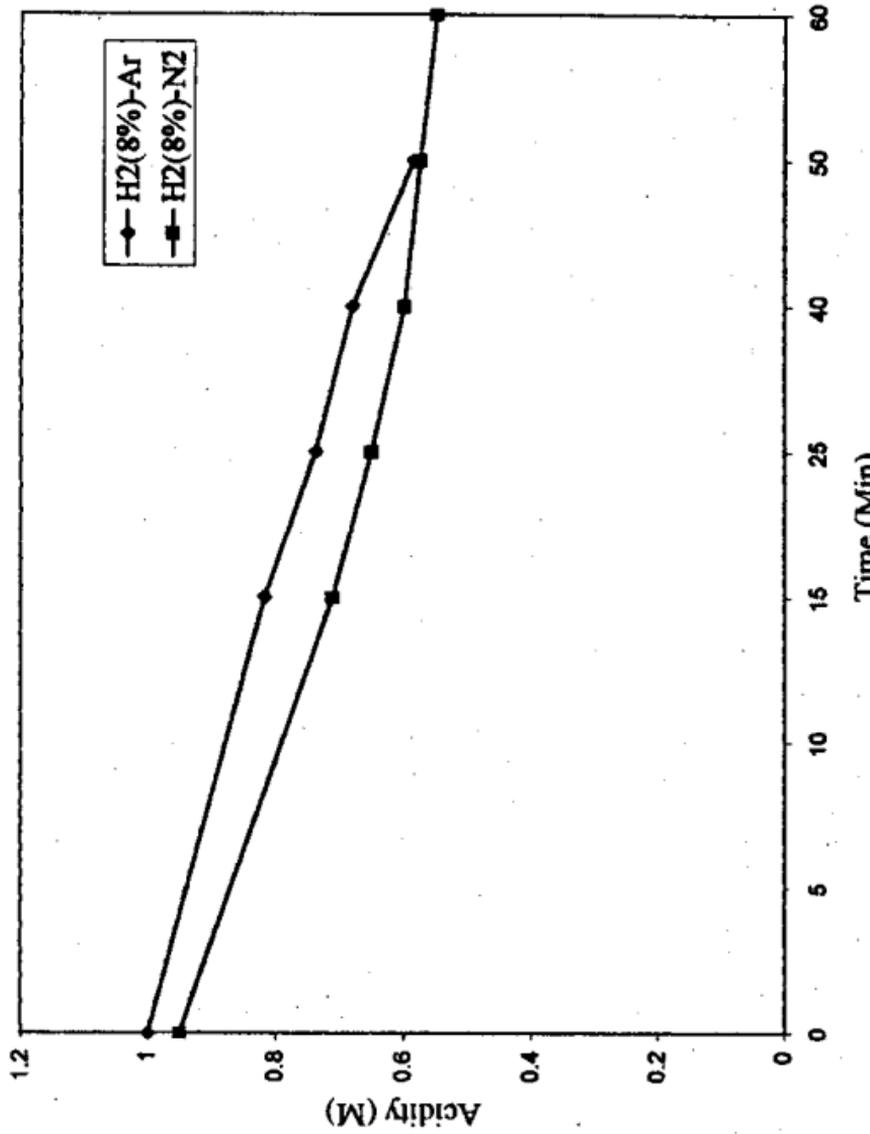
Fig 19 : Variation of hydrazine concentration during the reduction of uranyl nitrate with H_2 gas mixtures
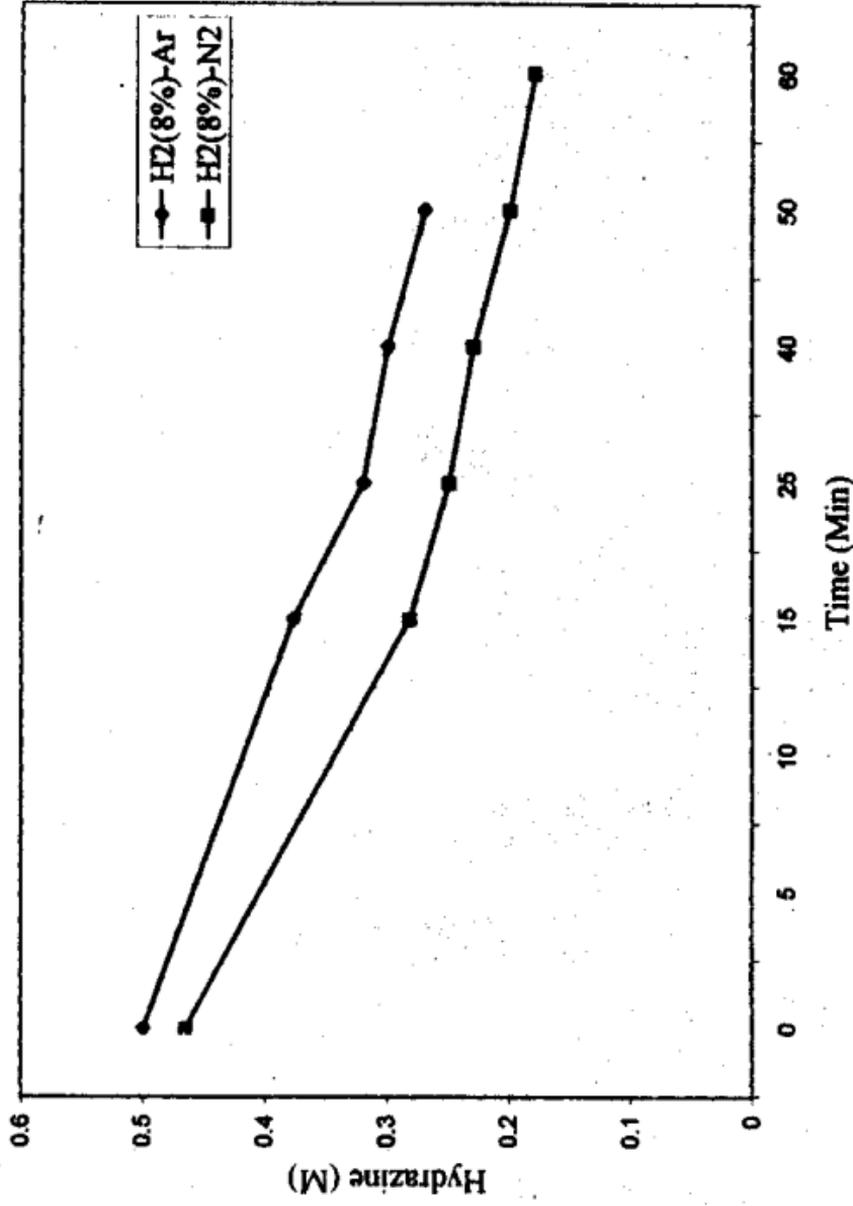
Legend:
- H2(8%)-Ar
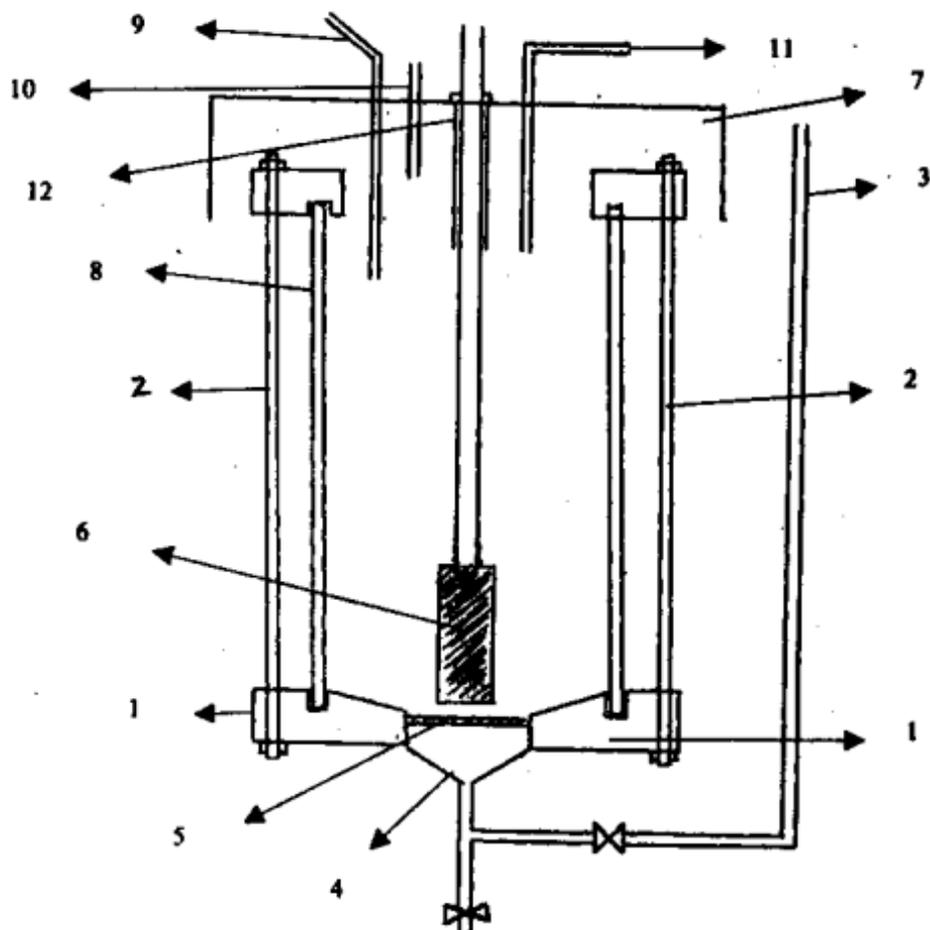- H2(8%)-N2

X-axis: Time (Min)
Y-axis: Hydrazine (M)

Fig 20 : Sketch of the reductor column used in pilot plant scale studies

1.HDPE flanges, 2.Fastening rods, 3.H₂ gas inlet, 4.SS conical cup

5.Filter disc (G-4). 6. SS cartridge filter, 7. SS crown, 8.Glass column

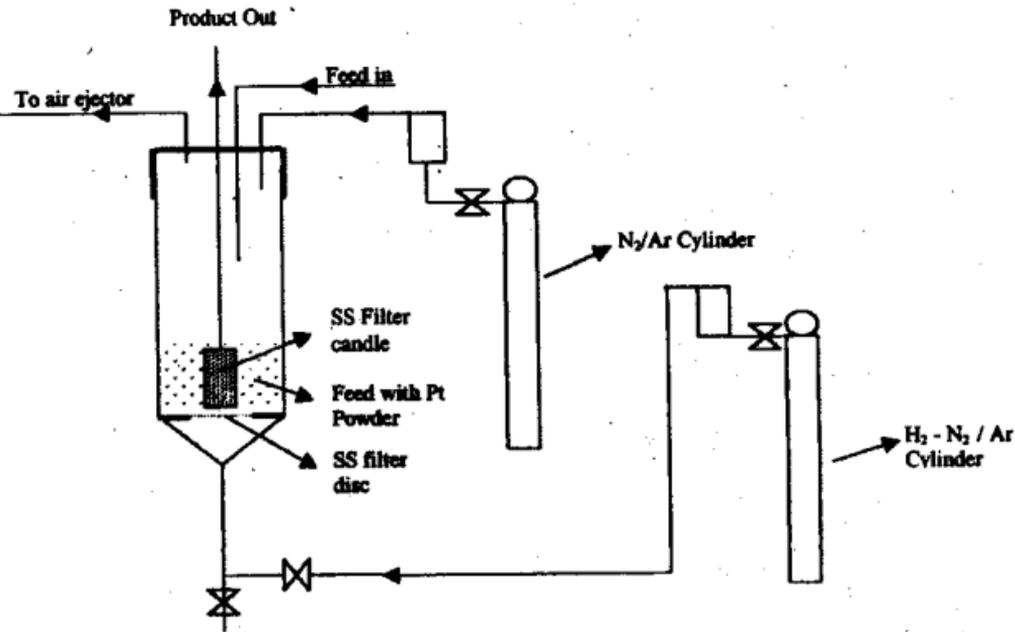9.Feed inlet, 10.N₂/Ar gas inlet, 11.Vacuum inlet, 12. Opening for filter system

Fig 21: Flowsheet for the production of uranous nitrate

Fig 22 : Pilot plant studies