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Reduction of uranium (VI to IV) by hydrogenation using Adams' catalyst

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ABSTRACT

Plutonium uranium reduction extraction using U(IV) as universal reductant for Pu partitioning is the only technology practiced internationally to recover U and Pu from spent nuclear fuels. Uranous requirement of Indian reprocessing plants is met by the electrolytic reduction of uranyl nitrate with 50–60% conversion. Though the current requirement can be met with this method, it increases the load on uranium purification cycle. In addition, it is a batch process with slow kinetics. In order to achieve higher conversion of uranyl nitrate to uranous nitrate, catalytic reduction method using hydrogen in presence of Adams' catalyst (PtO_2) was tried. Parametric studies have been performed in an autoclave to evaluate the effect of U(VI) concentration, the role of hydrazine nitrate and pressure. It is observed that kinetics is improved at higher pressures. The studies revealed that near total conversion of uranium from (VI to IV) can be achieved by the catalytic reduction route.

Keywords: Uranyl nitrate; Adams' catalyst; Hydrogenation; Uranous; Reduction

1. Introduction

Reprocessing flow sheet-based on plutonium uranium reduction extraction process essentially involves dissolution of used nuclear fuels followed by solvent extraction cycles. The first extraction cycle, comprises of co-decontamination and U/Pu partitioning. Partitioning involves the selective stripping of Pu from U. This is accomplished by the reduction of extractable Pu(IV) to the non-extractable Pu(III) oxidation state. Among the various reducing agents, U(IV) is most widely accepted and employed. In Indian reprocessing plants, uranous nitrate [U(IV)] is produced externally by conventional electrolytic reduction of U(VI) using titanium substrate insoluble anode with hydrazine nitrate as uranous nitrate stabilizer. Hydrazine nitrate scavenges the nitrous acid generated by autocatalytic decomposition of nitric acid and prevents the re-oxidation of U(IV) to U(VI) [1]. Limited conversion of 50–60% leading to increase in uranium processing load is the major drawback of the existing electrolytic route. Other limitations includes poor kinetics, frequent recoating of electrode and secondary waste generation during decontamination of anode. Use of cation exchange membrane to separate catholyte from anolyte could enhance percent conversion. However, developing the membrane

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indigenously for higher throughput appears to be a difficult task.

In order to achieve higher conversion of uranyl nitrate to uranous nitrate, catalytic reduction method using hydrazine was tried. In addition to its role as U(IV) stabilizer, it also acts as a chemical reductant and reduces U(VI) to U(IV) in the presence of Pt as follows [2]:

$$UO_2^{2+} + 0.5N_2H_5^+ + 1.5H^+ \xrightarrow{Pt} U^{4+} + 0.5N_2 + 2H_2O$$

Laboratory scale studies for the conversion of uranyl nitrate to uranous nitrate using hydrazine as reductant was carried out in the presence of finely divided PtO_2 (Adams' catalyst) [3]. Bench scale studies have been performed with 2 wt.% platinum loaded on alumina balls using hydrazine as reductant [4]. Near total conversion could be achieved with catalytic reduction using hydrazine. Use of hydrogen as reductant in place of hydrazine, enhances the reaction rate and make the process amenable for continuous production of U(IV). Laboratory scale studies on uranyl nitrate reduction using dilute hydrogen gas as at a pressure of 2 kg/cm^2 in presence of Adams' catalyst were reported [5] in a reductor made of SS-304L.

A reduction process with 99.9% hydrogen in presence of Adams' catalyst has been developed for the reduction of uranyl nitrate.

The reduction reaction of U(VI) by hydrogen [6] is as follows:

$$UO_2(NO_3)_2 + H_2 + 2HNO_3 \xrightarrow{Pt} U(NO_3)_4 + 2H_2O$$

Most of the experiments have been carried out using combination of hydrogen and hydrazine.

2. Experimental setup

2.1. Apparatus

Reduction studies of U(VI) to U(IV) have been carried out in an autoclave designed for a maximum pressure of 120 kg/cm^2. The operating volume of the reactor vessel is 1.5 L. A cooling coil is provided inside the reactor to remove the heat generated during the reaction. It is also provided with a thermowell & RTD to monitor the temperature during the progress of reaction, which is then displayed by the digital indicator. The reactor has a stirrer, magnetically coupled with a rotating pulley. The stirrer is provided with two impellers, one at the bottom and the other one at the middle of the stirrer shaft. Pressure inside the reactor is indicated by a glycerin-filled analog pressure gauge. Reactor is provided with two inlet connections for the reactants which reach up to the reactor bottom and one outlet connection for the gas. Bottom drain is also provided to withdraw the samples online or to drain out the liquid. All lines are of ¼′′ size made of stainless steel. The photograph of the system is given in Fig. 1.

Since the experiments involve the use of hydrogen, which is explosive in nature, precautions have always been taken to see that hydrogen is always accompanied with an inert gas so that during depressurization or release, dilution of hydrogen gas is ensured to avoid the H_2 concentration reaching the explosive limits.

2.2. Chemicals

Experiments have been carried out with PtO_2 (Adams' catalyst) (M/S. Arora Matthey Ltd., Kolkata, India). Electron microscope (SEM) image was taken to know the average size of Adams' catalyst and is shown in Fig. 2.

U_3O_8 was supplied by Uranium Extraction Division, Bhabha Atomic Research Centre, India. Nitric acid used for dissolution was of analytical grade.

2.3. Procedure adopted for hydrogenation studies

A stock solution of uranyl nitrate solution was prepared by dissolving U_3O_8 (natural) in concentrated nitric acid. From the stock solution, feed solution containing 100 g/L of uranium with varying free acidity and hydrazine have been prepared after adding required volumes of hydrazine nitrate and distilled water and used for experimental runs.

Pretreatment of the catalyst particles with nitric acid was found to be mandatory to activate the

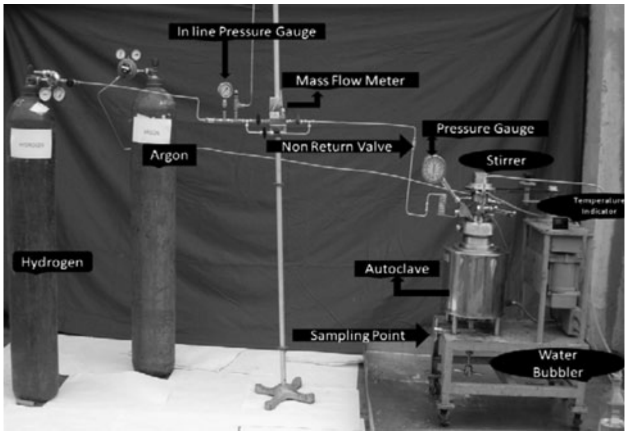

Fig. 1. Experimental set-up for catalytic hydrogenation studies.

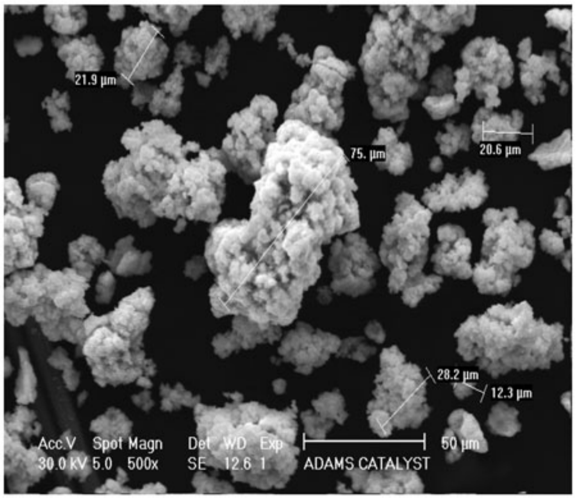

Fig. 2. SEM image of Adams' catalyst.

reaction sites. Accordingly, catalyst powder was pretreated prior to each experimental run. After charging the reactor with required volume of feed solution and catalyst quantity, lines are purged with argon. Argon supply line is then closed and hydrogen gas is passed through the reactor for 2–3 min to carry away the inert gas from the reactor. After closing the gas outlet line, desired pressure is built-up by operating the ball valve in the hydrogen line. Agitator is kept on. The samples withdrawn at regular intervals are analysed till quantitative conversion is achieved. After the run, hydrogen regulators are properly closed. Electric supply is switched off. Then the product solution is drained out and the reactor vessel is washed to avoid its pitting and corrosion.

In order to evaluate the performance of the reduction process, solution samples were analysed for total uranium concentration, uranous nitrate concentration, free acidity and hydrazine concentration. Modified Davis–Gray method and redox titration with standard potassium dichromate were used for total uranium and uranous analyses, respectively [7,8]. The accuracy and precision of these methods is within ± 0.2% and total error is within ±1%. Free acidity and hydrazine concentration were analysed by titration with standard alkali [9].

3. Hydrogenation studies with 3.34% hydrogen

Experiments were done on one litre scale with 3.34% H_2 (rest-N_2) gas at a pressure of 2 kg/cm^2 under agitated condition for uranyl nitrate solution having U: 102 g/L, free acidity of 0.97 and 0.77 M hydrazine with catalyst to uranium (C/U) ratio of 1:5 and the reduction progress in terms of percent reduction, acidity and hydrazine are summarized in Table 1.

Poor kinetics was observed during the reduction. Even after 4 h, merely 65% conversion could be obtained.

3.1. Effect of pressure

Since the conversion is only 60%, after 4 h at a pressure of 2 kg/cm^2, set of experiments were conducted by varying the pressure up to 35 kg/cm^2 to improve the kinetics for the above feed conditions and the effect of pressure on conversion is shown in Fig. 3. It is observed that percent conversion increases with pressure and near total conversion was achieved after 210 min of reaction time at a pressure of 33 kg/cm^2.

3.2. Effect of hydrazine nitrate concentration

In the conventional electrolytic route, hydrazine is added in the feed stream to maintain the valency state of uranous nitrate by suppressing the autocatalytic decomposition of nitric acid. In order to investigate role of hydrazine in catalytic reduction process, various runs were carried out at 33 kg/cm^2 for conversion of U(VI) to U(IV) with uranyl nitrate solution having uranium concentration of 101 g/L, acidity of 1.05 M and C:U ratio of 1:10 by changing the hydrazine concentration in the range 0–0.75 M under agitated condition. Reduction performance is depicted in Fig. 4.

Without hydrazine, conversion of U(VI) to U(IV) using 3.34% hydrogen was found to be difficult. It is clear from Fig. 4 that for hydrazine concentration in the range of 0.25–0.6 M, the reduction trend remains almost same but above 0.6 M hydrazine, better kinetics is observed. It is envisaged that in catalytic reduction process, hydrazine acts as reductant in addition to its role as nitric acid scavenger.

Table 1
Variation of percent reduction, acidity and hydrazine with time using 3.34% hydrogen at 2 kg/cm^2

Time (min)	% Conversion	Acidity (M)	Hydrazine (M)
0	0	1.25	0.77
30	11.2	1.21	0.71
60	23.8	1.2	0.68
90	34.0	1.17	0.60
120	41.2	1.14	0.54
150	47.8	1.13	0.46
180	52.9	1.1	0.39
210	60.1	1.09	0.32
240	65.0	1.09	0.28

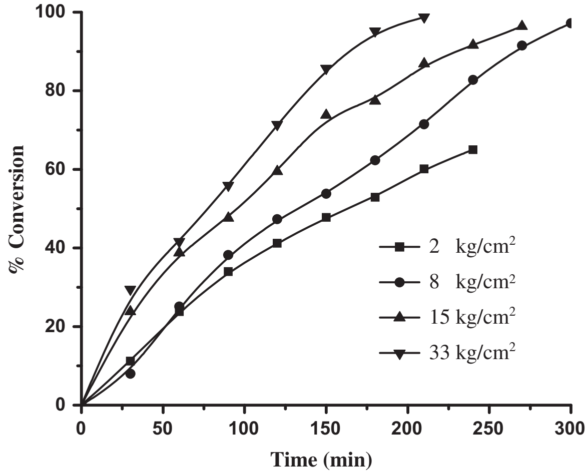

Fig. 3. Effect of pressure using 3.34% hydrogen for reduction of uranyl nitrate solution having U: 102 g/L, free acidity: 0.97 M and hydrazine: 0.77 M with a catalyst to U ratio of 1:5 under agitated condition.

4. Hydrogenation studies with 99.9% hydrogen

With an aim to enhance the reduction rate, experiments were performed at moderate pressures with hydrazine and 99.9% hydrogen. By maintaining a C:U ratio of 1:10, reduction of the feed solution containing U: 101 g/L, free acidity of 1.05 and 0.76 M hydrazine has been studied for pressures 15 and 33 kg/cm^2 under agitation. Behaviour is represented in Fig. 5.

Time required for quantitative conversion has been reduced drastically with 99.9% hydrogen under agitated condition even at a lower C:U ratio of 1:10, as compared to that required with 3.34% hydrogen at C:U ratio of 1:5.

Using 99.9% hydrogen at 33 kg/cm^2, uranyl nitrate solution with U: 101 g/L and 1.15 M acidity (Fig. 6), reduction process has been carried out with 0.75 M hydrazine nitrate and without hydrazine nitrate by maintaining C:U ratio of 1:10 under agitated condition.

Without hydrazine, initially the reduction rate was very low. But after 70 min duration, the rate is enhanced. It could be attributed to autocatalytic behaviour of U(IV). With hydrazine, near total conversion was obtained in 40 min.

4.1. *Effect of uranium concentration*

To investigate the behaviour of reduction by varying the concentration of uranium, runs have been carried out with 99.9% H_2 at 33 kg/cm^2. Uranyl nitrate solution (acidity 1.05 M and hydrazine concentration of 0.75 M) with a C:U ratio of 1:10 was used as the feed. Percent conversion is compared in Fig. 7. It is observed that under similar conditions, the reduction rate is reduced with U(VI) concentration due to the lower acidity of feed solution.

4.2. *Hydrogenation studies at higher pressures*

By maintaining the parameters U: 108.3 g/L, H^+: 1.1 M and hydrazine: 0.76 M and C/U = 1:10 constant, catalytic hydrogenation of uranyl nitrate solution was carried out using 99.9% H_2 at 45, 60 and 70 kg/cm^2.

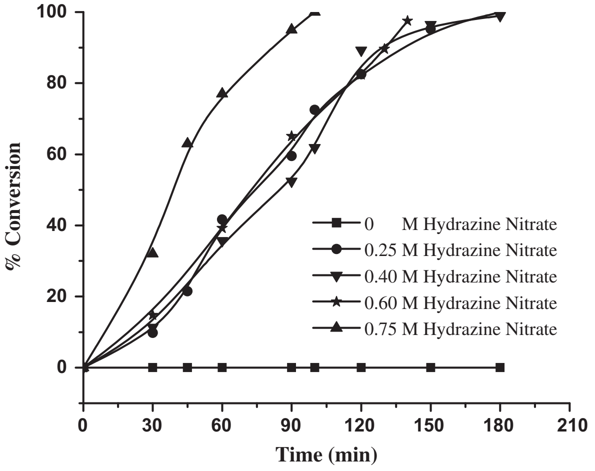

Fig. 4. Effect of hydrazine nitrate concentration using 3.34% hydrogen at 33 kg/cm^2 for reduction of uranyl nitrate solution having U: 101 g/L, acidity: 1.05 M and a catalyst to U ratio: 1:10 under agitated condition.

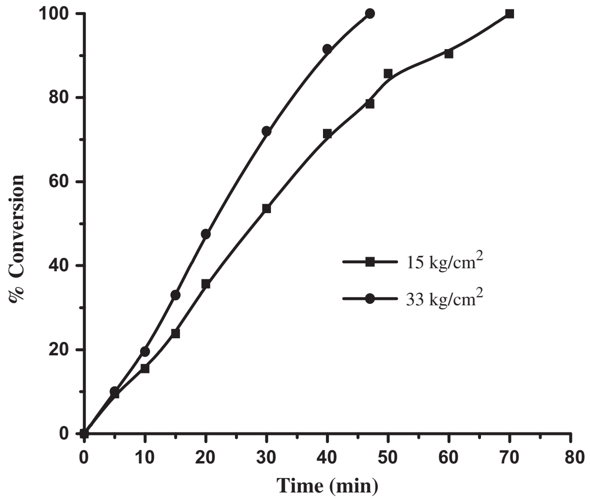

Fig. 5. Effect of pressure using 99.9% hydrogen for reduction of uranyl nitrate solution containing U: 101 g/L, free acidity: 1.05 M and hydrazine: 0.76 M with catalyst to U ratio of 1:10 under agitated condition.

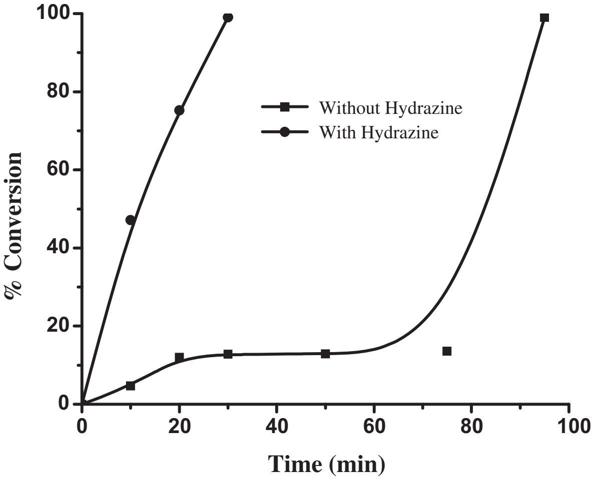

Fig. 6. Plot of percent conversion vs. time obtained with & without hydrazine using 99.9% hydrogen at 33 kg/cm^2 for reduction of feed solution having U: 101 g/L and acidity: 1.15 M.

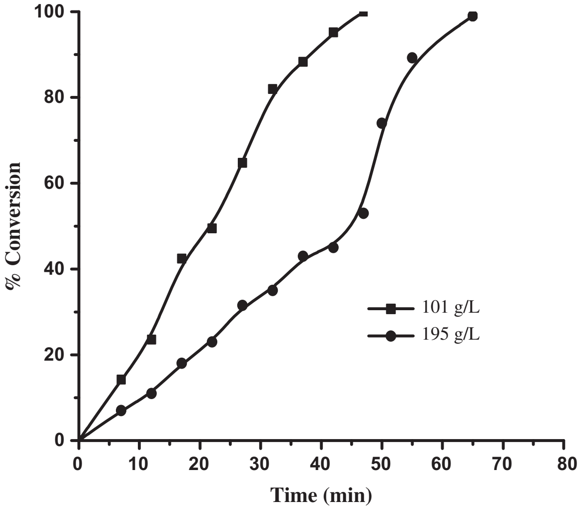

Fig. 7. Conversion trend with 99.9% hydrogen at 33 kg/cm^2 for reduction of feed solution having U: 101 and 195 g/L, acidity: 1.05 M and hydrazine concentration of 0.75 M with a C:U ratio of 1:10 under agitated condition.

Details of the performance are given in Figs. 8–10, respectively.

It is seen from Figs. 8–10 that the rate of conversion to U(IV), increases with increase in pressure and >99.99% conversion is achieved in 10 min at a pressure of 70 kg/cm^2. This could be attributed to the higher solubility of hydrogen at higher pressures. Acid and hydrazine consumption was found to more at 45 kg/cm^2. Temperature of the solution was raised from 31 to 71.2˚C when the pressure was set at 45 kg/cm^2. At pressures 60 and 70 kg/cm^2, temperature rise of around 20˚C was noticed.

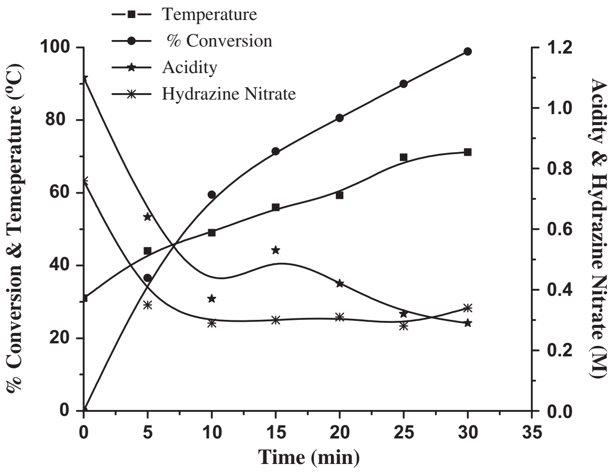

Fig. 8. Variation of percent conversion, temperature, acidity and hydrazine nitrate concentration with time at 45 kg/cm^2 using 99.99% hydrogen.

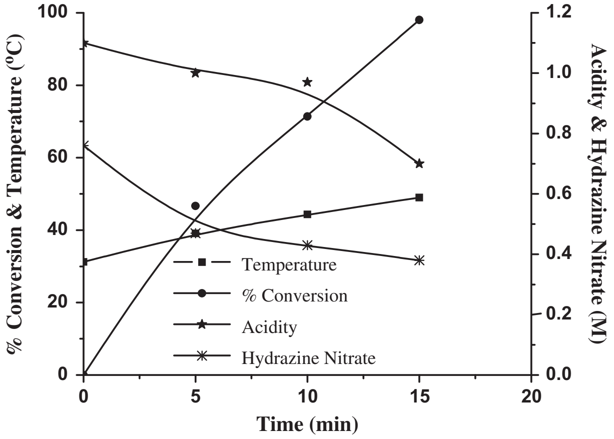

Fig. 9. Plot of percent conversion, temperature, acidity and hydrazine nitrate concentration with time at 60 kg/cm^2 using 99.99% hydrogen.

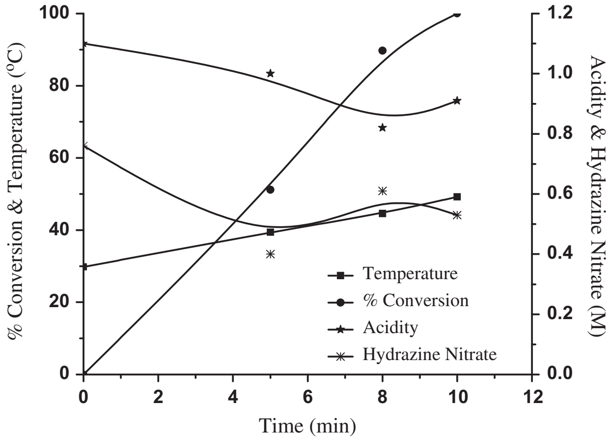

Fig. 10. Variation of percent conversion, temperature, acidity & hydrazine nitrate concentration with time at 70 kg/cm^2 using 99.99% hydrogen.

5. Conclusions

Studies conducted in the pressure range of 2–70 kg/cm^2 reveals that the reduction kinetics of U(VI) to U(IV) enhances with the increase in pressure and with the addition of hydrazine. Due to the fast kinetics in presence of catalyst, use of hydrogen and hydrazine together as reductants enhances the reaction rate and makes the process amenable for continuous production of U(IV). It has been confirmed that uranyl nitrate solution having 195 g/L of U(VI) can be subjected to hydrogen–hydrazine-based reduction process. Catalytic hydrogenation process is established on bench scale for near total conversion of U(VI) to U(IV).

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