

COGEMA Experience in Uranous Nitrate Preparation

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ABSTRACT

Separation and purification of plutonium by PUREX process is based on a sequence of extraction and back extraction which requires reducing plutonium Pu IV (extractable form) into Pu III (inextractable form)

Different reducers can be used to reduce Pu IV into Pu III.

Early plants such as that for Magnox fuel at Sellafield used ferrous sulfamate while UP1 at Marcoule used uranous sulfamate. These reducers are efficient and easy to prepare but generates ferric and/or sulphate ions and so complicates management of the wastes from the plutonium purification cycle.

Recent plants such as UP3 & UP2 800 at La Hague, THORP at Sellafield, and RRP at Rokkasho Mura (currently under tests) use uranous nitrate (U IV) stabilized by hydrazinium nitrate ($N_2H_5NO_3$) and hydroxyl ammonium nitrate (HAN).

In the French plants, uranous nitrate is used in U-Pu separation and alpha barrier and HAN is used in Pu purification.

Compared to sulfamate, U IV does not generate extraneous chemical species and uranyl nitrate (U VI) generated by reducing Pu IV follows the main uranium stream. More over uranous nitrate is prepared from reprocessed purified uranyl nitrate taken at the outlet of the reprocessing plant.

Hydrazine and HAN offer the advantage to be salt-free reagents.

Uranous nitrate can be generated either by electrolysis or by catalytic hydrogenation process.

Electrolytic process has been implemented in early plant UP1 at Marcoule (when changing reducer from uranous sulfamate to uranous nitrate) and was used again in UP2 plant at La Hague.

However, the electrolytic process presented several disadvantages such as a low conversion rate and problems associated with the use of mercury. Electrolysis cells with no mercury were

developed for the Eurochemic plant in Belgium and then implemented in the first Japanese reprocessing plant in Tokai-Mura.

But finally, in 1975, the electrolytic process was abandoned in favor of the catalytic hydrogenation process developed at La Hague. The yield of the operation and its simplicity were the main reasons for this choice. Nowadays, our catalytic hydrogenation process is used in all the commercial reprocessing plants worldwide: THORP at Sellafield, UP3 & UP2 800 at La Hague, and RRP at Rokkasho-Mura.

In this process, uranyl nitrate is reduced to uranous nitrate by hydrogen in presence of a platinum based catalyst. Most of the plants implement the reaction in the same kind of reactor: "co-current, up-flow and fixed-bed reactor".

For UP2 800 at La Hague, started in 1994, a new kind of reactor allowing a higher capacity has been developed. In this reactor, the catalyst bed is not fixed but circulating (fluidized bed).

The aim of the paper is to describe both reactor technology implemented in La Hague (fixed bed and fluidized bed), to show their performance in terms of capacity and yield and to compare their operating and maintenance principles.

INTRODUCTION

HLW vitrification

In the modern reprocessing plants, the PUREX process is used to recover uranium and plutonium from spent nuclear fuels. This process is based on solvent extraction, TriButyl Phosphate being used as an extractant. Uranium and plutonium are decontaminated from fission products and separated one from the other by means of a series of extraction and back-extraction operations. TBP being a neutral extractant, a negative counter ion is required to allow extraction of metallic cations. Nitrate complexes have proved to be suitable for this purpose. This applies to the extractable U (VI) and Pu (IV).

Plutonium/uranium separation and plutonium purification are based on the reductive stripping of plutonium: Pu (IV) present in the organic phase is stripped by contact with a reducing agent: Pu (IV) being reduced to the almost inextractable valence III is back-washed to the aqueous phase.

Pu valence control in the PUREX process

At the inlet of the extraction cycles, Plutonium is adjusted to the extractable valence IV by contact with nitrous ions. In the back-extraction operation, plutonium has to be reduced to the inextractable valence III. The reducer has to be combined with a stabilizer to prevent plutonium from being re-oxidized.

Several reducer/stabilizer pairs have been used: early plants such as the Magnox plant at Sellafield used ferrous sulfamate while UP1 at Marcoule used uranous sulfate. Ferrous and uranous ions are efficient reducers of plutonium (IV) and the sulfamate ion is an excellent stabilizer thanks to its strong anti-nitrous power. However, these reagents introduce non volatile species in the process, *i.e.* ferric and/or sulfate ions, that make the liquid waste management more complicated especially from the corrosion point of view.

In modern reprocessing plants, salt-free processes, *i.e.* processes that do not introduce new ions or waste other than water and gases in the radioactive streams are favored, in order to limit the volume of waste. For the reduction of plutonium, this led to the use of uranous nitrate or hydroxylamine nitrate, both stabilized by hydrazine nitrate. Uranous nitrate produces uranyl nitrate as waste, while hydroxylamine and hydrazine nitrate produce water and gases like nitrogen and N_2O .

Uranous nitrate is more efficient with rather diluted plutonium stream with fairly high acid content (typically U/Pu Partition), while hydroxylamine nitrate is best with low acid, concentrated plutonium stream (typically plutonium purification cycles). Thanks to its extractability, uranous nitrate is able to displace plutonium from any complexes with the solvent degradation products and hence to remove final traces of plutonium from unloaded solvent. This operation is commonly called plutonium barrier.

Early in the operation of UP1, the waste problem was identified and an attempt to solve it was performed by testing the electrochemical reduction of uranyl nitrate on a mercury electrode. This technique provided uranous nitrate to the plant, with two drawbacks: the presence of unwanted mercury and large amounts of uranyl nitrate in the solution of uranous nitrate, because of the limited efficiency of electrolysis process.

Electrochemical production of uranous nitrate was improved at Eurochemic plant by development of mercury free process. This equipment is also used in the first Japanese reprocessing plant at Tokai-Mura, designed by SGN. In the mid seventies, the first UP2 plant at La Hague shifted to an other process to prepare its uranous nitrate: catalytic reduction of uranyl nitrate by hydrogen, according to the chemical background described in [1]. Recent plants such as UP3 and UP2-800 at La Hague, THORP at Sellafield and RRP at Rokkasho-Mura (currently under tests) use uranous nitrate (U IV) prepared with the same process of catalytic reduction with addition of hydrazine nitrate ($N_2H_5NO_3$) as a stabilizer.

In La Hague plants as well as in Rokkasho Mura plant, the uranyl nitrate used to prepare the uranous nitrate is drawn from the main stream of decontaminated uranium at the outlet of the plant.

Uranous nitrate production in the present reprocessing plants

Chemical bases of the process

The reaction of reduction of U(VI) by Hydrogen is the following one:



The rate of this reaction increases with the pressure of Hydrogen and with the area of catalyst. Therefore, in industrial conditions, hydrogen is used at fairly high pressures (typically about 40 atm.) and the platinum is deposited on silica grains, in order to meet both high catalytic activity with good hydraulic properties of the bed of catalyst.

The effect of temperature and nitric acid are less simple.

The rate of the reaction increases with temperature, but it cannot be operated at temperatures significantly higher than room temperature, as at high temperature an other reaction occurs, the catalytic reduction of nitric acid by hydrogen, according to:



On the one hand, the nitrous acid evolves nitrous fumes that are adsorbed on the catalyst and poison it irreversibly: clearly this must be avoided at all cost, as if it occurs, the catalyst must be replaced.

On the other hand, the reaction (1) evolves a significant amount of heat and the reactor must be cooled: the start-up of a reactor must be performed carefully, in order to effectively start the reaction (1), without heating it too much to prevent the reaction (2) and (3) to occur.

The effect of nitric acid also is not simple. It must be noted that the reaction (1) consumes 2 moles of nitric acid per mole of uranium. On the one hand therefore, to avoid the unwanted hydrolysis of U(IV), the initial concentration of nitric must be equal or higher than twice the molar concentration of uranium plus about 0.5 mol/L.

On the other hand, high concentrations of nitric acid favors the reaction (2), so that the initial acidity must be limited.

As a result, there is a practical higher limit to the concentration of U(IV) that can be performed in industrial condition, about 200 g/L.

Description of the uranous nitrate preparation unit

An uranous nitrate preparation unit is composed of few pieces of equipment :

- The reactor fitted with the uranyl nitrate and hydrogen feedrate controllers and with the cooling device,

- A high pressure separator to separate the uranous nitrate solution from the hydrogen excess,
- A low pressure separator fed with nitrogen to remove the dissolved hydrogen from the liquid product. The hydrazine nitrate solution, the stabilizer is added to the product at this stage to avoid any re-oxidation of the uranous nitrate.
- A vent scrubber and a filter on the off-gas line to prevent traces of uranium from being released to the atmosphere.

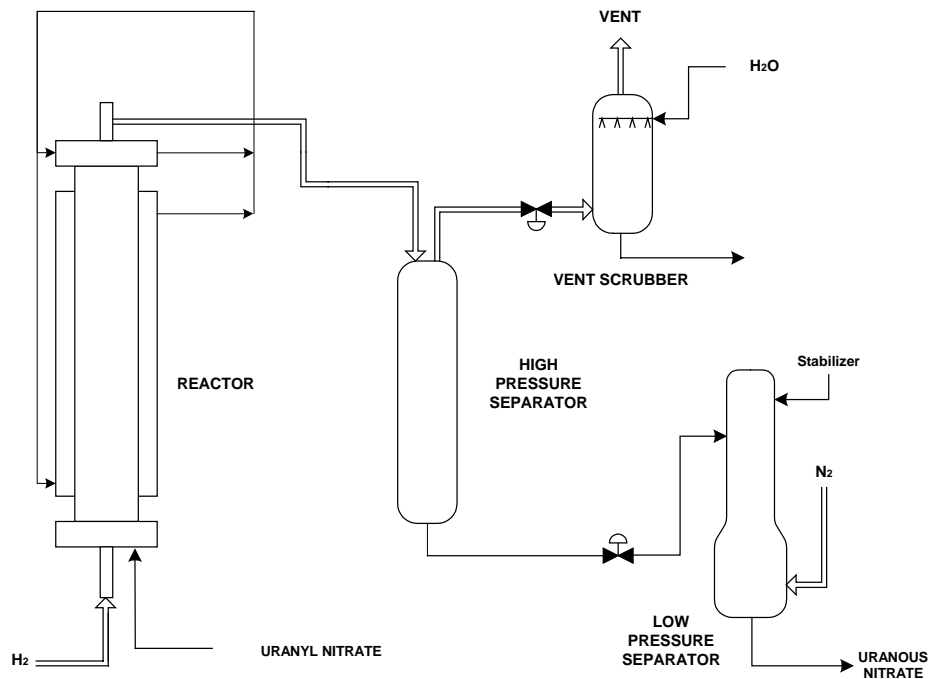


Fig. 1. Principle diagram of an uranous nitrate preparation unit

Two types of reactors have been used in La Hague:

- in the first one, hydrogen and uranium flow from the bottom to the top of the reactor and the catalyst bed is packed at the top part.
- in the second one, the catalyst particles are maintained in suspension in the liquid phase. This suspension is circulated in a loop inside the reactor, hydrogen acting as the driving gas of this circulation.

The first type was used for the first time in UP2 plant at La Hague and was replicated for UP3, THORP and RRP. The second type was installed in the new plutonium purification facility of UP2-800 plant, R4 started in active operation in 2002.

Provided that the start-up procedure is carefully applied, both of these reactors are quite easy to operate. From 1975 up to now no operating trouble has ever been recorded in the three units operated on La Hague side.

Fixed catalyst bed reactor

This type of reactor is composed of a 1.7 meter high and 15 centimeter diameter cylindrical shaft fitted with an external cooling jacket and an internal cooling pin fed with chilled water. About 6 liters of catalyst are introduced in the annular space around the cooling pin. Hydrogen and uranyl nitrate are fed at the bottom of the reactor through sintered stainless steel filters. When the reagents flow upwards in the reactor, the catalyst bed is packed and blocked at the top by a sintered stainless steel plate.

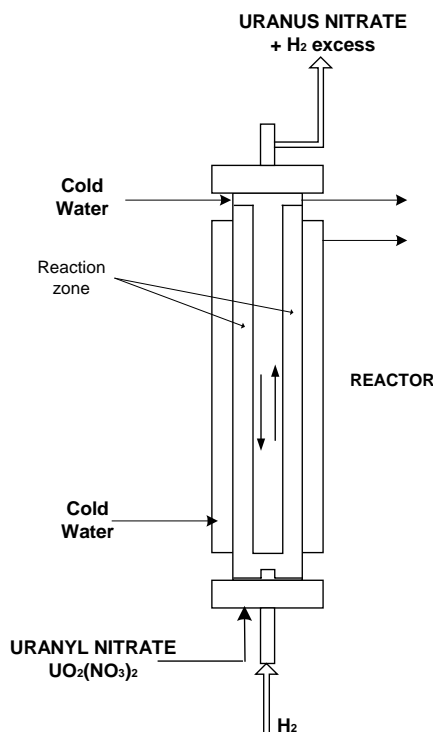


Fig. 2. Simplified drawing of the Fixed catalyst bed reactor

This reactor is able to prepare more than 400 kg of tetravalent uranium per day with a reaction yield (U VI to U IV conversion rate) higher than 96 %. Its main advantages are then its high efficiency and its compactness. It has also some drawbacks related to the maintenance needs:

- The catalyst particles undergo a progressive mechanical wear due to the liquid circulation through the catalyst bed. This kind of attrition of the catalyst grains has no influence on the reaction yield but the pressure drop of the catalyst bed increases regularly and the catalyst has to be changed periodically. In UP 3 the catalyst is usually changed once a year during the summer inter-campaign. The service life of a catalyst load corresponds to more than 2000 operating hours.
- The top sintered stainless steel plate which is in permanent contact with the catalyst bed is subject to corrosion and has to be replaced preventively every 350 operating hours. A galvanic coupling phenomenon between the fine platinum particles and the sintered metal is suspected.

Thanks to the very low activity of the recovered uranium used as the inlet product, these maintenance operations do not raise any radiological problem but they are time consuming especially because tightness of the unit has to be carefully checked prior re-starting.

Circulating bed catalyst reactor

The circulating bed catalyst reactor is composed of a central riser surrounded by an annular downcomer. Hydrogen is injected in the bottom part of the riser. Circulation of the catalyst suspension is driven by the density difference between the riser and the downcomer. The reactor behaves like a gas-lift. The hydrogen flow rate required to maintain the catalyst in suspension and to circulate the suspension in the reactor being much higher than the amount involved in the reduction reaction, the major part of the hydrogen leaving the reactor is recycled to the feeding nozzle by means of a pump. A filter is installed on the liquid outlet pipe to avoid any entrainment of catalyst with the uranous nitrate. Cooling devices are also installed inside and around the reactor.

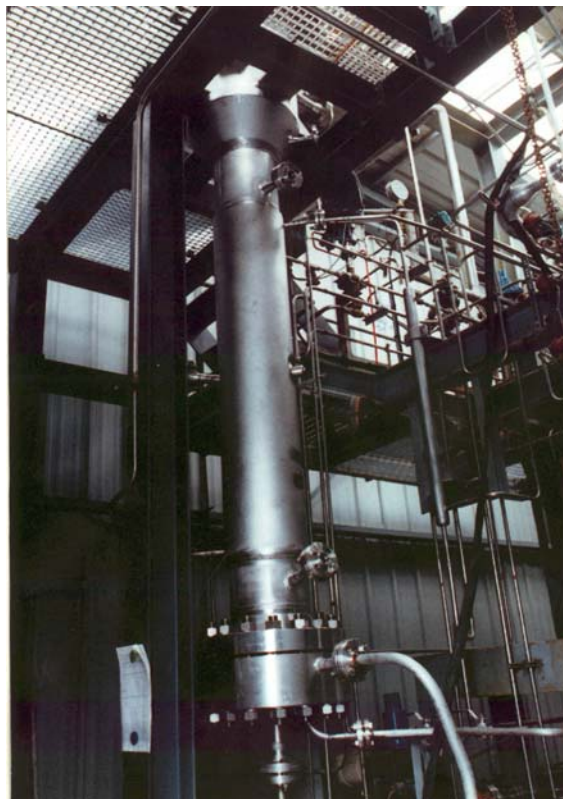


Fig. 3 Circulating bed catalyst reactor (pilot facility)

Its design throughput is 500 kgU/d with same reaction yield as obtained with fixed catalyst bed reactor.

In addition to its high capacity, the main advantage of this new reactor is that the maintenance needs are far lower compared with the fixed catalyst bed reactor:

- as the catalyst is in suspension in the liquid phase, there is no permanent contact between the catalyst and a metallic wall and up to now, no corrosion has been observed on this reactor.

Production at low capacity

Some tests have been performed recently to produce uranous nitrate at very low capacity using a continuous electrolysis cell. Results are quite positive, and a further development could be envisaged if necessary.

CONCLUSION

Uranous nitrate combined with hydrazine rapidly appeared to be the best reducer/stabiliser couple for the uranium/plutonium partition and the plutonium barrier steps of the PUREX process. COGEMA has gained a long industrial scale experience of uranous nitrate production using the hydrogen reduction. Two types of high efficiency reactors are used.

The first one has been used satisfactorily for more than 30 years. The second one is designed to reduce the maintenance needs and increase catalyst service life. Thanks to this characteristics and its high throughput, it is well adapted to high capacity modern reprocessing plants.

REFERENCE

1. Patent US 6759027: Method and installation for carrying out a three phase chemical reaction under pressure.