

ITALIAN RADWASTES MANAGEMENT: THE OPTIMIZATION OF A CHEMICAL PROCESS FOR THE U+Th BY-PRODUCT TREATMENT AND DISPOSAL

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ABSTRACT

ITREC plant located near the TRISAIA Research Centre, was built in the frame of a collaboration between CNEN and USAEC (United States Atomic Energy Commission) to study the feasibility of U-Th fuel cycle.

In 1975 the reprocessing pilot plant started up the first reprocessing campaign of about 20 fuel element coming from the Elk River Power plant (USA).

About 4 cubic meter of unconditioned liquid wastes were produced by pre-nuclear tests and currently stored on site.

A chemical process based on the precipitation of U+Th by-product by addition of hydrogen peroxide was studied to reduce the liquid wastes in a solid encapsulated form.

The final product is ready to be encapsulated and stored in the National Storage Site.

INTRODUCTION

The process described in this paper is suitable for the treatment of uranium and thorium powder, scraps and pellets recycle during fuel element fabrication as well as liquid wastes coming from pre-nuclear and nuclear tests.

Main process steps are:

- preparation and adjustment of the feed solution,
- precipitation of uranium and thorium peroxide by means of hydrogen peroxide,
- centrifugation of the precipitate
- drying, calcination and reduction of Uranium/Thorium dioxide by means of hydrogen at high temperature.

The main characteristic of this process is that the precipitation takes place in a narrow range of pH thus avoiding the co-precipitation of most of the impurities eventually presented.

PARAMETERS THAT MAY AFFECT PRECIPITATION WITH PEROXIDES

There are some factors that can complicate precipitation, mainly:

- pH of solution
- hydrogen peroxide concentration

- concentration of ions to precipitate
- possible anions interference
- possible cations interference

pH of solution

Quantitative precipitation comes out in a pH range between 1 and 3, considering the presence of certain hydrogen peroxide excess.

We can contemplate that at higher pH values, salts between Uranium and hydroxide, as well as between Thorium and hydroxide can form, and they could release great quantity of ions in solution.

Hydrogen peroxide concentration

An excess of 0.3-0.5 M as to that required by the balanced equation is enough for a complete reaction and a good reaction rate.

A further excess of 0.002 M is moreover sufficient to avoid the peroxide product re-dissolution .

Ions concentration in the solution.

Uranium and Thorium ions concentrations must be not lesser than 1% in weight for a good precipitation.

If concentration were below this value, a previous concentration step has to be foreseen.

Ions interference

- **Anions**

Some anions interference with a complete precipitation.

The effect increases going through acetates, chlorides, sulphates and fluorides.

Sulphate effect is lower if magnesium ion is present, while fluoride effect could be undo by addiction of an equimolar concentration of aluminium nitrate. Nitrates cause a little effect.

- **Cations**

Some cations affect hardly the precipitation.

Some of them give interference by forming mixed salt with uranium and thorium (especially at high pH values), while other cations catalyse the decomposition of hydrogen peroxide.

Fe³⁺ is very effective, especially if it is present at valuable concentrations. We can minimise its effect by including a Fe precipitation step, or a malonic acid addiction, or performing the precipitation with peroxides at low temperature (20° C).

Also Cobalt, Manganese and Cerium can strongly catalyse hydrogen peroxide decomposition if in alkaline solution. Alkaline and alkaline-earth metals can also slow down the reaction rate, while other metals, such as Zinc, Cadmium, Nickel, Aluminium, Chrome and Copper don't affect the reaction.

There is also a possible hydrogen peroxide decomposition due to temporary alkaline pH gradients forming inside the reactor. To obviate this difficulty, reaction can be performed without any ammonia addition.

Although pH decrease, reaction will still be quantitative with a sufficient hydrogen peroxide addition.

CHEMICAL COMPOSITION OF NUCLEAR WASTES

About five cubic meters of unconditioned liquid wastes are currently stored.

The total amount of Thorium and Natural Uranium is respectively 286 and 34 kilograms with a nitric acidity of 2-3 M.

Probably other inorganic ions coming from analytical and process tests as well as some little quantities of organic compounds arising from solvent extraction tests are dissolved in the wastes, too.

EXPERIMENTAL

The uranyl nitrate solution as well as thorium nitrate solutions were prepared using distilled water.

The sodium hydroxide and the hydrogen peroxide were analytical grade reagents.

The standard conditions used for the tests were:

Uranium concentration: 7 g/l
Thorium concentration: 57 g/l
HNO₃ : 2 M

pH was adjusted using a NaOH solution.

In Fig. 1, the increase of pH during the adjustment step is shown.

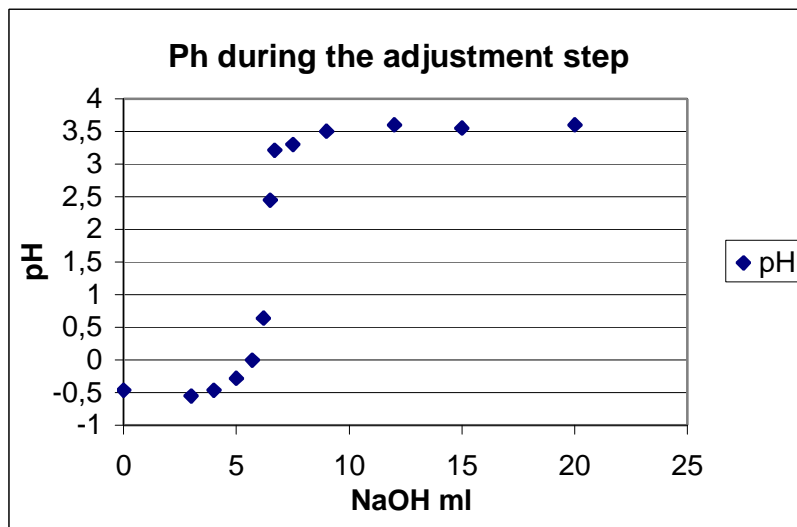
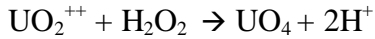


Fig. 1 pH recording during the adjustment step.

Optimum pH value for this step was found 2.8-3.5 and no cooling was necessary.

The reaction took place, under continuous stirring, in the precipitation tank by adding to the adjusted solution the necessary amount of H_2O_2 :



For thorium as final product, the stoichiometry is more complex.

The very probable formula is $Th(OO)_3A^- \cdot 2.5 H_2O$ where A represent the anion.

However, some anions are usually replaced from oxygen so the near true composition is $Th(OO)_3 \cdot 2A_{(0.5)}^-(O^-)_{0.15}$.

Since Hydrogen peroxide is consumed and hydrogen ion liberated the precipitation progress is governed by controlling the addition of H_2O_2 and the acidity of the solution.

If hydrogen peroxide and alkali are added in a molar ratio of 1:2 and the solution is well stirred, the pH is approximately constant until the precipitation is complete.

During the reaction the pH of the solution decrease to about 0.6, see fig.2, requiring a further addition of NaOH to neutralise partially the solution.

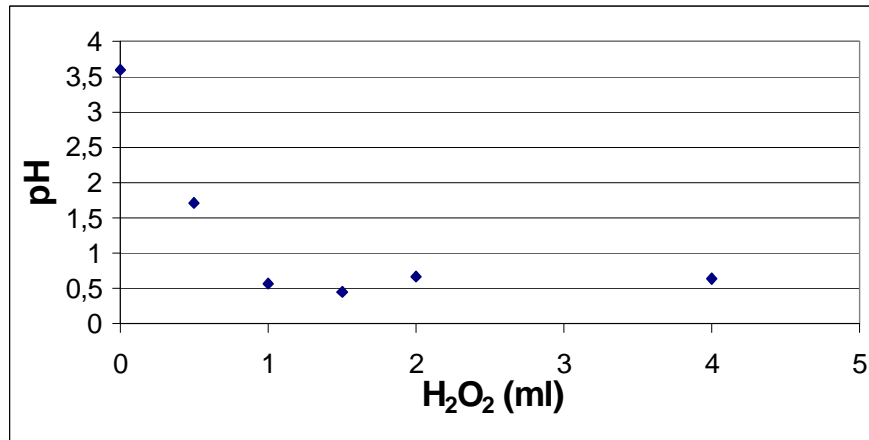


Fig.2 pH recording during the precipitation step

NaOH was added until a value of pH of 1.6 was reached. After that, the control of the pH starts to become less reliable.

So, we had choose another methods , which does not require a strict control of the pH that is to add the stoichiometric quantity of H_2O_2 plus an excess without neutralising the nitric acid produced.

RESULTS

Using the conditions chosen, the amount of Uranium and Thorium in the mother waters, detected from samples taken in the precipitation storage tank, analysed with radiometric and spectrophotometric methods, is of a few p.p.m. and this result was considered acceptable.

This procedure appeared not only extremely flexible but also very reliable as regards the pH regulation system.

FINAL REMARKS

Th and U precipitation's safely work in tested process conditions.

It is necessary to take care of pH value measurement during the process. In fact a change of pH from suitable value can result in serious problems such as incomplete precipitation if acidity product during reaction is not immediately neutralised.

On the other hand, excessive increase in pH, due to wrong or not homogeneous alkali adding, could result to Th hydroxide formation instead of peroxide with relative process problems.

REFERENCES

L.ARCURI, L. PIETRELLI, C.RIZZELLO “ Experience with a Uranyl nitrate—Uranium Dioxide Conversion Pilot Plant” RT/COMB/(84)/9 ENEA (1984).