# Uranium recovery from liquid waste composed of uranyl nitrate solution

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**Abstract**

The object of this study was to find a route for the treatment of uranyl nitrate solutions generated in the decontamination of equipment in a nuclear installation by chemical precipitation. Through experimental planning by central composite rotation design (CCRD) it was possible to optimize the treatment of this solution. The initial concentration of uranium in solution was 13.9 g∙L-1 and after treatment with hydrogen peroxide with a concentration of 200 g∙L-1 with pH adjustment of the solution equal to 1.75 was possible to recover 99.7 % of the uranium present in the initial solution.

## INTRODUCTION

During the operation of a nuclear facility several instruments and equipment may get contaminated. This contamination may be loose or fixed, being a loose contamination easily transferred to other surfaces and the fixed contamination does not [1]. The hazard of a loose contamination is a greater than that of a fixed contamination [2] as it poses as an additional internal contamination threat. To minimize risk, costs, facilitate waste management, and reduce the dose that the employees are exposed a periodical decontamination of the machinery is needed.

For the past 20 years the Brazilian Nuclear Industries (INB – in Portuguese) enrichment, reconversion and fuel manufacturing facility has used diluted nitric acid (HNO3 15 %) as a chemical method to remove loose contamination from equipment throughout the factory.

This acid has been stored in 50 L plastic drums and, in March 2021, have accumulated 3.000 L of a radioactive acid waste that need to be treated to meet the final deposition specifications [3].

Several methods for chemical recovery of the dissolved uranium contained in acid solution have been developed. Some methods, such as ion exchange resins [4] and ionic liquid extraction [5] were developed to concentrate the uranium, considering the enrichment, that may lead to critical concentration and is unadvisable to use.

Alkaline precipitation methods, with calcium hydroxide (Ca(OH)2) [6] or ammonium hydroxide (NH4OH) are highly efficient to remove the uranium, but they lead to a product that are not suitable to use in INB manufacturing process. An adequate route to treat this solution and recover the uranium is through a uranium peroxide precipitation seen in **Eq. 1** [7].

$UO\_{2}^{2+}+H\_{2}O→UO\_{2}\left(O\_{2}\right).xH\_{2}O+2H^{+}$ **Eq. 1**

This work aims to optimize the uranium recovery using a Central Composite Rotational Design (CCRD) considering pH, reaction time and hydrogen peroxide mass as study factors.

## Experimental

### Instrumentation

A PerkinElmer Optima 2100 DV ICP-OES was used for quantitative measurements. Stirring was accomplished by a magnetic stirrer (IKA C-MAG HS 7, Germany). Statistica® version 10.0.228.2 was used for calculations.

### Reagent and chemicals

Hydrogen peroxide 50 % and Ammonium hydroxide 25 % were purchased from Vetec (Brazil) and were used without any further dilution. The waste samples were collected from a 50 L plastic drum labeled as 0615031 at INB’s. Into a 50 mL sample was added the hydrogen peroxide, and mixed for 2 minutes, after that the ammonium hydroxide was added and the stirring was turned off and the solution was put to rest for the designated time. After this step the solution was filtered and analyzed for uranium content.

### Optimization strategy

The study was based on a CCRD with adjusted pH, resting time and hydrogen peroxide added mass as independent variables. The residual uranium concentration was used as dependent variable.

### General procedure

The study was based on a CCRD with adjusted pH, resting time and hydrogen peroxide added mass as independent variables. The residual uranium concentration was used as dependent variable.

## Results and discussion

With the recovery values ​​obtained with the exploratory experiments and with a focus on having the shortest possible time, the lowest expenditure of reagents and, of course, the greatest possible uranium recovery, even with a view to releasing the effluent, a CCRD experiment planning was prepared.

The advantage of applying the design of experiments is the reduction in the number of tests and the need to repeat them, as well as the simultaneous analysis of the variables and evaluation of the experimental error.

 Based on the best uranium recovery values ​​according to the findings in the preliminary tests, it was possible to establish the main variables to be studied, as well as their levels, aiming to find the optimum point to have more uranium removal from the solution aiming at lesser financial expenditure for this.

It is noteworthy that the number of blocks adopted was 1 because it is a small planning, and a total of 16 experiments were carried out, and 15 unique experiments, since the central point was done in duplicate. Independent variables that were shown to have a greater influence on the studied system were inserted in the planning according to the results of the preliminary tests. Table 1 shows the result of the concentration of uranium in uranyl nitrate solution after carrying out the planned experiments using the CCRD elaborated with the Statistica® program. The experiments highlighted in gray, according to Table 1, were the ones that showed the best performance in removing uranium from the solution. Therefore, in this table the time, pH and dosage of hydrogen peroxide were varied.

TABLE 1. RESULTS OF PLANNED EXPERIMENTS WITH CCRD.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Experiment** | **pH** | **Time (hours)** | **Hydrogen peroxide (g∙L-1)** | **Residual concentration of U in the solution (g∙L-1)** |
| 1 |  | 1,00 | 4,0 | 100 | 1,51 |
| 2 |  | 1,00 | 4,0 | 200 | 0,24 |
| 3 |  | 1,00 | 12,0 | 100 | 0,61 |
| 4 |  | 1,00 | 12,0 | 200 | 0,33 |
| 5 |  | 2,50 | 4,0 | 100 | 9,1.10-2 |
| 6 |  | 2,50 | 4,0 | 200 | 4,8.10-2 |
| 7 |  | 2,50 | 12,0 | 100 | 8,4.10-2 |
| 8 |  | 2,50 | 12,0 | 200 | 4,0.10-2 |
| 9 |  | 0,50 | 8,0 | 150 | 0,48 |
| 10 |  | 3,00 | 8,0 | 150 | 2,1.10-2 |
| 11 |  | 1,75 | 1,3 | 150 | 0,28 |
| 12 |  | 1,75 | 14,7 | 150 | 9,4.10-2 |
| 13 |  | 1,75 | 8,0 | 66 | 0,16 |
| 14 |  | 1,75 | 8,0 | 234 | 0,12 |
| 15 C \* | 1,75 | 8,0 | 150 | 3,9.10-2 |
| 16 C\* | 1,75 | 8,0 | 150 | 3,6.10-2 |

\* C - Refers to the central point of the CCRD.

\*\* Used for pH adjustment.

\*\*\* Nitric acid 65 % for pH adjustment - acidification of the solution.

In addition to this high removal obtained that extends the value range of uranium in solution, the difference between predicted and observed values ​​can be attributed to analytical uncertainties, sampling variations and technicians who performed the analyzes, in addition to the instrumental uncertainty inherent in the glassware, pipettes and instrument used to carry out the determination of uranium in solution. In Figure 1 it is possible see the observed vs. predicted values.



FIG 1. *Observed vs. predicted values.*

In Figure 2, it is possible to observe the normal probability distribution of the residues and that they are close and well distributed in relation to the line, which is a good sign for the model applied in this study.



FIG 2. *Normal probability distribution of the residuals.*

Even with the best condition obtained, the treated uranyl nitrate solution is not found within the limit recommended by the regulator in the licensing of the nuclear installation, which is 5.10-3 g∙L-1 for uranium in solution. Thus, it will be necessary to carry out another stage of precipitation, now with lime to reach this limit.

## Conclusions

Through experimental planning by CCRD, it is possible to confirm that hydrogen peroxide and lime bring satisfactory results in uranium precipitation. With the experiment planning tool, it was possible to optimize this treatment, aiming to generate the minimum amount of waste, the lowest possible use of reagents, gain in operational time, and mainly, to define the best treatment condition for the uranyl nitrate solution, obtaining the highest precipitation. possible uranium to remove this element from the solution and return this precipitate to the production of UO2 powders and pellets.

As a result, maximum removal was achieved by precipitation with 50 % H2O2 at 200 g∙L-1 in solution, pH equal to 1.75 and a reaction time of 8 hours, where 99.7 % of uranium was removed in solution. Therefore, the initial solution had 13.9 g∙L-1 and 36.10-3 g∙L-1 of 5 % enriched uranium remained in solution. The uranyl peroxide precipitate can be returned for UO2 production. To reach the release limit, a future study will be necessary as to polish the solution with calcium oxide, thus reaching values lower than 5.10-3 g∙L-1 of uranium in solution and generating the minimum of radioactive waste.

## Further information

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## References

[1] IAEA Technical Report Series 120 – Monitoring of radioactive contamination on surfaces. <https://inis.iaea.org/collection/NCLCollectionStore/_Public/02/004/2004458.pdf>. Accessed 25 May 2021.

[2] CANTEACH – Radiation protection “Green book” – chapter 9 - <https://canteach.candu.org/Content%20Library/20031309.pdf>. Accessed 25 May 2021.

[3] Norma CNEN NN 8.01. <http://appasp.cnen.gov.br/seguranca/normas/pdf/Nrm801.pdf>. Accessed 25 May 2021.

[4] Smirnov A L, Rychkov V N, Titova S M et al. (2018) Precipitation of uranium from nitrate-sulfuric eluates by aqueous ammonia solution. J Radioanal Nucl Chem. 317:863–69.

[5] Takao K, Arakawa K, Mori T, Harada M, Ikeda Y (2015) Outer-Sphere Extraction of Uranyl (VI) from HNO3(aq) to 1-Butyl-3-methylimidazolium Nonafluorobutanesulfonate Ionic Liquid −Towards Decontamination of Uranium Wastes. Bulletin of the Chemical Society of Japan. 88.

[6] Chen B et al (2012) Heavy Metal and Phosphorus Removal from Waters by Optimizing Use of Calcium Hydroxide and Risk Assessment. Environment and Pollution. 1:38-54.

[7] Kim KW, Hyun JT, Lee KY, Lee EH, Lee KW, Song KC, Moon JK (2011) Effects of the different conditions of uranyl and hydrogen peroxide solutions on the behavior of the uranium peroxide precipitation. J Hazard Mater. 193:52-58.