THE FACTORIAL PLANNING USE AS A TOOL FOR OPTIMIZATION OF THE SOLUBILIZATION OF UF_4 PROCESS

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Abstract: We seek to optimize the leaching process of uranium tetrafluoride (UF_4), analyzing the variables of time, temperature and use of catalyst. The results show that the temperature is the main factor for maximum solubilization of the material, indispensable feature to optimize the material leaching.

Keywords: Uranium, Uranium Tetrafluoride, leaching, Minitab.

1. INTRODUCTION

This article refers to the operating conditions of leaching of Uranium Tetrafluoride (UF_4) optimization using factorial planning and subsequent quantification of mass and the content of Triuranium Octoxide (U_3O_8) solid insoluble residue. This study aims to clarify questions about the future generation of solid waste from leaching of approximately 57,000 kg of material deposited on the Institute of Nuclear Energy Research (IPEN).

Factorial design is a statistical tool that allows to simultaneously evaluate the effect of a large number of variables, from a reduced number of experiments.

UF_4 is a uranium halide highly insoluble in water [1]. Although this material is an intermediate to the uranium hexafluoride (UF_6) [1], [2], it don't meet the actual standard specifications to uranium concentrate [3]. In order to meet the international specifications the material needs a chemical transformation. We decided to try an ore approach to total dissolution and later precipitation of uranium concentrate (yellow cake). The experiments realized are based only on the recovery of the uranium from UF_4 and not on the precipitation and quality of the final product.

The first step to this treatment is choosing the leeching agent and oxidant [1], [4]. From previous knowledge of the reaction [5] sulfuric acid (H_2SO_4) and sodium chlorate ($NaClO_3$) were the reactants studied. The reaction which best describes the system in question is indicated below:

$$3.UF_{4(s)} + ClO_3{}^-{}_{(aq)} + 3.H_2SO_4 + 3.H_2O \rightarrow 3.[UO_2SO_4]_{(aq)} + Cl^-{}_{(aq)} + 12.HF_{(g)}$$

Iron is an ion that may participate and enhance the reaction rates of the dissolution of uranium [4] and may be added as a catalyst to the reaction. The temperature may also enhance the reaction rate, but may pose a difficulty to choose the appropriate area to process the material, and reaction time will determinate the velocity which the UF_4 mass will be consumed. To identify the which one of the factors involved with this transformation are more

significant a chemometric method will be utilized. This methodology is well established in the industry and provides a statistical way to optimize industrial processes [6], [7].

2. THEORETICAL BASIS

In scientific research the general procedure is to formulate hypotheses and check them directly or by its consequences. For this we need a set of observations and the design of experiments is then essential to indicate the scheme under which the hypotheses can be verified. The hypotheses are verified by using statistical analysis methods that depend on the manner in which the observations were obtained. Therefore, design of experiments and analysis of results are closely linked and should be used in sequence in the scientific research of the various areas of knowledge. The factorial design is a statistical tool that allows to simultaneously evaluate the effect of a large number of variables to a small number of experiments. This technique is presented by the authors Mary R. M. Marinho & Walman B. de Castro in the article: Planejamento Fatorial : Uma ferramenta poderosa para os pesquisadores.[8], as well by Neto, B. B.; Scarmino, I. S.; Bruns, in the book: Como fazer experimentos: Pesquisa e desenvolvimento na ciência e na indústria;[6].

Once known chemical reactions as shown in the report RT-DRM-01-07 Rev. 00 – Processamento em batelada de concentrados de UF_4 para recuperação de urânio, na forma de DUA, nas instalações da INB;[5], the leaching of oxidizing agents, sulfuric acid and sodium chlorate were used based on the authors Katz, J. J.; Rabinowitch, E. [1] and Merritt, R. C. [4].

3. MATERIAL AND METHODS

All tests were conducted using the following equipment and reagents:

- Water bath with digital temperature control;
- Mechanical agitator with Teflon coated rod and digital control of rotation;
- Gas exhaust system;
- Electronic analytical scale;
- Digital thermometer;
- Polypropylene Becker;
- Set of vacuum filtration (Buchner funnel, kitassato, tubing, filters, etc.);
- Concentrated sulfuric acid (H_2SO_4);
- Sodium chlorate ($NaClO_3$);
- Carbon steel wool (catalyst);

The tests were carried out preparing a pulp with the percentage of solids and then adding the oxidant in solution of 500 g L-1 and concentrated sulphuric acid slowly in plastic beaker of suitable volume for testing and mechanical agitation in rotation that favored the homogenization without generating waste material (approximately 200 rpm) in accordance with the pre-established programming in order to develop an initial empirical model that demonstrates the behavior of the solubilization of uranium from UF_4. A full factorial design considering the following variables and their interactions:

A. Catalyst;
B. Time

C. Temperature;

The analyses were directed to the evaluation of the kinetics of the reaction, so the statistical model was considered only the main parameters-catalyst, time, temperature-related to this property, and other parameters, such as Acid-UF_4 Ratio (AUR), Oxidant-UF_4 Ratio (OUR) and $\%_{solids}$, have not been studied.

Table 1 below illustrates the conditions used in the tests of solubilization of uranium from UF_4. AUR was maintained at 0.5 ton_{H2SO4}/ton_{UF4}, the percentage of solids ($\%_{solids}$) was maintained at $18\%_{m/m}$, and OUR was kept in 0.1 ton_{H2SO4}/ton_{UF4}. The other parameters (catalyst, time and temperature) were varied.

Table 1 - Conditions used for the solubilization of UF_4.

Order	UF_4 mass [g]	AUR [ton/ton]	OUR [ton/ton]	$\%_{solid}$ [$\%_{m/m}$]	Catalyst [$\%_{catalyst/UF4}$]	Time [hr]	Temperature [°C]
1	100	0,5	0,1	18	0,0	6	20
2	100	0,5	0,1	18	0,0	6	70
3	100	0,5	0,1	18	0,5	6	20
4	100	0,5	0,1	18	0,5	6	70
5	100	0,5	0,1	18	0,0	24	20
6	100	0,5	0,1	18	0,0	24	70
7	100	0,5	0,1	18	0,5	24	20
8	100	0,5	0,1	18	0,5	24	70

Chemical analyses were performed by spectrophotometry with DBM (dibenzoylmethane). Statistical analysis was performed with Minitab ® 16.2.4 software.

4. RESULTS AND DISCUSSION

4.1. Optimization

From the results obtained in the tests planned on Table 1 it is possible to assemble the Table 2, which contains the mass of residue obtained for each test and its yield of solubilization. The yield of solubilization calculation is given by the ratio of the variation of solid material in relation to initial test mass, as formula below.

$$RS_{[\%]} = 100 \times \frac{(m_i - RI)}{m_i}$$

Where:

$RS_{[\%]}$ = solubilizing income;

m_i = initial mass;

RI = insoluble residue;

Table 2 - Insoluble residue and solubilization yield for optimization tests of leaching.

Testing	insoluble residue [g]	Solubilization yield [%]
1	81,0	19,0
2	19,6	80,4
3	67,9	32,1
4	7,8	92,2
5	82,8	17,2
6	12,1	87,9
7	73,0	27,0
8	8,0	92,0

From the information contained in Table 1 and Table 2 it is possible to draw the array of factorial planning with the codes to their factors and response, detailed below in Table 3.

Table 3 - Results of factorial 2^3 planning for optimization of the uranium UF_4 solubilization.

Factors		**(–)**	**(+)**
A	Catalyst (%)	0,0	0,5
B	Time (hours)	6	24
C	Temperature (°C)	20	70
Results: Not soluble residue [%]			
Testing	A	B	C	Result
1	-	-	-	81,00
2	-	-	+	19,60
3	+	-	-	67,90
4	+	-	+	7,80
5	-	+	-	82,80
6	-	+	+	12,10
7	+	+	-	73,00
8	+	+	+	7,98

The Figure 1 below illustrates the value of results and their correlations among the factors evaluated in the test.

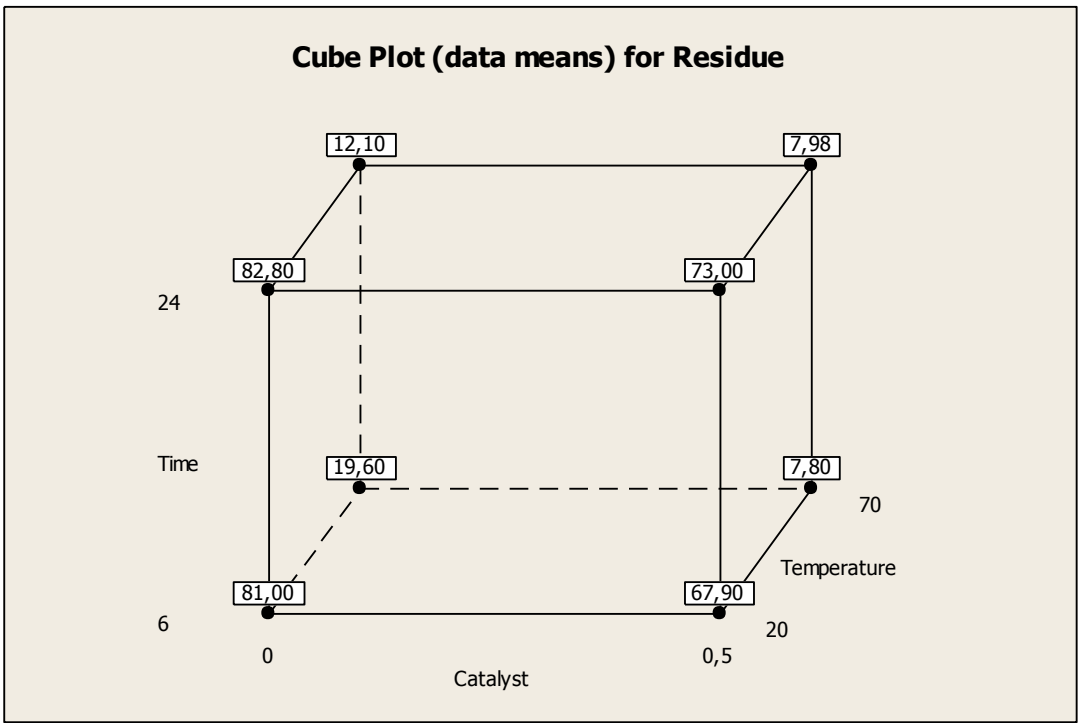

Figure 1 – Cubic plot for residue.

From the results obtained it is possible to evaluate the behavior of the results according to each evaluated factor .The Figure 2 below illustrates the variation of response with the levels of the three factors. This variation is evaluated on the basis of the average of the values obtained only on factor change illustrated in each chart.

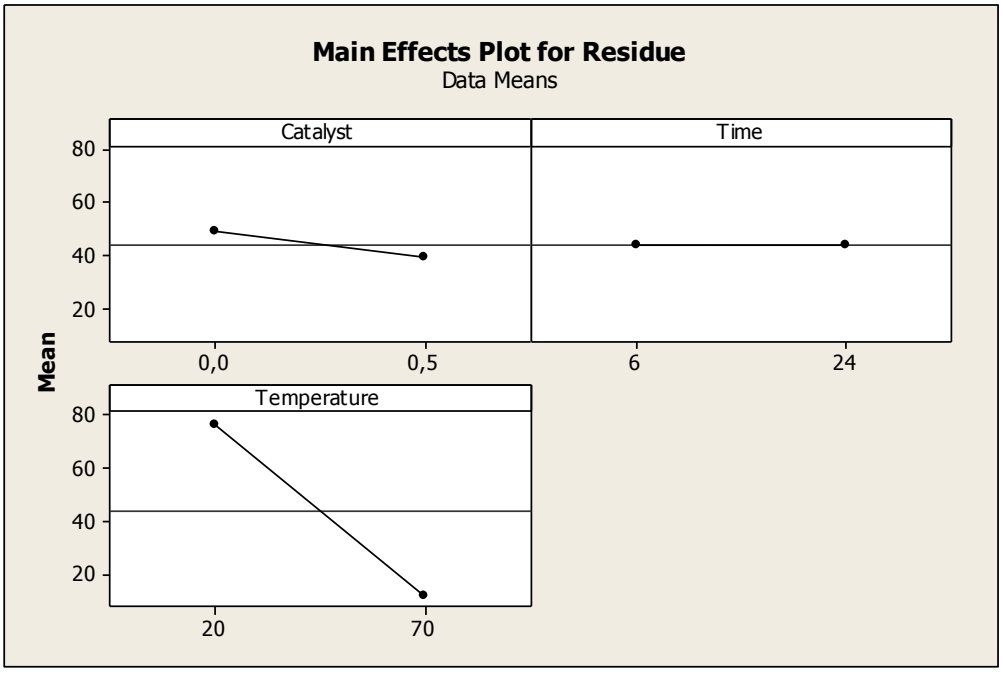

Figure 2 – Main effects plot.

On Figure 2 you can see that the temperature is factor with the greatest influence on the average result of solubilization, and the higher the temperature the lower the amount of insoluble residue resulting from the test. To obtain a more accurate assessment of the system

it is possible to generate Pareto chart (Figure 3) and the normal graphic effects (Figure 4). In both you can see that the Temperature factor stands out among the other factors studied. As if unaware of the behavior of the interaction between the factors initially estimated the results of the model considering all interactions.

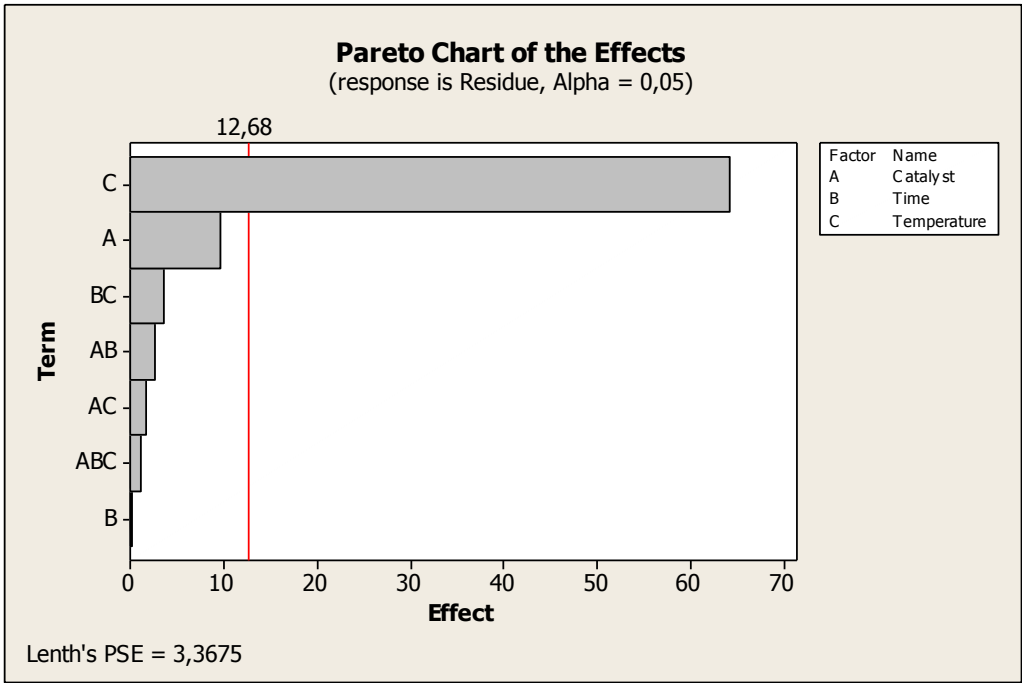

Figure 3 – Pareto chart of influence of the effects and interactions

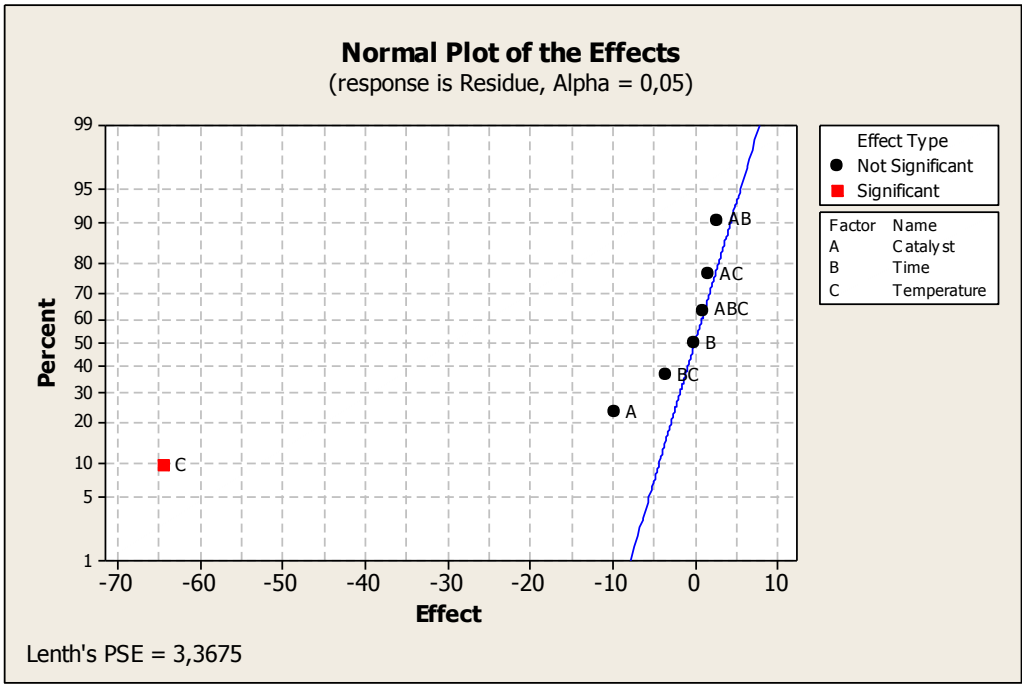

Figure 4 – Normal plot of the effects and interactions

The results of the charts above indicate that interactions among the studied factors may not have significant influence on the system .This means that the model can require statistical adjustments.

For the calculation of the model were used only the main factors and second-order interactions, with a factorial adjustment model presents the values described in Table 4 below.

Table 4 - Estimated Effects and coefficients for calculation of residue, whereas all interactions.

Term	Effect	Coefficient	Coefficient Standard error	T	P
Constant		44,02	0,5475	80,41	0,008
Catalyst	-9,70	-4,85	0,5475	-8,86	0,072
Time	-0,10	-0,05	0,5475	-0,10	0,939
Temperature	-64,30	-32,15	0,5475	-58,73	0,011
Catalyst*Time	2,75	1,37	0,5475	2,51	0,242
Catalyst*Temperature	1,74	0,87	0,5475	1,59	0,357
Time*Temperature	-3,55	-1,78	0,5475	-3,25	0,190

S = 1,54856 PRESS = 153,475

R^2 = 99,97 % R^2 (pred) = 98,20 % R^2 (adjusted) = 99,80 %

The P-value indicates whether the given factor may or may not be excluded from the model. If the value is greater than the value of significance adopted (0.05) remove, sequentially, the factor with the greatest difference, and then adjusts the model again until all terms are statistically significant, meaning that the value of p is less than 0.05.

The template in question removes the time factor and their interactions and subsequently the interaction factor Catalyst*Temperature. The model, then, is again adjusted and withdraws the interaction Catalyst*Temperature. The Table 5 below indicates the final model adjusted.

Table 5 - Estimated Effects and coefficients for calculation of residue, whereas statistically significant factors.

Term	Effect	Coefficient	Coefficient Standard error	T	P
Constant		44,02	1,105	39,83	0,000
Catalyst	-9,70	-4,85	1,105	-4,39	0,007
Temperature	-64,30	-32,15	1,105	-29,09	0,000

S = 3,12590 PRESS = 125,072

R^2 = 99,43 % R^2 (pred) = 98,53 % R^2 (adjusted) = 99,20 %

The value of R^2 indicates adjustment of the model to the data presented, while the value R^2 (pred) denotes the quality of model prediction. From the values obtained in statistical tests it is possible to assume that the template fits, reliably, to the experimental data.

To the result obtained in this test the largest calculated coefficient corresponds to the Temperature factor, having a value of -32.15. You might want to warn that the goal of the test is to minimize the amount of residue after solubilization and that the larger the absolute value of the coefficient calculated for larger interaction factor and/or the influence of this factor

and/or interaction on the mathematical model and the sign of the coefficient refers to the proportionality of this influence. The absolute value (32.15) indicates that the variable Temperature has the greatest influence on solubilization of uranium, while the sign (-) indicates that this influence is inversely proportional, i.e. the higher the temperature the lower the amount of residue. The catalyst factor is also statistically significant, however presents a much smaller influence on the result. The Figure 5, below, indicates the estimated influence of two factors on the outcome of the process.

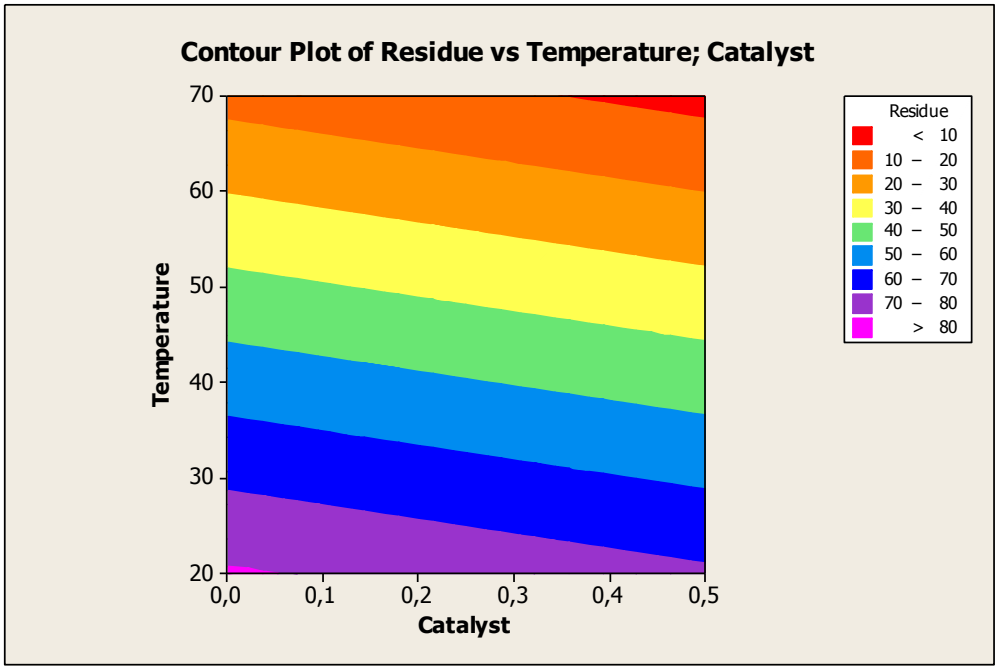

Figure 5 - Contour graph of the influence of temperature and Catalyst in the residue.

4.2. Insoluble residue

UF_4 processing proposal consists of solubilizing steps in batches, where the liquor is separated from the insoluble material, which is kept inside of reactors for later reprocessing with new addition of oxidant, acid and uranium concentrate.

In order to simulate what would be the final residue of this operation were carried out fresh tests solubilizing from solid material obtained from the previous test. The conditions of this new test (Table 6) were such that favored the maximum solubilization of the material in question. Essentially a solubilization with the same proportions of acid (RAM = 0.5 ton/ton) and oxidant (ROM = 0.1 ton/ton), obeying the great effects of the factors (temperature, reaction time and addition of catalyst) checked in step of optimization.

The mass of the insoluble solid residue obtained from this second operation of leaching was quantified and the results are presented in Table 6.

Table 6 - Terms used for the tests of leaching of waste generated from the essays of solubilization of UF_4.

Testing	Initial mass [g]	Insoluble residue first leaching	AUR [ton/ton]	OUR [ton/ton]	$\%_{solids}$ [$\%_{m/m}$]	Time [hr]	Temperature [°C]	Insoluble residue 2nd leaching

		[g]						[g]
9	100,0	81,00	0,5	0,1	18	6	70	3,13
10	100,0	19,60	0,5	0,1	18	6	70	1,85
11	100,0	67,90	0,5	0,1	18	6	70	2,94
12	100,0	7,80	0,5	0,1	18	6	70	1,42
13	100,0	82,80	0,5	0,1	18	6	70	2,89
14	100,0	12,10	0,5	0,1	18	6	70	1,57
15	100,0	73,00	0,5	0,1	18	6	70	2,63
16	100,0	7,98	0,5	0,1	18	6	70	1,30

According the initial conditions proposed in mass Table 1 (UF_4 mass = 100 g) the percentage of insoluble residue in relation to an initial mass is calculated directly from the mass of waste presented in Table 6, for example, 1 g of residue = 1% of insoluble residue. (1 g of residue = 1% of insoluble residue). From the results above it is possible to establish a residual mass ratio and the initial mass of the tests. Assumes that this second leaching ensures complete removal of material liable to solubilization for purposes of calculation, in which the residual mass refers, in its entirety, the insoluble residue.

Depending on the consideration of solubilization of material testing total demonstrated in table 6 can be considered as replicatas and to calculate the confidence interval, it is assumed that these have a normal distribution. The statistical estimators from this analysis can be found on Table 7 below.

Table 7 - Statistical Estimators to insoluble residue leaching of UF_4.

Estimator	Value fond
Mean	2,216 %
Confidence interval (95 %)	$\pm$ 0,633
Population average estimator	2,216 $\pm$ 0,633 %

For the calculation of the average and the confidence interval were used the following formulas:

$$\mu = \bar{x} \pm t_{0,05;n-1} \frac{s_x}{\sqrt{n}} \qquad \bar{x} = \frac{\sum_{i=0}^{n} x_i}{n} \qquad s_x = \sqrt{\frac{\sum_{i=0}^{n} (x_i - \bar{x})^2}{(n-1)}}$$

Where:

μ = average population estimator;

$\bar{x}$ = average;

x_i = i-th sample;

s_x = sample standard deviation;

n = number of replicates;

$t_{0,05;n-1}$ = value of table t (two-tailed) with 95 % of confidence for n-1 degrees of freedom;

The resulting final mass of these trials was insufficient to perform comprehensive analyses of material characterization. Meanwhile have chosen a sample (sample 12) for quantification of the radionuclides present. The choice of 12 test was not random, having been used as a parameter of choice the maximum solubilization of material (*i.e.* least amount of residue generated), condition consistent with multiple leechings of the material. Was not chosen to test sample 16 due to difficulties of recovery of the sample in question.

Chemical analyses were performed by semiquantitative EDXRF (for determination of the levels of their macroelements), spectrophotometric analysis for quantitative determination of the activities of U-nat Th-tot overall, and for determining the activity ^{226}Ra, ^{228}Ra and ^{210}Pb through radiometric techniques. The results can be observed in Table 8 below.

Table 8 - Certain Levels in the solid residue insoluble 12 test.

Element	Content	Analytical technique
SiO_2 (1)	55,041 %	EDXRF
Na_2O (1)	42,915 %	EDXRF
Al_2O_3 (1)	1,253 %	EDXRF
Fe_2O_3 (1)	0,083 %	EDXRF
Cr_2O_3 (1)	0,078 %	EDXRF
NiO (1)	0,027 %	EDXRF
CuO (1)	0,018 %	EDXRF
U-nat	46 kBq/kg (0,189 %)	Spectrophotometry
Th-total	2,7 kBq/kg	Spectrophotometry
^{226}Ra	1,0 kBq/kg	Radiometry
^{228}Ra	2,1 kBq/kg	Radiometry
^{210}Pb	7,2 kBq/kg	Radiometry
Total activity (2)	166 kBq/kg	–

(1) Semiquantitative analysis
(2) Calculated

Considering the total mass of the material available for processing and reuse (57,000 kg) and the data obtained in this report it is possible to estimate the quantities of total insoluble residue processing and elements of interest. The Table 9 below illustrates the expected final quantitative (mass and activity) to the residue and radionuclides.

Table 9 - Quantification of waste, estimated levels and final activity of the UF_4 available for reprocessing.

Origin	Quantitative		
	Minimum	Medium	Maximum

Total residue	900	kg	1.260	kg	1.620	Kg
	149,4	MBq	209,2	MBq	268,9	MBq
U-nat	1,70	kg	2,39	kg	3,06	Kg
	41,4	MBq	58,1	MBq	74,5	MBq
Th-total	2,4	MBq	3,4	MBq	4,4	MBq
^{226}Ra	0,9	MBq	1,3	MBq	1,6	MBq
^{228}Ra	1,9	MBq	2,6	MBq	3,4	MBq
^{210}Pb	6,5	MBq	9,1	MBq	11,7	MBq

5. CONCLUSIONS

Only one leaching operation does not fully solubilizes the available material. Optimization tests demonstrate that: the temperature is a crucial factor for maximum solubilization of the material; in relation to other factors studied the use of catalyst has influence, but this is less than the influence of temperature and time variation and interactions among the factors do not have significant influence on the system.

When considering the extrapolation of the system to an industrial scale, it is possible to assume that, in order for the reaction to complete satisfactory time, industrial reactors should be heated. In heating condition proposal, and whereas the insoluble residue will undergo reprocessing only 6:0 leaching is sufficient to ensure a reasonable condition of processes, eliminating the use of catalyst in the process.

The simulation of sequential leaching of the material demonstrates that the insoluble residue, for the sample tested, corresponds to 2.216 $\pm$ 0.633% of original material. This residue presents the following activity specific for certain radionuclides: U-nat: 46 kBq/kg; Th-tot: 2.7 kBq/kg; ^{210}Pb: 7.2 kBq/kg; ^{226}Ra: 1.0 kBq/kg; ^{228}Ra: 2.1 kBq/kg.

It is expected that a total of 57 tons, this percentage corresponds to, at most, 1.62 tons of residue insoluble solid, with the following maximum total activity for radionuclides: U-nat: 74.5 MBq (corresponding to a total of 3.06 kg); Th-tot: 4.4 MBq; ^{210}Pb: 11.7 MBq; ^{226}Ra: 1.6 MBq; ^{228}Ra: 3.4 MBq. it is estimated that the total activity maximum final 268.9 MBq.

The activity presented by this residue makes it necessary to control this material, Radiological Protection responsibility being an indication of storage best practice.

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