



## RECOVERY OF URANIUM FROM SLAG GENERATED IN THE MAGNESIOTHERMIC PRODUCTION OF METALLIC URANIUM

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### ABSTRACT

The Nuclear Fuel Center of IPEN-CNEN/SP has recently concluded a program for developing the fabrication technology of the nuclear fuel based on the LEU  $U_3Si_2$ -Al dispersion, which is being used in the IEA-R1 research reactor. The uranium silicide ( $U_3Si_2$ ) fuel production starts with the uranium hexafluoride ( $UF_6$ ) processing and uranium tetrafluoride ( $UF_4$ ) precipitation. The  $UF_4$  is then converted to metallic uranium by magnesiothermic reduction. The  $UF_4$  reduction by magnesium generates  $MgF_2$  slag containing considerable concentrations of uranium, that could reach 20 wt% of uranium. The uranium contained in that slag should be recovered and this article presents the results obtained in uranium recovering from that slag. The uranium recovery is made by acidic leaching of the calcinated slag. The calcination transforms the metallic uranium in  $U_3O_8$ , promoting the pulverization of the metallic uranium pieces to facilitate the leaching operation. The process variables considered were: nitric molar concentration; acid excess concerning the stoichiometric content and leaching temperature. As a global result of this experimental work, uranium recovery reached the level of 96% of process yield.

**Key-words:** uranium recovery; metallic uranium,  $U_3Si_2$ , nuclear fuel.

## 1. INTRODUCTION

Energy and Nuclear Research Institute (IPEN-CNEN/SP) produces radioisotopes, radiopharmaceuticals and radioactively marked substances, which are also processed and distributed. Materials used in nuclear medicine, supplied by IPEN, serve approximately one million patients a year. Considering the social strategic importance of radiopharmaceuticals production in Brazil and for the continued expenditure growth to import radioisotopes needed to reach production target, the Brazilian Commission of Nuclear Energy (CNEN) decided to invest in this critical area, especially in the IPEN's Laboratories. As a result, from 1995 onwards, a major financial input allowed important revamps to start the radiopharmaceuticals production facilities, promoting an increasing

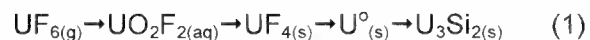
of radioisotopes production based on the IPEN's research reactor - IEA-R1. It was also decided to increase the power of the IEA-R1 from 2 to 5 MW and change the continuous operation pace to 100 hours per week, creating conditions for more radioisotopes production.

For many years, IPEN-CNEN/SP worked on the development on manufacturing process for dispersion type fuel elements to be used in IEA-R1, since the market in nuclear materials is in a sense unpredictable and the IEA-R1 depends entirely on necessary fuel elements for its reactor operation. To implement this fuel fabrication in this context, IPEN's Nuclear Fuel Center started to produce the fuel elements based initially on LEU  $U_3O_8$ -Al dispersion. After increasing the power of IEA-R1, it became necessary to increase the uranium concentration of fuel plate meat, which was obtained by replacing  $U_3O_8$  by  $U_3Si_2$  in Al-dispersion. The uranium meat density in the fuel plate has risen from 2 to 3 gU/cm<sup>3</sup> (1) (2) (3). The manufacturing technology of the new fuel-based Al- $U_3Si_2$  based on precipitation of  $UF_4$  from  $UF_6$  hydrolyzed solution, using stannous chloride as reducing agent. The  $UF_4$  obtained is then reduced to metallic uranium with magnesium as reducing agent using metalothermic route (4). As a byproduct of this reduction, we obtain  $MgF_2$  slag containing substantial amounts of uranium. Historically, there was around 20wt% of uranium in the slag, since the typical yield of magnesiothermic reduction is 80% uranium (5) (6).

This paper presents the results obtained in the recovery process of uranium from the generated slag in the magnesiothermic reduction process of  $UF_4$  to get metallic uranium. The recovered uranium is then reconverted to  $UF_4$  and returns to the fuel fabrication cycle.

## 2. EXPERIMENTAL

The manufacturing process of the fuel dispersion-based silicide (LEU  $U_3Si_2$ ) adopted in the Nuclear Fuel Center IPEN-CNEN/SP is represented by the following processing chain:



The  $UF_6$  is hydrolyzed. From the hydrolyzed solution is precipitated the  $UF_4$ , using stannous chloride as reducing agent and adding hydrofluoric acid. The reduction of uranium tetrafluoride ( $UF_4$ ) to metallic uranium is performed by magnesium as a reducing agent. The produced metallic uranium is melted with metallic silicon in an induction furnace to obtain the silicide ( $U_3Si_2$ ) as a nuclear material. (3) (2)

During the process of reduction of  $UF_4$  to uranium metal, It is generated a slag containing fundamentally magnesium fluoride ( $MgF_2$ ) with uranium as metal and minor quantities of magnesium oxide (MgO) and uranium oxides in the form of  $UO_2$  and  $U_3O_8$ . According to the reaction below, the  $MgF_2$  (the raw material used in this work) is the slag generated in the magnesiothermic process (7):



Table 1 shows the main chemical characteristics of slag used in this work. This slag was obtained early in the development of the production process of uranium metal, containing high content of uranium. Nowadays, the average content level is up to 20% in weight. In this work, it was used previously produced slag containing high amount of uranium to allow better analysis of uranium recovery process yield.

The slag directly obtained from the uranium production was first calcinated to promote the formation of metallic uranium powder. During this process, metallic uranium is oxidized to  $U_3O_8$  in order to facilitate maximum leaching. For the calcination, it was used a 10 kW resistive furnace power for applying different temperatures and time periods for calcination. Uranium metal is unstable, pyrophoric and extremely reactive. Slag containing levels exceeding 70wt% in uranium, without calcination, could suffer spontaneous combustion as quoted in the literature (8) (9). On the other hand, the stable oxide  $U_3O_8$  has low chemical reactivity, easily handled, justifying so the implementation of calcination step for the slag.

Table 1 – Chemical characteristics of slag produced during metallic uranium fabrication

Composition	Content (%)
U	31,1
F	24,9
S	0,01
Metallic impurities	Content ( $\mu\text{g g}^{-1}$ )
Ca	8800,0
Si	5000,0
Mg	4000,0
Al	1200,0
Sn	1200,0
Fe	476,5
Ba	164,7
Mn	74,9
Pb	60,1
Cu	27,4
Zn	15,6
Ni	5,6
Cr	4,6
Mo	< 3,0
Co	< 0,4
Li	0,6
V	0,4
Cd	< 0,1

After calcination, the process followed to crushing in order to decrease the particles amount containing oxidized compounds of uranium, increasing so the specific open surface of the material, providing a better reaction speed in the later leaching process. To reduce particle size, it was used a ball mill with alumina balls, having jar dimensions of 30 x  $\varnothing$ 20 cm with a capacity of 10 liters.

After grinding the slag, an operation of nitric leaching began. Initially, it was added to the reactor part of HNO<sub>3</sub> leaching solution with a ratio of 0.025 moles of HNO<sub>3</sub> per gram of uranium. Then, it was slowly fed the slag and the remaining solution of HNO<sub>3</sub>. This process was conducted during 12 hours, with reaction temperature control and with a constant stirring of 300 rpm. An impure uranyl nitrate solution (UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>) was got. This solution was then vacuum filtered and treated for purification with organic solvent, the tributylphosphate diluted in 30%vol with isoparaffins.

After UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> purification, the solution was reacted with gaseous ammonia to precipitate ammonium diuranate uranyl (ADU), which is calcinated at 600°C for a period of 3 hours, thereby obtaining pure U<sub>3</sub>O<sub>8</sub>.

The U<sub>3</sub>O<sub>8</sub> produced was transformed into uranium tetrafluoride (UF<sub>4</sub>) under reaction with stannous chloride (SnCl<sub>2</sub>) and hydrofluoric acid (HF) inside a precipitation reactor. The obtained UF<sub>4</sub> was then treated under argon atmosphere in an heating furnace at 400°C in order to remove crystallization water. Once UF<sub>4</sub> is duly qualified then it returns to production route of uranium metal as raw material for the magnesiothermic reaction.

### 3. RESULTS AND DISCUSSION

In the experiments of calcination, it was observed a homogeneous calcinated slag made at 600°C for a period of 3 hours. The calcinated slag was characterized by x-ray diffraction and the results are shown in Figure 1. As could be seen, the heat treatment under air atmosphere converted all the uranium present in the slag into U<sub>3</sub>O<sub>8</sub>. The diffraction peaks that do not agree with pure U<sub>3</sub>O<sub>8</sub> correspond to crystalline compounds that remained in the slag after uranium removal during leaching. They are mainly fluorides.

Table 2 – Slag granulometry from uranium magnesiothermic process (after calcination)

Size (µm)	Mass (g)	(%)
> 420	564,5	16,1
420 - 250	26,7	0,7
250 - 150	80,2	2,3
150 - 75	1321,4	37,7
< 75	1515,8	43,2
Total	3508,6	100,0

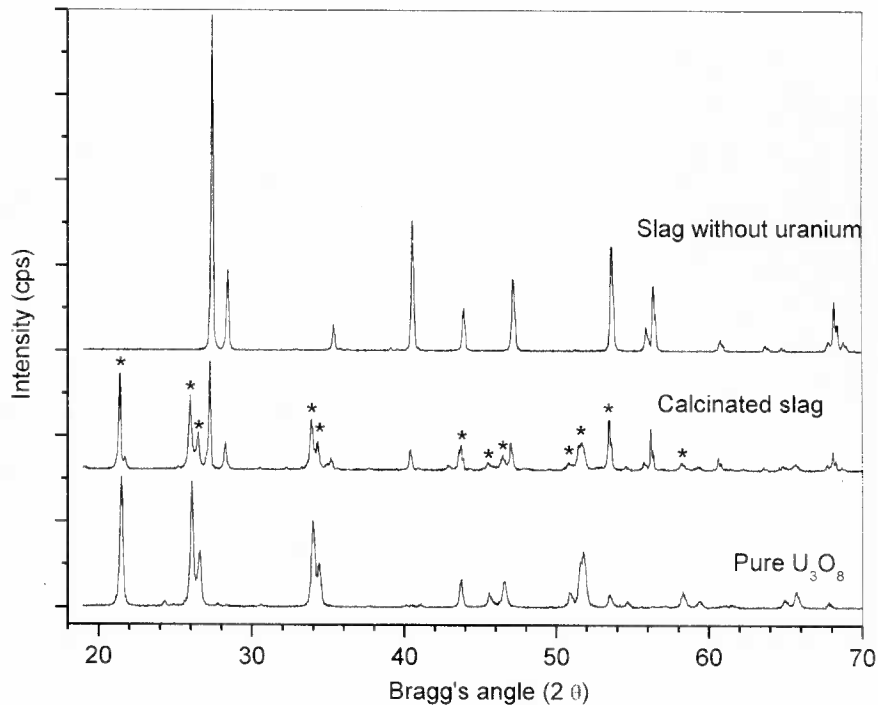
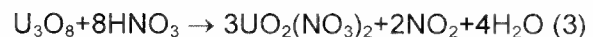


Figure 1 – Diffractograms showing the presence of  $U_3O_8$  after calcination.

The slag was ground in a ball mill for 8 hours with rotation speed of 200 rpm. The slag was then classified by granulometry through sieving. It resulted in a wide size distribution range, as illustrated in Table 2. The material obtained after grinding showed 90wt% of particles within the range of 75 and 150  $\mu m$  (100 - 200 mesh). This material was used in the leaching tests.

It is desirable that the process of uranium recovery from scrap generated, during metallic uranium fabrication, could produce a uranium compound that allows the reuse of recovered material that could be easily incorporated it in fuel cycle production. The dissolution of uranium slag calcinated (basically  $U_3O_8$ ) with  $HNO_3$  results in a solution of uranyl nitrate,  $UO_2(NO_3)_2$ , which is a compound widely used as feedstock in the nuclear fuel cycle and the processes, and well known solution in IPEN -CNEN/SP laboratories in order to produce uranium materials. For this reason, nitrate leaching was found to be adequate for this recovery production line.

The main chemical reaction for calcinated slag nitric leaching is represented by the reaction:



According to this stoichiometric balanced equation, the nitric acid consumption is 0,011 mol by 1 gram of uranium. It was found that the consumption of required nitric acid was greater than the stoichiometric due to the presence of fluorides in the slag, as  $MgF_2$  and  $CaF_2$ , which are quasi-insoluble or poorly soluble. To guarantee the full leaching of calcinated slag, leading the  $U_3O_8$  to a solution of  $UO_2(NO_3)_2$ , in order to make it suitable for recovery process, it was set a nitric acid consumption to 0.025

mol.g<sup>-1</sup> of uranium, which is an excess of 120% of stoichiometric nitric acid. The leaching process variables were time, 2 levels of temperature, 25°C and 45°C, and the concentration of nitric acid at 1 and 3 molar. The leaching process was carried out in batches of 300g of calcinated slag, previously classified in the mesh range from 150 to 75 µm (100 - 200 mesh).

During leaching, samples were collected in intervals of 1 hour and analyzed in order to determine the free acidity of leached solution and uranium and fluoride concentration. After 12 hours of leaching, the results of the uranium concentration in solution allowed figure out how was the performance of process yield in terms of uranium removal from the slag. The results are shown in Figure 2 and Table 3.

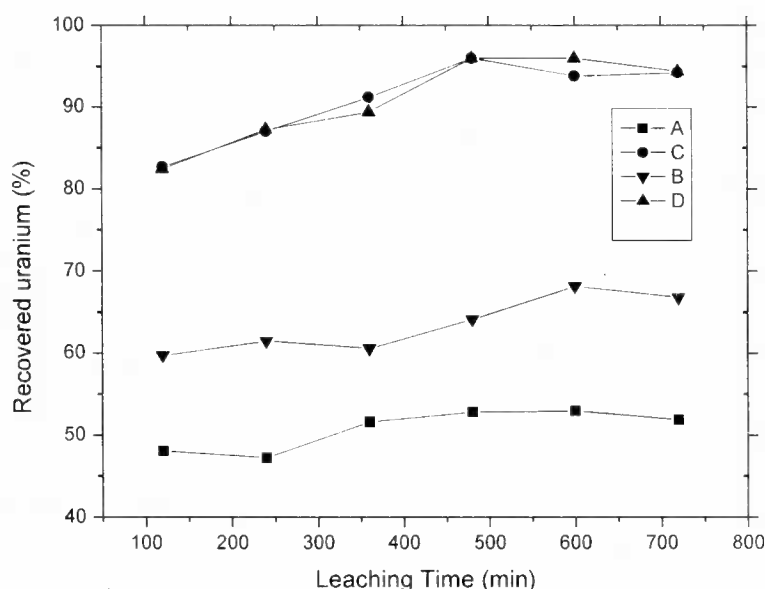


Figure 2 – Recovered uranium (%) by leaching time in the conditions shown in table 3.

Tabela 3 – Performance of nitric leaching of reduction slag

Experiment	Temperature (°C)	HNO <sub>3</sub> (Molar)	U-yield (%)	Fluoride (g/l)	Free acidity (Molar)
A	25	1,0	53	0,002	0,01
B	25	3,0	77	0,002	1,00
C	45	1,0	96	0,002	1,00
D	45	3,0	95	0,006	1,00

Leaching time= 12 horas

The results shown in Figure 2 and Table 3 suggest that the best conditions for leaching would be using process temperature at 45°C and HNO<sub>3</sub> concentration with 1 or 3 Molar

(experiments C and D). After 12 hours, the nitric leaching, it was got a yield of 96% in the uranium extraction from slag with a minor residual fluoride content of only 0.002 g/L. It was chosen to HNO<sub>3</sub> concentration at 1 Molar, since it provided the lowest solubility of fluoride present in the slag. It also provides better economy in terms of acid consumption and less acidic nuclear residues.

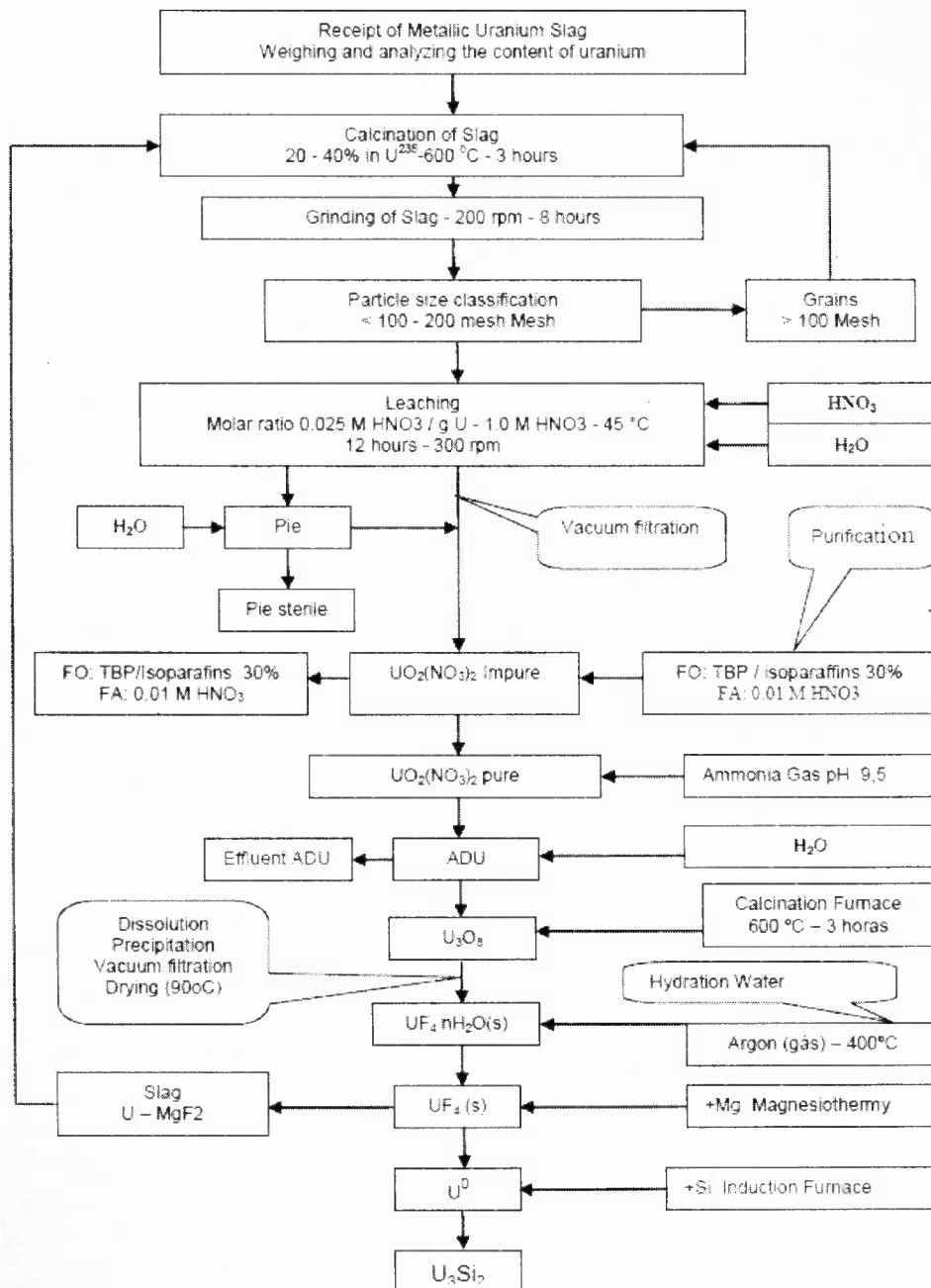


Figure 3 - Block diagram of the recovery process of uranium present in slag generated in the production of uranium metal.

In addition, the leaching being carried out at low temperature (45°C) with low nitric concentrations (1 to 3 Molar) are favorable since it helps keeping the Mg and Ca fluorides with poor solubility, avoiding also the corrosion effect caused by fluoride ions, ensuring stable and more secure leaching from operational routine standpoint [2,3,4].

The residues dissolution with nitric excess of 120%, i.e., molar ratio of 0.025 HNO<sub>3</sub> per gram of uranium, result in an impure solution of UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> with free acidity in the range of 1 Molar, which is very suitable for direct addition in purifying system using solvent extraction in the last phase of the recovery.

Figure 3 illustrates the whole process flow diagram developed in this work for the recovery of uranium contained in the slag which is generated in the production of uranium metal.

#### 4. CONCLUSIONS

It was developed a process to recover LEU uranium from generated scrap in the production of metallic uranium, which can contain significant amounts of uranium, in the range of 20 wt%. The experimental process yield reached a maximum value of 96% in uranium recovery. Pre-treatment steps are necessarily to be made with the slag, such as calcination and grading. These steps made metallic uranium present in the slag to be oxidized to U<sub>3</sub>O<sub>8</sub>. This substance was easily dissolved in nitric acid medium. The uranium recovery process developed in this work, whose flowchart is shown in Figure 3, is being implemented as a routine recovery production of fuel IPEN-CNEN/SP.

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