ANALYSIS OF SLAG FORMATION
DURING UF$_4$ MAGNESIOTHERMIC REDUCTION

A. M. SALIBA-SILVA[(1,2)], B. AGUIAR[(1)], E. U. CARVALHO[(1,2)],
D.G. DA SILVA[(1)], H. GRACHER RIELLA[(2,3)], M. DURAZZO[(1,2)]

[(1)]Nuclear Fuel Center of IPEN/CNEN-SP
CCN - Av. Prof. Lineu Prestes, 2242 – Cidade Universitária
05508-000 – São Paulo, SP, Brazil - email: saliba@ipen.br
[(2)]Science and Technology Brazilian Institute – Innovating Nuclear Reactors
[(3)]Federal University of Santa Catarina, Florianópolis, SC, Brazil

ABSTRACT

Metallic uranium is a fundamental raw material to produce nuclear fuel element for research reactors based on U$_3$Si$_2$ or on the future fuel U-Mo. Magnesiothermic reduction of UF$_4$ is a normal route in IPEN´s nuclear fuel cycle to produce uranium as a metal ingot. The main concern about the reducing scale to produce LEU metallic uranium (around 1000 g) is the relative low yield, around 85%, compared to calciothermic reduction. Nevertheless, the magnesiothermic reduction has many advantages of lower cost and being safer method to deal with uranium processing. The magnesiothermic process, as a batch, is closed inside a sealed crucible and virtually it is not possible to analyze the kinetics of the reaction. Only the real time acoustic and visual inspection results during the crucible opening were used in these studies to achieve a general idea of the whole reaction ignition by the physical arrangement of the products. In the present studies, in order to have a qualitative idea of the kinetics during the ignition moment, it was used the slag projected over the lateral inner face of the crucible to sketch the general magnesiothermic evolution. The used methods were metallographic observation and X-Ray diffraction followed by Rietveld refinement. Results of these analyses led to conceive a general reaction development during the first 800-1200 ms between the ignition and final settlement of the products. A relevant information from these studies led to the conclusion that uranium is not majorly present in the lateral slag projection over the crucible during the reaction and the temperature level may be reached 1500°C or more, after the ignition.

1. Introduction

The nuclear reactor IEA-R1 fuel elements and irradiation targets to produce radioisotopes for nuclear medicine are made using metallic uranium. This element is alloyed to produce the subsequent products, such as the U_3Si_2, UAl_x and future nuclear fuel alloy U-Mo. There are several possibilities to produce metallic uranium[1, 2]. Magnesiothermic reduction of UF_4 is known process since early 1940's [3, 4]. IPEN decided to use this route in 1970-80's for production 100 kg ingots of natural uranium. For LEU U-production, it is necessary to handle safe mass (less than 2.2 kg U), to avoid possible criticality hazards. IPEN presently produces around of 1000g LEU ingots via magnesiothermic process and in future may produce 2000 g or more [5, 6]. This range of LEU U weight is rather small if compared to big productions of natural uranium. Metallic uranium is reported [7] to be produced with 94% metallic yield when producing bigger quantities. The magnesiothermic process downscaling to produce LEU has small possibilities to achieve this higher metallic yield. This is due to the design of crucibles, with relatively high proportion of surrounding area, which is more prone to withdraw evolved heat from the exothermic reaction during uranium reduction. Normally, calciothermic reduction of UF_4 is preferred worldwide, since the exothermic heat is -109.7 kcal/mol if compared to smaller amount of -49.85 kcal/mol produced using magnesium as the reducer [8]. Nevertheless, IPEN chose magnesiothermic because it is easier to be done avoiding no handling of toxic and pyrophoric calcium. Moreover, the magnesiothermic process is cheaper, so, it brings economical compensation for its worse metallic yield than calcium reduction process. In addition, the recycling of slag and operational rejects is highly efficient and virtually insignificant LEU uranium is lost [9, 10].

The magnesiothermic reaction is given by:

$$UF_4 + 2Mg = U + 2MgF_2 \qquad \Delta H = -49.85 \text{ kcal/mol (at 640°C)} \qquad (1)$$
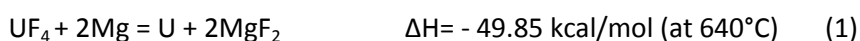
As magnesium thermodynamics is less prompt to ignite than calcium, the batch reactor is heated up to the temperature around $640°C$. The routine shows that this ignition normally happens some degrees below this temperature [7] [11].

In this work, it is discussed formation of slag during the magnesiothermic ignition and projected towards the lateral wall of graphite crucible. The evidences in the slag solidification, after the reaction process to reduce UF_4 towards U°, can guide the interpretation of the reaction blast. Based on RX-diffraction analysis throughout the transversal section of wall solidified slag, it is possible to give a general idea of chemical and physical events.

2. Experimental and Results

IPEN's UF_4 production is made through a wet route [12, 13]. The microstructure appearance of UF_4 produced is presented in Figure 1 a-b, which is a typical representation of the UF_4 morphology produced by the wet route. As could be noticed in Figure 1a, there are crystallites of different sizes and morphologies. The UF_4 powder is supplied to produce metallic uranium by UF_4 reduction by magnesiothermic arrangement.
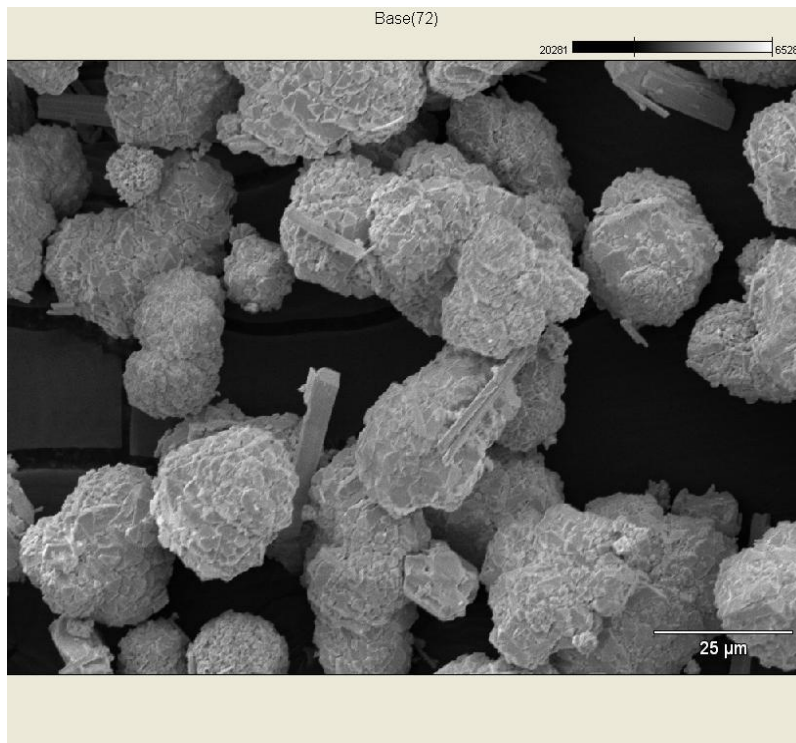
Figure 1- SEM Microstructure of UF_4 produced by
IPEN's wet route, using $SnCl_2$ as precipation agent.

The IPEN's magnesiothermic reduction process of UF_4 to metallic uranium could be synthesized as: (1) single batch using 1815 ± 5g of the mixture Mg + UF_4 (1540 ± 1g LEU UF_4) containing 15% excess of stoichiometric Mg content. For purpose of homogenization, the charge of UF_4 + Mg is divided into 10 layers tapped one by one inside the crucible. (2) A variable amount of CaF_2 is tapped over the UF_4+Mg load in the crucible to fully complete the reaction volume. This amount is dependent on tapped density and UF_4+Mg blending, which varies in function to UF_4 fabrication. (3) The crucible is inserted inside a stainless steel cylindrical reactor vessel, made of ABNT/ANSI 310, with argon fluxing during batch processing (1 L/min with 2 kgf/cm^2 of pressure). As shown in Figure 2 (a-b), the whole crucible + reactor is placed in resistor pit furnace with four programmable zones having the possibility of raising the temperature up to 1200°C. (4) The reaction vessel is heated up to 620°C. At this level, the reaction ignition is expected. The total heating time and waiting for ignition is about 180 minutes from heat time to temperature setting point. (5) The reaction of UF_4 with Mg produces an intense exothermic heat release inside the crucible. It produces metallic uranium and MgF_2 slag in liquid form. Both products deposit in the crucible bottom are easily taken apart after opening the crucible. Some slag, during the reaction blast, is project over the crucible wall. The full reaction happens during 800-1200ms from ignition to final deposit, as controlled by accelerometer.
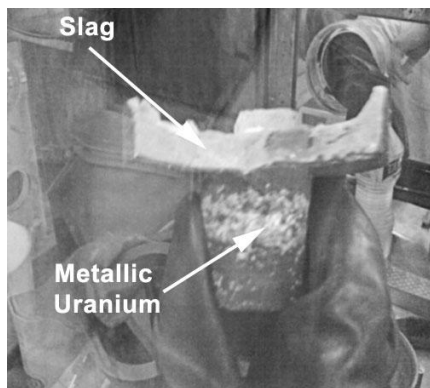
In Figure 2 (c-d), it is shown the metallic uranium removed from the crucible with the top slag and after removed the slag around the ingot.
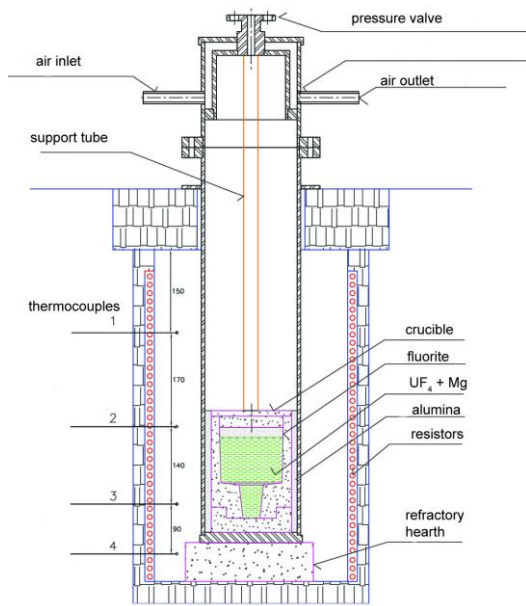
(a)   (b)

(c)   (d)

Figure 2 – (a) Schematic drawing of pit furnace, reactor vessel and crucible; (b) Charging of the reactor vessel inside the pit furnace; (c) Raw metallic uranium and upper deposited slag after removing from the crucible; (d) Metallic uranium after cleaning.

In Figure 3 (a-b) it is displayed the sample of projected slag in lateral crucible wall, with the views of transversal section and inner side.

In Figure 3 (c), it is possible to see in details that different structures deposited during the process of magnesiothermic reaction. It is important to notice that there are 4 layers in this sample, named in the order of solidification:

- Layer 1 – it is the layer that had contact with the crucible wall. It is believed to have been formed in the first stage of the blast, when there was the first disarrangement of the initial charge. There was a partial melting of the charge, including the CaF_2 that was originally placed on the top of the charge

arrangement to complete the hollow volume inside the crucible. This first layer had a dark color.

- Layer 2 – This layer follows layer 1 in the sequence of solidification. It has a general view of compressed longitudinal strips parallel to the wall, indicating that this solidification happened under heavy pressure. It has a light greenish color.
- Layer 3 – Between layer 2 and 3, there are a plane of bubbles of extraneous material if compared to the layer solidification. These bubbles, still under studies, seem to be results of reacting UF_4+Mg+U nuclei during reaction that could have been thrown during the blast to this region of ongoing layer solidification. Layer 3 was solidified on the top of this. It resembles much lighter material than layer 2.
- Layer 4 – This layer is similar to layer 3. It is represents the region of last slag crystallization.

The X-Ray diffractograms of the parallel planes of the transversal sections, obtained by metallographic preparation, was made by polishing along the transverse axis. They are shown in Figure 3 (d). Table 1 presents the main results of normalized data for the 2 major phases (MgF_2 and CaF_2) occurring in this projected slag at the crucible wall. In general terms, this solidified slag reflects the photography of crystals formation during the events following the ignition of magnesiothermic reaction.

In this work, it will be also considered the Rietveld results, obtained by GSAS software [14] using the XDR diffractograms, to discuss a broad guideline of magnesiothermic reaction kinetics accounted by the solidification structures. It will be used the texture index as an overall guide. The texture index obtained by the refinement can be defined as an indication of randomness of crystals solidified. If the texture is fully random then the index is 1, otherwise texture index > 1; single crystal has the texture is infinite.
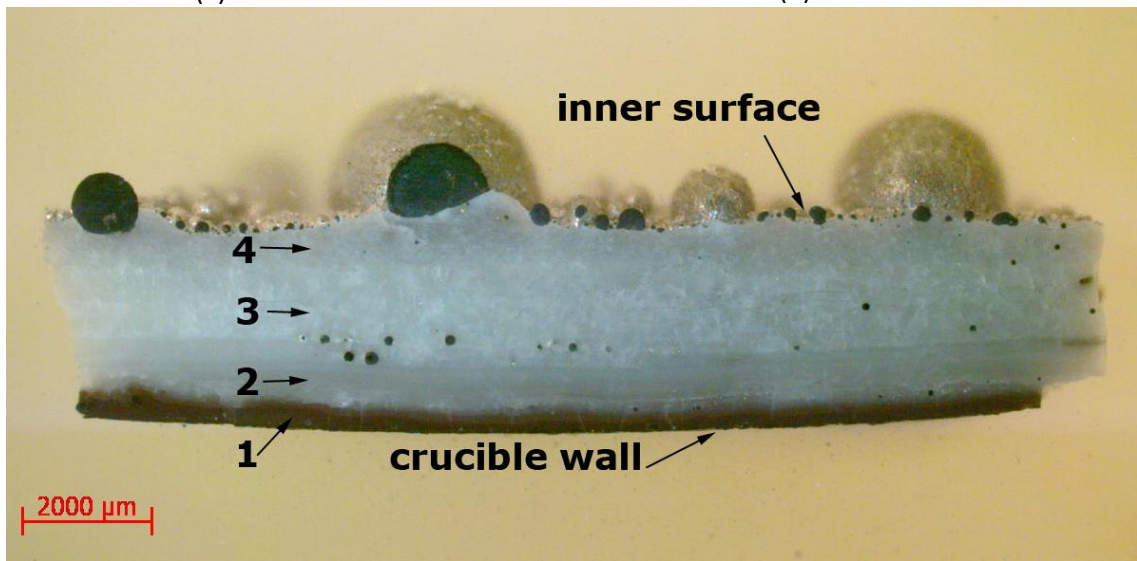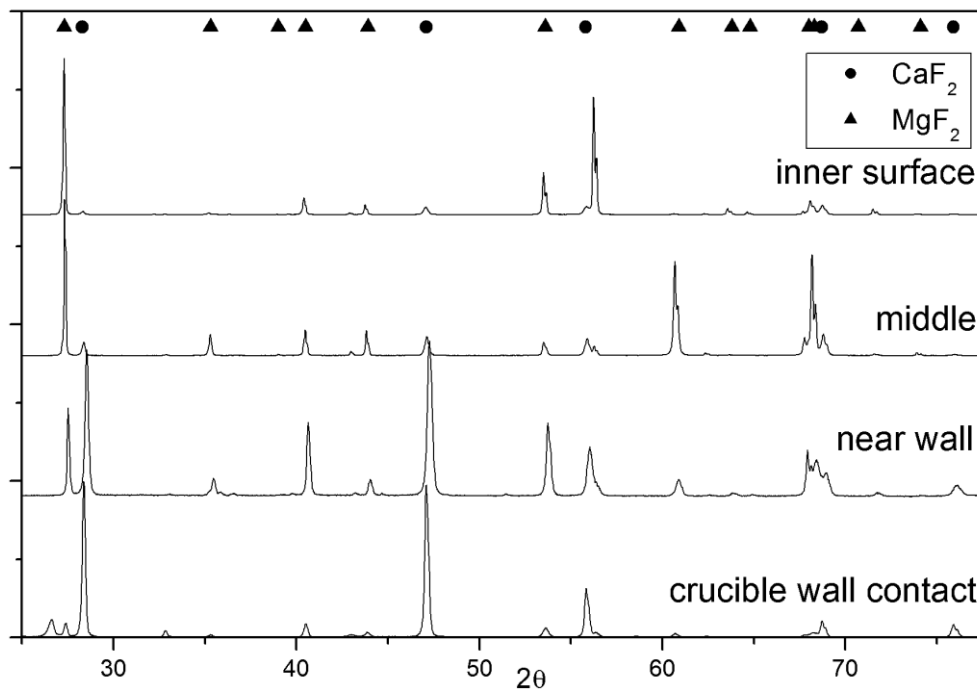
Figure 3 – Wall projected slag analysis. (a) Transversal section view of the slag sample; (b) Sample view from the inner side; (c) Lens magnified view of tranversal section view; (d) XRD diffractograms of each zone.

Table 1 – Rieltveld results for the major phases contents MgF_2 and CaF_2 (normalized to 100%) found in the lateral projected slag.

XRD Zones	#	%MgF_2	%CaF_2	χ^2	Text MgF_2	Text CaF_2
Near Inner Surface	4	81.3	18.7	41.0	2.04	1.68
Middle	3	87.0	13.0	37.2	3.39	1.90
White Band near Wall	2	66.3	33.7	6.6	8.15	1.03
Crucible Wall	1	25.7	74.3	33.9	1.12	1.00

Discussions

This present discussion tries to elucidate the sequence of events just after the ignition of magnesiothermic reaction leading UF_4 to metallic uranium:

It is feasible to suppose that the metallic magnesium also oxidizes during the heating of the load before the ignition, due to oxygen remaining in the atmosphere of the reactants. This, in a certain grade, prevents the reaction to happen before it reaches the ignition moment, since there is not a direct contact of magnesium to UF4. In routine reaction, all reactants reaches the temperature level of approximated 640°C, which is considered the ignition temperature. This point is very near to magnesium melting temperature at 651°C. As a possible hypothesis, the ignition is promoted by magnesium vapor breaking through the thin layer of magnesium oxide covering the magnesium particle. The Mg vapor reaches the nearest UF_4 powder grains. The first reaction happens between a solid UF_4 and magnesium vapor. At this point, it provokes the first spark of ignition promoting a high exothermic reaction (reaction 1) forming locally the first quantity of metallic uranium and magnesium fluoride. The following-up is a chain reaction between solid UF_4 grains and Mg vapor. It evolves vigorously throughout the reactants in a driven explosion blast.

This full mass reacts in approximately 800 to 1200 msec. In this short time, it is not safe to rely in any equilibrium thermodynamic system. All the physical-chemical events happen very quickly and under a substantial rising of pressure, not yet quantified. After the opening of the reaction chamber, it is observable that even the CaF_2, put on top of the reactants to compensate UF_4 density variation, is partially melted. The melting point of CaF_2 is 1418°C. This is an indication that the temperature during reaction reaches values higher than that, probably rising higher than 1500°C. At this temperature, all loaded Mg would be vaporized (boiling point at 1091°C). If any remainder UF_4 exists, it may exist either as a liquid or as a gas (melting point at 1036°C; boiling point at 1417°C).

Analyzing the slag in Figure 3, it may be said that there are at least 4 great events during the reaction moment, characterized by the solidified layers. These events could be discussed on the basis of relationship of MgF_2 and CaF_2 contents.

Closer to the crucible wall, the solidified slag shows a much greater content of CaF_2 than MgF_2 (3:1 proportion) and displays a dark crystal. This darkness of the crystal, from Rietveld analysis

did not have enough acquired carbon from the graphite crucible. It might have helped to darken the structure of the first layer. As the Rietveld's results indicate virtually no texture for CaF_2, it indicates that the solidified CaF_2 is near to polycrystalline fluoride formed under high pressure. Fluoride is a crystal that tends to have a dark greenish-violet color. From this analysis, for this first layer, it is able to conclude that the temperature went above the CaF_2 melting point, taking away the CaF_2 put in the top load, in the region of starting ignition, melt it and project it towards the crucible wall. The liquefied CaF_2 had relatively short time to solidify the projected liquid at the crucible wall, with great nucleation sites but without limited growing. The texture of the crystal is very near to 1 (polycrystalline).

At this stage, it is plausible to say that the magnesiothermic reaction actually happens between the reactants UF_4 and Mg both in vapor state, since the temperature became high enough for exothermic heat, and produced molten metallic uranium and MgF_2. As observed in XRD analysis, virtually not much uranium was projected towards the crucible wall. So only the lighter products (CaF_2 and MgF_2) were blasted towards the wall and solidified. Most liquid uranium droplets went directly towards the crucible bottom and solidified there. All the temperature was quite above uranium melting point at 1036°C and even much higher than the MgF_2 at 1280°C. The proportion variation of CaF_2 composing all layers' zones throughout the projected molten material, it is possible to say that the temperature was above 1417°C (melting temperature point of CaF_2). Since the crystal structure of the projected slag displayed no material fluency downwards, this is an indication that the difference of temperature was not so high from the melting points under probably high pressure. As the texture of crystallized slag raised from layer 2 to 4, it may indicate that the crystals were formed under less stress with the process of nucleation and growing with a relative high temperature above the melting temperature.

Almost no magnesium was identified inside the slag sample; nevertheless, there is "magnesium bubbles" layer between layer 2 and 3, which was not yet fully studied, but being a result of a very vigorous blast, probably marking the peak of the magnesiothermic reaction. This is confirmed by the most texturized crystals (nucleation followed by growing) in layer 3 and 4. In addition, the amount of MgF_2 increased steeply in layer 3, showing that the major part of the reaction had already been happened, when this part of the sample was formed.

Finally, the last deposition over the final inner layer surface, was from magnesium forming bubbles over the inner layer of the slag at temperatures below 651°C, as shown in Figure 3 (a,b and c). In the transverse views, there are bubbles of many sizes, showing that this process lasted enough to allow nucleation and growing. In fact, 15% excess of magnesium loaded with UF_4 was more than enough to assure full reaction.

Conclusions

From projected slag at the midway of crucible wall, it was analyzed the sequence of events just after the ignition of magnesiothermic reaction to produce metallic uranium. The major characteristics of these events, based on XRD and Rietveld analysis, reveal the sequence of the reaction just analyzing the crystallization of the slag. The major constituents of the slag were CaF_2 and Mg_2F. Mg_2F is crescent in content from the crucible wall towards the inner side. In the same direction also increases the texture of the crystallized materials. There was no

fluency of the material, showing that the solidification happened in temperatures above the melting point of CaF_2 (1417°C). From the slag, it is possible to see, the reaction peak moment from a plane formed by projected magnesium small bubbles inside the slag sample. The further deposited CaF_2 and Mg_2F happened with increasing of crystallographic texture indicating that the temperature declined as this structure was being formed. Magnesium deposited finally over the crystallized layer, indicating that this process had enough time to happen, displaying spheres of several sizes showing that a mechanism of nucleation and growing took place in this process as the crucible decreased its temperature.

Acknoledgements

References

[1] Harper J, Williams AE. Factors influencing the magnesium reduction of uranium tetrafluoride. Extraction and Refining of Rarer Metals. London: The Institute of Mining and Metallurgy; 1957. p. 143-62.

[2] Katz JJ, Rabinowitch E. Part 1 - The elements, its binary and related compounds. The Chemistry of Uranium. New York: McGraw-Hill; 1951.

[3] Huet H, Lorrain C. Magnesothermal Process for Preparation of Metallic Uranium. Energ Nucl-Paris. 1967;9:181-&.

[4] Kubaschewski O. High-Temperature Reaction Calorimetry - Potentialities, Limitations and Application of Results. Thermochim Acta. 1978;22:199-209.

[5] Perrotta JA, M. Neto A, Durazzo M, Souza JAB, Frajndlich R. IRRADIATION EXPERIENCE OF IPEN FUEL AT IEA-R1 RESEARCH REACTOR. In: RERTR ANL-, editor. 1998 International RERTR Meeting. São Paulo: RERTR; 1998.

[6] Saliba-Silva AM, Souza JAB, Frajndlich EUC, Perrotta JA, Durazzo M. First Results of U3Si2 Production and its Relevance in the Power Scaleup of IPEN Research Reactor IEA-R1m. In: RERTR ANL, editor. 1997 International RERTR Meeting. Jackson Hole, WI: RERTR; 1997.

[7] Beltran AD, Rivaz Diaz M, Sanchez AF. Fabricación de Uranio Metal. Energia Nuclear - Publicacion Bimestral de la Junta de Energia Nuclear (España). 1972:294-320.

[8] Rand MH, Kubaschewski O. The Thermochemical Properties of Uranium Compounds. London: Oliver & Boyd; 1963.

[9] Saliba-Silva AM, Urano de Carvalho EF, Riella HG, Durazzo M. Research Reactor Fuel Fabrication to Produce Radioisotopes. In: Singh N, editor. Radioisotopes - Applications in Physical Sciences: InTech; 2011.

[10] Fornarollo F, Frajndlich EUC, Durazzo M. Recuperação de Escórias geradas na produção de urânio metálico. Revista Brasileira de Pesquisa e Desenvolvimento. 2006;10:158-64.

[11] Saliba-Silva AM, Martins IC, Oliveira ET, Pereira JV, Durazzo M. ESTUDOS TÉRMICOS E FÍSICOS PARA VIABILIZAR A REDUÇÃO METALOTÉRMICA DE URÂNIO METÁLICO A PARTIR DE UF4. Revista Brasileira de Pesquisa e Desenvolvimento. 2006;8:85-90.

[12] Frajndlich EUC, Saliba-Silva AM, Zorzetto MA. ALTERNATIVE ROUTE FOR UF6 CONVERSION TOWARDS UF4 TO PRODUCE METALLIC URANIUM. In: RERTR ANL-, editor. 1998 International RERTR Meeting. São Paulo: RERTR; 1998.

[13] Saliba-Silva AM, Durazzo M, Urano Carvalho EF, Riella HG. Fabrication of U3Si2 Powder for Fuels Used in IEA-R1 Nuclear Research Reactor. Materials Science Forum. 2008;591-593:194-9.

[14] Larson AC, Von Dreele RB. General Structure Analysis System (GSAS). Los Alamos National Laboratory Report; 2000.