



Manufacturing low enriched uranium metal by magnesiothermic reduction of UF₄



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ABSTRACT

This work presents an experimental description of thermal and physical studies to attain a practical manufacturing process of uranium metal enriched to 20% U²³⁵ (LEU – Low Enriched Uranium) by metallothermic reduction of UF₄, with nuclear purity, for reduced amounts (1000 g of uranium) and with radioactive safety. Uranium metal is needed to produce nuclear fuel elements based on uranium silicide (intermetallic U₃Si₂) and irradiation targets to produce Mo⁹⁹. This process is a part of Brazilian efforts to fabricate the fuel elements for its research reactors, primarily aiming at the production of radioisotopes for nuclear medicine. The magnesiothermic reduction is influenced by variables which are related to the starting material UF₄ and the thermal conditions for its reduction. These variables are investigated. The physical arrangement of the crucible/reduction reactor/furnace system and the management of the furnace thermal input in the reduction reactor during the heating were studied. Thermal simulation experiments provided delineation for the reactants' thermal progress before the ignition of the metallothermic reaction. The heat input to the reduction system has proved to be the main variable that influenced the efficiency of the process. The levels of metallic yield and reproducibility have been improved, making the production process reproductive and economically viable. The typical yield in the production of uranium metal was above 80%. Unrecovered uranium metal is present in the MgF₂ slag and can be recovered at the level of 96% yield. The process of recovering the uranium from the slag is also discussed.

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1. Introduction

The production of uranium metal is necessary to produce the intermetallic U₃Si₂ which is the modern basis for manufacturing the nuclear fuel used in nuclear research reactors (Keiser et al., 2003; White et al., 2014; Finlay and Ripley, 2001; Nuclear Regulatory Commission, 1988). Uranium metal is also necessary for manufacturing irradiation targets to produce ⁹⁹Mo by nuclear fission (International Atomic Energy Agency, 2013). These targets are based on the UAl_x-Al dispersion or thin foils of uranium metal (Lisboa et al., 2015; Stepnik et al., 2013; Jollay et al., 2011).

There are several possibilities for producing uranium metal (Harper et al., 1957; Katz and Rabinowitch, 1951). In the decade of 1930–40, uranium was produced from metallothermia with Na and Ca from UCl₄. In the 1950s, in the context of worldwide interest in nuclear technology, several technologies were developed to obtain uranium metal: by electrolysis from the KUF₅ salt, by UO₂

metallothermia with Ca and Mg, and by metallothermia of UF₄ with Ca and Mg. Magnesiothermic reduction of UF₄ is a known process since the early 1940's (Huet and Lorrain, 1967; Kubaschewski, 1978).

Normally, calciothermic reduction of UF₄ is preferred worldwide since the exothermic heat is –109.7 kcal/mol if compared to a smaller amount of –49.85 kcal/mol produced using magnesium as the reducer (Rand and Kubaschewski, 1963). Nevertheless, the Nuclear and Energy Research Institute – IPEN/CNEN-SP in the nationalization process to produce its own nuclear fuel for research reactors and target fabrication (Osso et al., 2013; Obadia and Perrotta, 2010), decided for the magnesiothermic process of uranium tetrafluoride (UF₄) since it is easier to be done avoiding handling of toxic and pyrophoric calcium. Moreover, the magnesiothermic process is cheaper since magnesium is cheaper than metallic calcium. Thus, there is an economic compensation despite the unfavorable thermochemistry of reduction with magnesium when compared with reduction with calcium.

Magnesiothermic reduction employs metallic magnesium as a chemical reducer of uranium. Magnesium is mixed with stoichiometric excess to uranium tetrafluoride (UF₄), which is produced

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from UF₆ hydrolyzed in HF solution. The hydrolyzed solution is then reduced by stannous chloride to UF₄ (Frajndlich et al., 1998; Saliba-Silva et al., 2008). UF₄ is a greenish substance which, mixed with magnesium, can be reduced to uranium metal under adequate thermal conditions. This reaction is intensely exothermic. The reaction is:



$$\Delta H = -49.85 \text{ kcal/mol (at } 640 \text{ }^\circ\text{C)}$$

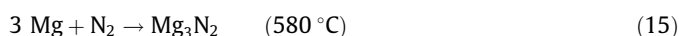
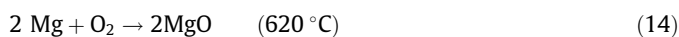
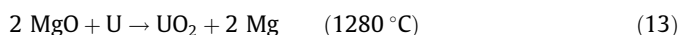
The reaction products utilize the resulting exothermic heat and melt to form the uranium ingot at the bottom of the crucible and the slag. The supernatant slag, which is formed essentially by MgF₂, solidifies at the top of the ingot. Considering the calculations of Rand and Kubaschewski (1963), the sum of the heat produced by this reaction and the latent heat to melt the products give a reaction heat of -49.85 kcal/mol . Therefore, this is the resulting heat available to heat the products. Assuming that 49 cal/mol is required to raise one degree centigrade of the reaction products, it has been shown that the possible increase in temperature would be only $1017 \text{ }^\circ\text{C}$. This average heating is based on water, as a calorimetric reference, which uses $7 \text{ cal/}^\circ\text{C}$ for each atomogram. In the case of $2\text{MgF}_2 + \text{U}$, there are 7 atoms present which, therefore, need $49 \text{ cal/}^\circ\text{C}$ (Rand and Kubaschewski, 1963). However, this heat is not sufficient to reach the melting reaction products if the reaction occurred at room temperature (U melts at $1132 \text{ }^\circ\text{C}$ and MgF₂ at $1255 \text{ }^\circ\text{C}$). Therefore, these fusions are only possible if there is a pre-heating of the reactants before the reaction, as predicted by Harper et al. (1957) for this process.

In addition to these thermal problems, chemically there are a number of undesirable secondary reactions that can contaminate and reduce the reaction yield. Among these reactions, we have:

1- In the presence of moisture:



2- Other undesirable reactions:



As can be seen from reactions (2)–(15), there is a potential formation of various undesirable products (UO₂, UO₂F₂, UF₃, MgO and

Mg₃N₂) during the reduction process. These products lower the yield of the system and can impair the production of uranium with nuclear purity. In this way, it is seen that the reduction system should be properly designed so as to avoid all such secondary reactions.

Our research center decided to use this route in 1970–80's for producing 100 kg ingots of natural uranium. However, for low enriched (LEU) U-production, it is necessary to handle safe mass (less than 2.2 kg U) to avoid possible criticality hazards. We started studying the magnesiothermic reduction in the late 1990's to produce small amounts of enriched uranium (around 1000 g LEU ingots) (Perrotta et al., 1998; Saliba-Silva et al., 1997). This range of LEU U weight is rather small if compared to big productions of natural uranium. Uranium metal is reported (Beltran et al., 1972) to be produced with 94% metallic yield when producing bigger amounts of raw material. The magnesiothermic process downscaling to produce LEU has small possibilities of achieving this higher metallic yield. This is due to the design of crucibles, with a relatively high proportion of surrounding area, which is more prone to withdrawing evolved heat from the exothermic reaction during uranium reduction. The reduction reaction initiates by means of spontaneous ignition. As magnesium thermodynamics is less prompt to ignite than calcium, the batch reactor must be heated up to a temperature around $620 \text{ }^\circ\text{C}$. The routine shows that this ignition normally happens some degrees below this temperature (Beltran et al., 1972).

In general, the production of uranium metal takes into account the following recommended procedures:

- a) Physical Containment. The reaction charge and products must be kept fully contained during the loading, heating, reaction, cooling and disassembly processes without causing environmental damage and nuclear contamination.
- b) Chemical Insulation. In order to prevent undesirable reactions, the system must be inerted with noble gas (continuous argon flux) for keeping the system free from the presence of oxygen and moisture.
- c) Thermal Supply System. The reduction reactor system and graphite crucible system with the reduction charge shall allow a suitable thermal flow for heating the entire charge with a thermal profile such as to ensure controlled and minimized thermal differences between the different regions of the charge at the moment of ignition.
- d) Charging and Discharging. The charging of the reagents (UF₄ + Mg) for reduction must be done inside a glove-box to avoid hygroscopy and contamination of the reduction charge with O₂ and contamination of the external environment with nuclear material. The crucible should be handled for closing and opening inside a glovebox. The opening of the crucible to extract uranium ingot and the slag is fully carried out inside an inerted atmosphere to prevent pyrophoricity (uranium is a pyrophoric material and the eventual burning of uranium turns it into highly toxic powdery oxide, harmful to health when inhaled).
- e) Uranium Recovery. The generation of nuclear waste should be minimized to the maximum, with safe handling for charging and discharging. Unreacted material and uranium metal entrapped in the slag must be recovered since uranium metal is an expensive, rare and dangerous material.

Based on these recommended procedures, we designed an infrastructure to produce small amounts of LEU metal. However, in the initial reduction tests, the process did not prove to be reproducible since the yield in produced uranium metal varied over a wide range, from 20% or less to 90% or even more.

The objective of the present work was to investigate the possible causes that affected the yield of the process in order to achieve

a stable and reproductive process for the production of LEU metal with the best possible yield. Some variables related to UF_4 powder were investigated. A physical adaptation of the furnace and reactor set was performed and thermal parameters were developed in order to establish a routine for the production of LEU metal. The routine for uranium metal production must also consider the recovering of unreacted UF_4 or unseparated uranium. The development to achieve better procedures for uranium recovery from the MgF_2 slag was also envisaged.

2. Experimental procedures

2.1. Magnesiothermic reduction of UF_4

A standard reactant charge was fixed at 1815 ± 5 g of the UF_4 + Mg mixture (1540 ± 1 g UF_4), containing 15% excess Mg in addition to the stoichiometric amount. In this charge, there is a theoretical mass of 1154 g of uranium metal in the form of UF_4 . The objective was to obtain around 1000 g of LEU metal.

The preparation of the charge was done keeping a homogeneous mixture of UF_4 with Mg. As these materials have a great difference in densities ($\rho_{\text{UF}_4} = 6.72$ g/cm³ and $\rho_{\text{Mg}} = 1.74$ g/cm³), a stratified charge was made. For homogenization purpose, the charge of UF_4 + Mg was divided into 10 layers tapped one by one inside a graphite crucible, each layer containing the blend in the desired proportion. This operation was performed inside a glove box using a V type homogenizer mixer.

The height of the charge inside the graphite crucible varied mainly due to the variability of the tapping operation of the charge layers, which was performed manually. To fill the empty space between the top of the charge and the graphite crucible cap, a variable amount of CaF_2 was tapped over the UF_4 + Mg charge in the crucible to fully complete the reaction volume. CaF_2 was used for being readily available.

The charge bulk density was calculated based on the volume of the crucible filled with the charge. The occupied volume was calculated from the measured value of the distance from the top of the charge to the edge of the graphite crucible, which has a known height. This measurement was carried out using a ruler inside the glove box. Due to the difficulty in reading the measured value, the error in the reading was considered to be 2 mm. The maximum associated error in the calculated charge bulk density was considered to be around 0.05 g/cm³.

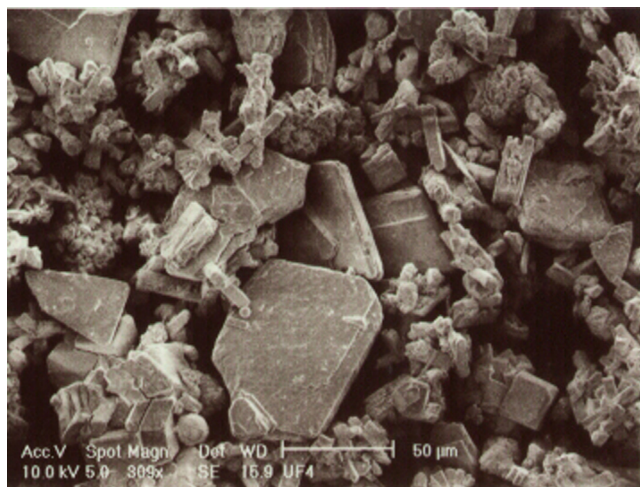


Fig. 1. Scanning Electron Microscopy (SEM) showing UF_4 particle morphology (secondary electrons).

The typical appearance of UF_4 used in this work is presented in Fig. 1 (Frajndlich et al., 1998). The magnesium used was in the form of granules of size $-12 + 50$ mesh (0.3–1.7 mm). The purity was 99.8%.

The crucible was made of fully machined graphite volume with enough resistance to produce safe nuclear uranium amounting to around 1000 g. This crucible was designed to withstand the blast impact of metallothermic reaction, as well as thermal cycles of heating and cooling without excessive wear in order to be used in several batches. Fig. 2 shows a view of the graphite crucible with the UF_4 + Mg charge. The graphite crucible was not lined.

After closing the graphite top cover, the crucible was inserted inside an ANSI 310 stainless steel cylindrical reactor vessel, which allows argon fluxing during batch processing (1 L/min with 2 kgf/cm² of pressure). As shown in Fig. 3, the whole crucible + reactor was placed in an electric-powered pit furnace with four programmable zones having the possibility of raising the temperature up to 1200 °C. The reaction vessel was heated and the reactants ignited spontaneously. The reaction of UF_4 with Mg produces an intense exothermic heat release inside the crucible. It is considered as an adiabatic reaction. It produces uranium metal and MgF_2 slag in liquid form. Both products deposit in the crucible bottom and are easily taken apart after opening and discharging the crucible. The exact moment of spontaneous ignition and reaction time was detected and recorded by sound waves, using an accelerometer.

The whole system developed for the magnesiothermic reduction of UF_4 is shown in Fig. 4. This figure shows the graphite crucible set and the reduction reactor inserted in the furnace inner for heating. The dimensions shown in Fig. 4 correspond to the current system. The reduction reactor consisted of a cylindrical vessel with pipes necessary for the introduction of argon and the exit of gases inside the reactor. The reactor head is cooled with airflow. This vessel can withstand positive pressure up to 4 atm.

After the reaction, there was a 10-min wait for full solidification of the reaction products inside the furnace. Then, the furnace energy was turned off and the reactor vessel was lifted out of the furnace. There was another wait for a period of 16 h to provide complete cooling before its opening for discharging. This avoids uranium metal pyrophoricity, which may happen when this metal is exposed to atmospheric oxygen.

The unassembly of reduction set was performed inside a glove box inertized with argon. The top and bottom crucible covers were then removed. By means of rubber soft hammering, it was able to withdraw the uranium ingot. The MgF_2 slag was removed by



Fig. 2. View of the graphite crucible with the UF_4 + Mg load after tapping the 10 layers.



Fig. 3. Charging of the reactor vessel inside the pit furnace.

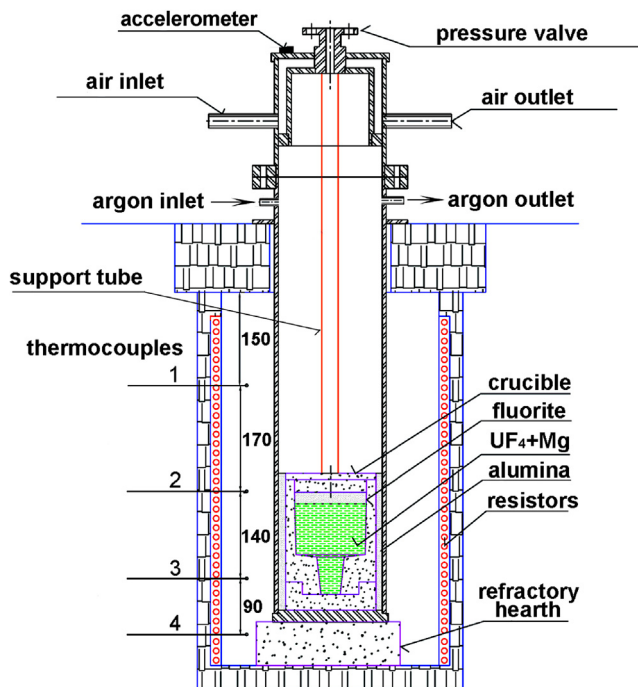


Fig. 4. Schematic drawing of pit furnace, reactor vessel and crucible.

mechanical cleaning. The uranium metal was pickled in nitric acid 65%vol and the final mass of uranium metal was measured and its density evaluated by Archimedes' method. Fig. 5 shows the reacted

charge with the slag at the top and the uranium metal at the bottom (A) as well as the uranium ingot after pickling (B).

Following these procedures, the efficiency on uranium metal fabrication was tested by processing 20 precipitation batches of UF_4 made on a large scale (50 L) and employing optimized $UO_2F_2 + HF + SnCl_2$ solution at a temperature range of 92 ± 3 °C with resting time for precipitation during 24 h (Frajndlich et al., 1998; Saliba-Silva et al., 2008). About 3000 g of natural UF_4 was produced for each batch. The magnesiothermic process was used to reduce this material to uranium metal by using 40 magnesiothermic reduction operations. After each reduction, the metallic yield was calculated as the ratio between the mass of uranium metal produced after reduction and the total uranium contained in the UF_4 prior to this reduction.

2.2. Uranium recovery from slag

The slags directly obtained from the tests described above were first calcinated in air to promote oxidation. During this process, uranium metal was oxidized to U_3O_8 in order to facilitate maximum leaching. For the calcination, a 10 kW resistive furnace was used to apply different temperatures and time periods for calcination. Uranium metal is unstable, pyrophoric and extremely reactive. Without calcination, slags containing levels exceeding 70 wt % uranium are pyrophoric and could suffer spontaneous combustion. On the other hand, the stable oxide U_3O_8 has low chemical reactivity and is easily handled, justifying the implementation of calcination step for the slag treatment.

After calcination, the material was crushed in order to decrease the size of particles containing oxidized uranium compounds. The crushing increases the specific open surface of the material, which provides a better reaction efficiency in the latter leaching process. To reduce particle size, a ball mill was used with alumina balls and 10 L capacity pot with dimensions of $30 \times \varnothing 20$ cm. The slag was ground for 8 h with a rotation speed of 200 rpm. The slag was then classified by granulometry through sieving. The obtained material after grinding showed all particles with a size smaller than 150 μm . This material was used in the leaching tests.

After crushing, the material was treated with a nitric leaching operation. The leaching solution was prepared with a ratio of 0.025 mol of HNO_3 per gram of uranium. Part of this solution was added to the reactor and the slag was slowly fed together with the remaining HNO_3 solution. This process was conducted during 12 h, with reaction temperature control and with a constant stirring of 300 rpm. An impure uranyl nitrate solution ($UO_2(NO_3)_2$) was then obtained. This solution was vacuum filtered and treated for purification with an organic solvent, the tributylphosphate diluted to 30 vol% with isoparaffins.

After $UO_2(NO_3)_2$ purification, the solution was reacted with gaseous ammonia to precipitate ammonium diuranate (ADU). The ADU was calcinated at 600 °C for 3 h, thereby obtaining pure U_3O_8 . The U_3O_8 produced was converted into uranium tetrafluoride (UF_4) by reacting with stannous chloride ($SnCl_2$) and hydrofluoric acid (HF) inside a precipitation reactor.

The UF_4 was then treated under argon atmosphere in a heating furnace at 400 °C in order to remove crystallization water. Once UF_4 is duly qualified it returns to production route of uranium metal as a raw material for the magnesiothermic reaction.

3. Results and discussion

3.1. Metallic yield

As shown in reactions (4)–(7), the UO_2F_2 and UO_2 content in dried UF_4 is the main source of oxidized products that will not

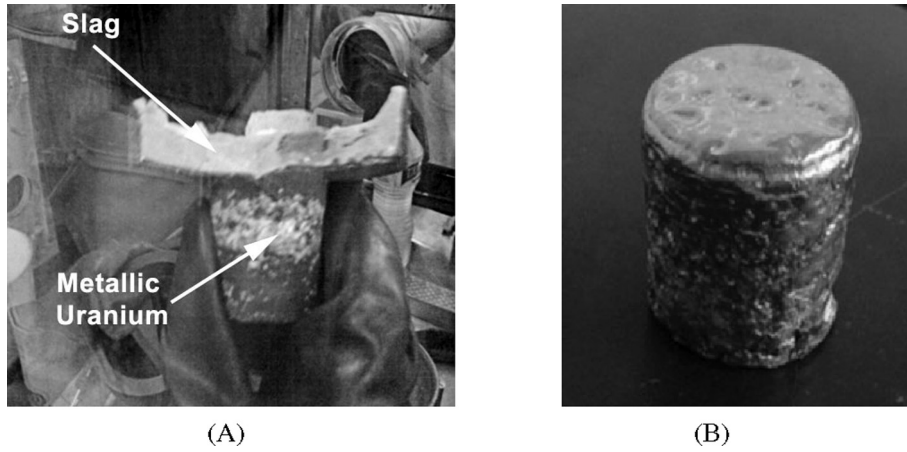


Fig. 5. (A) Raw uranium metal and upper deposited slag after its removal from the crucible; (B) Uranium metal after cleaning.

be reduced by magnesiothermic means, so it is one of the possible sources of metallic yield loss. The influence of their presence, as identified by chemical analysis, on the metallic yield was studied. The UO_2F_2 content varied from very small quantities (almost zero) to the maximum content that was observed experimentally in 20 produced batches, around 0.42 wt%. The UO_2 content varied from 0.02 to 0.28 wt%.

Fig. 6 shows the influence of the UO_2F_2 content in UF_4 on the metallic yield of the reduction to uranium metal. It would be expected that the presence of UO_2F_2 would be relevant in magnesiothermic reaction since it leads to having less U-production caused by no reactivity of U-oxides and Mg in this reaction process. This would impact directly on the metallic yield performance. Probably, besides the UO_2F_2 crystals previously formed during UF_4 drying, more UO_2F_2 and UO_2 could be formed during magnesiothermic heating when moisture (at 100 °C) and crystallization water (>400 °C) evolve. Reactions (2)–(6) show that this oxidation is very prone to happening under moisture presence with a high temperature (around 600 °C) and with relatively long residence time inside a confined vessel.

Fig. 7 shows the influence of the UO_2 content in UF_4 on the metallic yield of the reduction to uranium metal. All individual data are shown.

The bulk density of the charge varied in the range of 1.70 to 2.05 g/cm^3 . The height of the CaF_2 layer varied between 12 and

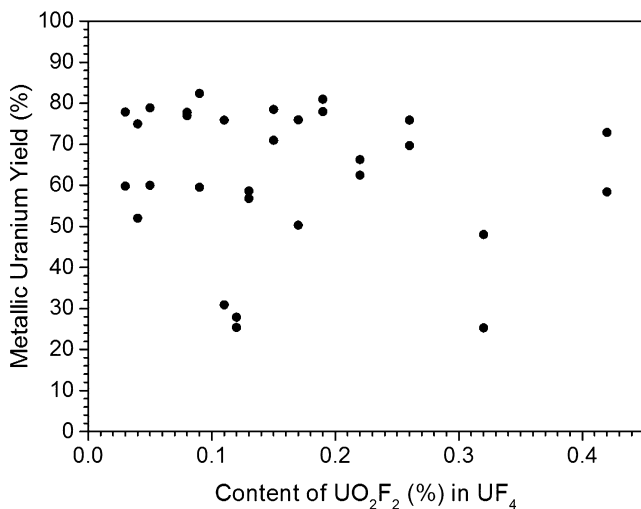


Fig. 6. Influence of UO_2F_2 content in dried UF_4 on metallic yield.

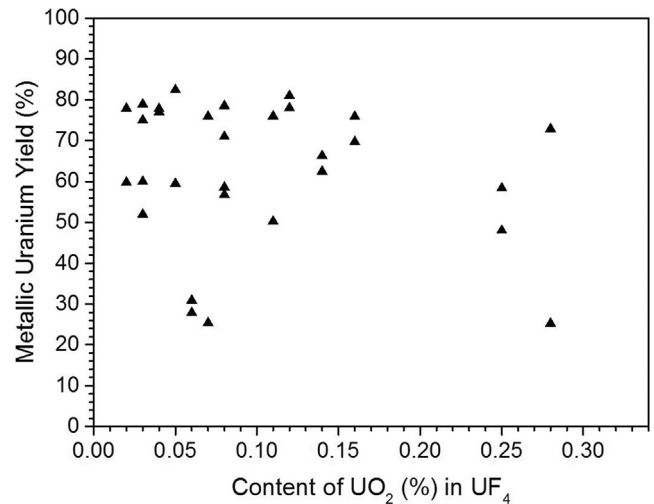


Fig. 7. Influence of UO_2 content in dried UF_4 on metallic yield.

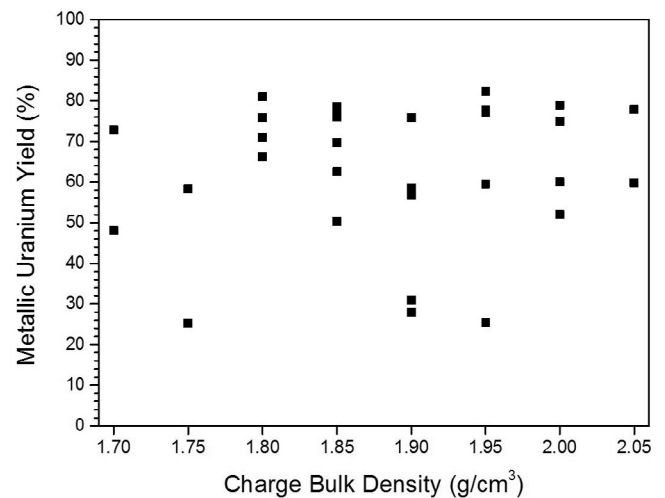


Fig. 8. Influence of charge bulk density on metallic yield.

32 mm. Fig. 8 shows the influence of the charge bulk density on the metallic yield of the reduction to uranium metal. All individual data are shown. The results show that there is no apparent correlation between the charge bulk density and the yield of the

reduction process. Although the thermal conductivity of the charge is affected by the density variation, the high yield variation cannot be attributed to the variations in the charge bulk density.

Figs. 6–8 show the great variability observed in the metallic yield, which cannot be explained by the presence of UO_2F_2 and UO_2 in the $\text{UF}_4 + \text{Mg}$ reduction charge or by the charge bulk density variations. Considering the great variability observed in the metallic yields, it cannot be affirmed that there is a correlation between the metallic yield and the UO_2F_2 and UO_2 concentrations in the range studied. The same can be said about the charge bulk density. The variation of the charge bulk density also reflects the variation of other physical characteristics of UF_4 that could affect the yield of the reaction, such as particle size and reactivity (specific surface area). Therefore, these physical characteristics do not appear to play an important role in the observed variability in metallic yields. Another powerful variable must be acting.

Fig. 9 shows the variation of the metallic yield obtained in the first 30 reductions performed with natural uranium. A great variability was observed, from 20 to 86%.

Seeking to understand the big variations observed in the metallic yield in the first magnesiothermic reductions, the slags formed after each reaction were fully inspected, trying to correlate any distinctive attribute or aspect with the reaction yield. The magnesiothermic operational routine and evidence after dismounting the crucible to remove uranium ingot lead to the reasoning about the moments before, during and after the ignition. The sequence of events that is proposed to take place during the magnesiothermic reduction of UF_4 is illustrated in Fig. 10. The proposed sequence of events would be as follows:

1. Crystallization water and moisture are released during heating and this water is expected to promote the surface oxidation of UF_4 (reactions (2)–(6)). The evidence for this is the production of water collected at an external Erlenmeyer, through which passes the fluxed argon and evolved gases from the system. These gases promote an extra bubbling inside the Erlenmeyer when the load first reaches temperatures around 100 °C. When the charge reaches the range between 400 °C and 500 °C, the heating process reveals, for the second time in the heating process, another extra bubbling showing the evolution of crystallization water developing from the charge. This observation indicates that UO_2F_2 and UO_2 are being formed and will reduce the yield of the process to some degree.

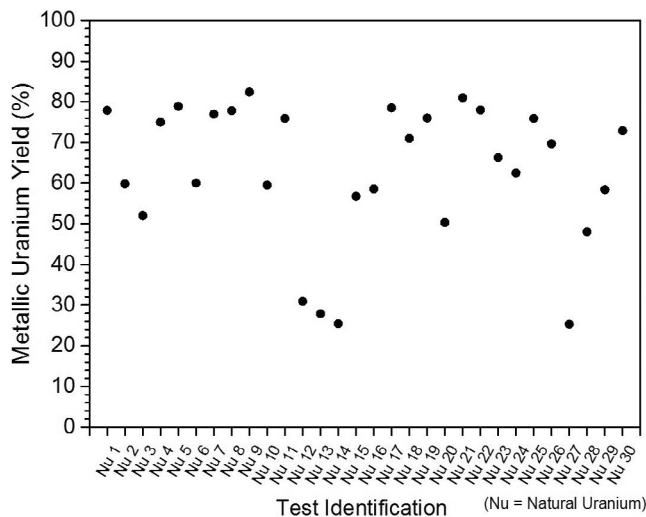


Fig. 9. Initial variability of yield in the uranium metal production by magnesiothermic reduction of UF_4 .

2. It is feasible to suppose that the metallic magnesium also oxidizes (reaction 14). This, in a certain grade, prevents the reaction from happening before it reaches the ignition time moment, around 600 °C, which is very near to magnesium melting temperature at 651 °C.
3. The reaction moment happens quite near the magnesium melting point. As a possible hypothesis, the reaction ignition is promoted by the vapor of magnesium breaking 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 uranium metal and magnesium fluoride. The following-up is a chain reaction between solid UF_4 grains and Mg vapor that evolves vigorously throughout the reactants in a driven explosion blast. From this moment onwards, the temperature swiftly promotes the nucleation of sparks erupting all through the whole mass of reactants.
4. This full mass reacts in approximately 500 to 800 ms. In this short time, it is not feasible to rely on any equilibrium thermodynamic system. After the opening of the reaction chamber, it is observable that even the CaF_2 put on top of the reactants is partially melted. The melting point of CaF_2 occurs at 1418 °C. This is an indication that the temperature during reaction reaches higher values than 1500 °C. At this temperature, all loaded Mg will be vaporized (boiling point at 1091 °C). If any remainder UF_4 exists it may be in vapor state (boiling point at 1417 °C).
5. At this stage, it is plausible to say that the magnesiothermic reaction firstly will be between solid UF_4 and Mg vapor, but will be hectic adiabatic explosion above 1100 °C after full melting of UF_4 (melting point at 1036 °C) and magnesium vapor (boiling point at 1091 °C), vapor-liquid reaction. Also, formed uranium (melting point 1131 °C) and all slag (MgF_2 fuses at 1280 °C) would be molten and goes down towards the crucible bottom.

The results of careful inspections of the crucible after reduction showed that the distribution of the MgF_2 slag inside the crucible had a direct relationship with the metallic yield. Three situations could clearly be observed:

- a) When the yield was good (above 80%), the slag was concentrated at the bottom of the crucible, over the uranium metal ingot. The presence of unreacted UF_4 and uranium metal in the slag was not observed visually.
- b) In the case of intermediate yields, between 80 and 70%, a considerable volume of adhered slag in the sidewalls of the crucible was observed. A smaller amount of slag was observed over the uranium metal ingot. Droplets of solidified uranium metal were observed entrapped within the adhered slag to the side of the crucible.
- c) In the case of low yields, below 70%, most of the slag was found on the walls and cover top of the crucible. Large quantities of uranium metal droplets could be seen entrapped within the slag.

These observations suggested that the most important factor that determines the yield of the reaction is the particular location where the ignition occurs within the charge. If the ignition or the blast onset occurs at the top of the charge, the front of the exothermic reaction shifts from above downwards, providing heat to efficiently melt the reaction products and to promote an effective separation between uranium metal and MgF_2 . The heavy uranium metal goes towards the crucible bottom, and the less dense slag solidifies above it during cooling. The efficient melting of the slag allows the uranium metal droplets, which are produced during

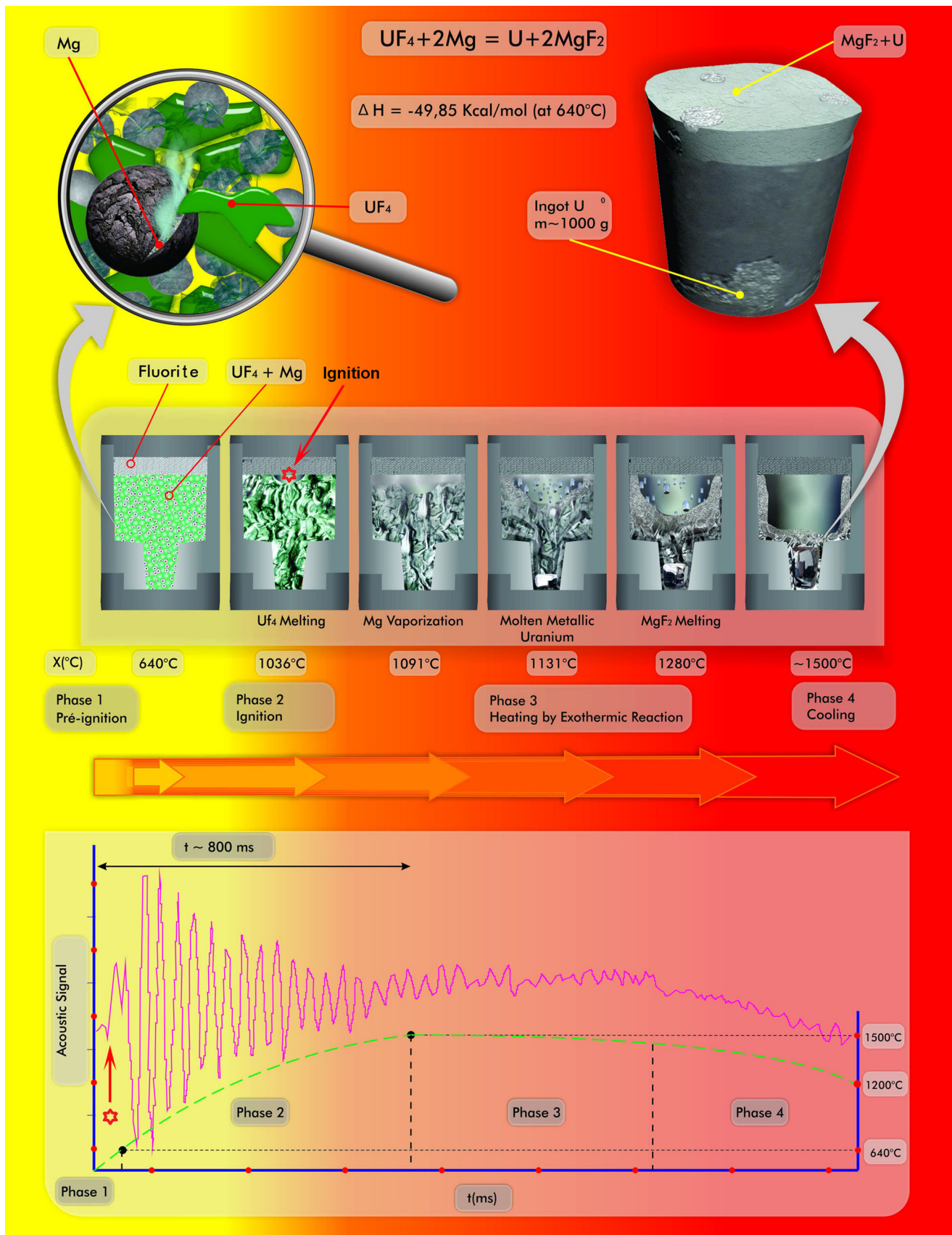


Fig. 10. Sequence of events during magnesiothermic reduction of UF₄ towards U metal.

the reaction, to separate from the slag duly and also going towards the crucible bottom. The efficiency of uranium metal separation from the slag defines the metallic yield of the reduction process.

When ignition occurs at the bottom of the crucible (or even at the center of the charge), the heat front of the exothermic reaction moves in opposition to the movement of the molten uranium metal produced. The blast throws the MgF_2 slag into the top cover and towards the side walls of the crucible, which solidifies at those places and partially entraps the uranium metal produced in the reaction (see Fig. 11). The yield greatly decreases in these cases because, although the reduction occurs, the produced uranium metal is not efficiently separated from the slag.

In order to collect data of the heating profile inside a UF_4 charge, with no Mg reducer, thermocouples were inserted inside the graphite crucible. The thermocouples were duly placed inside the graphite crucible to collect the heating profile at six points; at the top, middle and bottom positions of the charge. The side thermocouples (4, 5 and 6) were at a distance of about 5 mm from the crucible wall. This assembling was schematically made as shown in Fig. 11. The furnace has four independent heating zones with four thermocouples (F1tc to F4tc). Inoxidable steel protected k-type thermocouples were used (numbered 1 to 6) to record the temperatures inside the graphite crucible.

A preliminary experiment using the charge of $UF_4 + Mg$ allowed us to get the moment of charge ignition starting the reaction to produce uranium. This was a sacrificial test for the thermocouple. The thermocouple was placed at the top center position of the charge (position 3). The temperature of ignition was found to be around 620 °C.

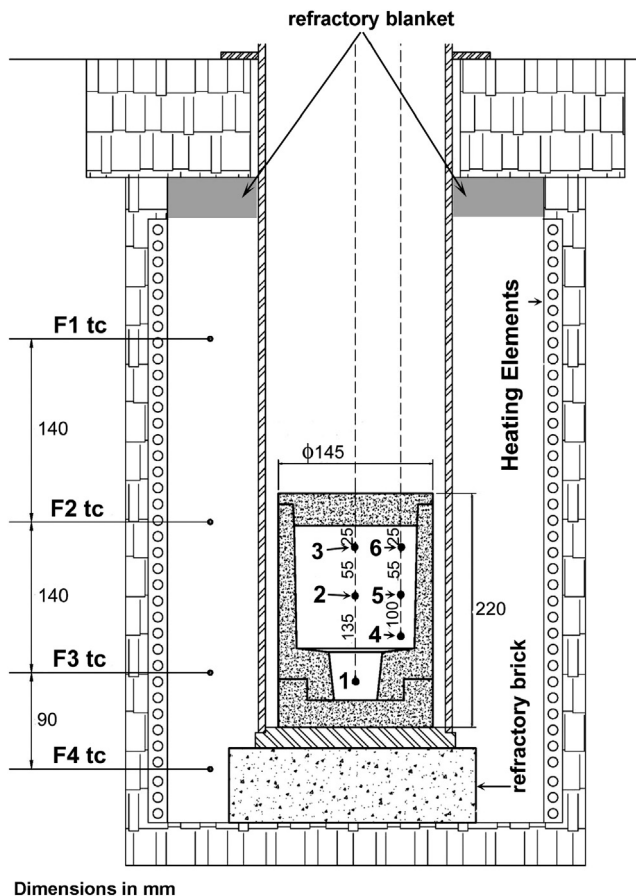


Fig. 11. Schematic assembly of the reduction reactor/crucible system inserted in the well.

A second experiment was carried out using only UF_4 , without Mg, and using six thermocouples placed accordingly inside the reduction reactor (Fig. 11). The heating of the reduction reactor started inside a cold furnace. The data for temperature profile lead to the graph presented in Fig. 12. All the four heating zones of the furnace were powered up to step up until 550 °C at a heating rate of 5 °C/min. The charge was left to soak for 60 min at this temperature and then the four heating zones of the furnace were powered up to reach 1000 °C at a rate of 5 °C/min. This profile is called “wild” heating procedure, since no fine control of heating setups and heat transfer was made. This profile was the one used in the initial tests, as shown in Fig. 9.

The results display crude differences between temperature evolution inside several regions of the bomb. The major one between top and bottom was 170 °C. The time to ignition, as recorded by the accelerometer, also varied over a wide range, from 220 to 330 min. Naturally, this is the profile that we would get without the possibility of checking the thermal profile evolution. This is the kind of result we had in the previous history of wide metallic yield variation in the uranium reduction procedures we had carried out, trying to do the reductions with no knowledge of the thermal profile. Fig. 12 shows the temperature profiles inside the “pseudo” charge of pure UF_4 following the “wild” heating procedure.

In practice, the reaction products should be heated to a temperature slightly above 600 °C for ignition of the reaction. From the data calculated by Rand and Kubaschewski (1963) only a preheating of 500 °C would be necessary, but in practice this value was around 570–620 °C, which indirectly confers a greater fluidity on the reaction products. This has been confirmed in practice by the preliminary experiment using the charge of $UF_4 + Mg$ to determine the temperature of ignition.

Assuming that the ignition occurs at 620 °C, as determined empirically, by examining the temperature profiles shown in Fig. 12, it is found that ignition occurs at the bottom of the charge. The highest temperatures are indicated by thermocouples 1 and 4, both at the bottom of the graphite crucible. This is an unfavorable situation and should be avoided, because when ignition occurs at the bottom of the crucible the heat from the exothermic reaction moves in opposition to the movement of the produced molten uranium metal. As already mentioned, the blast throws the MgF_2 slag into the top cover and sides of the crucible, which solidifies in these places and entraps the produced uranium metal. The yield declines in this case due to poor separation. The largest variations that were observed in the yields recorded in Fig. 9 should be related to the position in the charge where the ignition occurs. The more the ignition position moves to the top of the charge,

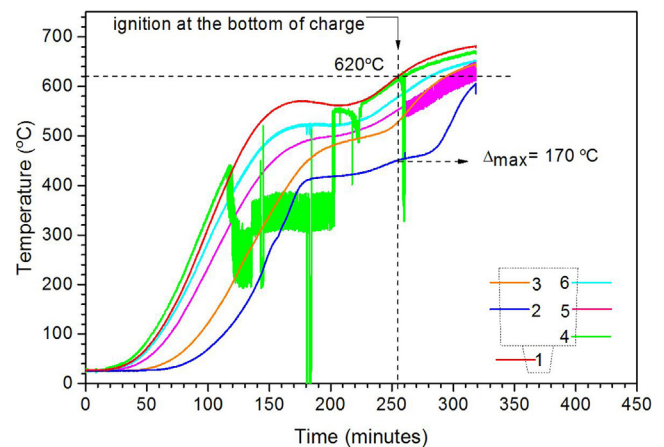


Fig. 12. Thermal profiles derived from the “wild” heating procedure.

the higher the metallic yields will be. If the ignition occurs in the regions at the bottom of the crucible, the yields will be lower.

Another unfavorable condition is related to the large temperature variation inside the charge at the moment of ignition, as shown in Fig. 12. The temperature difference reaches 170 °C between thermocouples 1 (bottom of the crucible) and 2 (center of charge). At the moment of ignition, the central region of the charge is around 450 °C, which is below the minimum preheating temperature calculated by Rand and Kubaschewski (1963).

The long time in which the charge remains at high temperatures before ignition should also have a negative impact on the efficiency of the reduction process. In Fig. 12 it can be observed that the charge remains up to 150 min at temperatures above 400 °C, which favors the occurrence of undesirable reactions that may cause the decrease in the metallic yield.

Based on these observations and discussion, it was clear that a new heating program should be developed. The new program must ensure a favorable temperature evolution within the charge, in the following aspects:

- the top of the charge should reach the ignition temperature (around 620 °C) before the bottom of the charge or even the central region. This ensures that the ignition will occur at the top of the charge, which favors the separation of the uranium metal by the reaction front displacement from top to bottom;
- keeping the top of the charge always at a higher temperature at the moment of ignition, the maximum temperature variation between the charge regions should be minimized so that no region is below 500 °C, as proposed by Rand and Kubaschewski (1963).
- the ignition should occur as soon as possible, avoiding exposure of the charge to high temperatures soaking for a long time.

Several heating programs were unsuccessfully tested. All simulations using UF_4 as charge (without magnesium) resulted in faster heating at the bottom of the charge. This was caused by the geometry of the system. The solution of the problem would depend on delaying the bottom heating of the graphite crucible and accelerating the top heating. This was accomplished by inserting a refractory brick (see Fig. 11) below the reduction vessel and inserting a refractory blanket into the open space between the reduction vessel and the wall of the furnace above the heating zone. With these small modifications, it was possible to develop a new heating program that favored the separation of the uranium ingot after the reduction reaction.

The new heating program consisted of raising all four furnace heating zones to 640 °C with the highest heating rate allowed by the furnace system, around 10 °C/min (varied from zone to zone). All heating zones were left for 240 min at this temperature and then the furnace was powered up to reach 1000 °C at a rate of 5 °C/min. The buck mass of the refractory brick placed below the reduction vessel slowed down the bottom heating of the graphite crucible. The better thermal insulation at the top of the reduction vessel accelerated the heating of the graphite crucible top. Fig. 13 shows the new heating profiles after the implementation of these modifications.

The thermal profiles achieved after these modifications were satisfactory since all the parameters seeking better heating were met.

The border top of the reduction charge in the crucible was the first position to achieve 620 °C (thermocouple 6). This is the likely place of the spontaneous ignition. The charge positions where the temperature was just below 620 °C were the center top and center of the charge in the central region (thermocouples 3 and 2), which

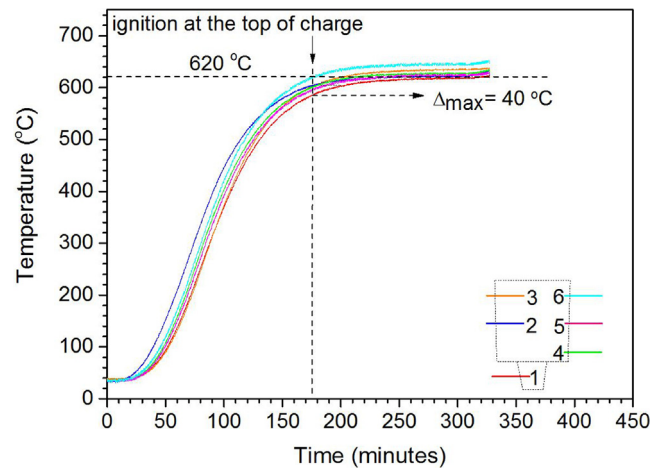


Fig. 13. New thermal profiles after adjusting the geometry of the system and heating procedure.

was also a favorable situation for the ignition path. The bottom of the charge (thermocouple 1) was the position that had the lowest temperature (580 °C) at the ignition flash. This means that it has the lowest probability to ignite the reaction at this location, which would be most unfavorable.

From the simulation, the maximum temperature difference between all regions of the reduction charge was only 40 °C, ensuring that all regions were above 500 °C at the time of ignition, which meets the minimum preheating suggested by Rand and Kubaschewski (1963).

The heating time until the ignition decreased significantly with the new heating program was from 255 to 175 min. The time at which the charge remained above 400 °C decreased from 150 to 85 min.

Based on these positive results, a further 10 reduction tests with natural uranium were carried out using this new heating program and the new system conditions. The results showed that the times elapsed until the ignition were reproducible, as shown in Fig. 14. The ignition time was determined experimentally with the use of an accelerometer. Fig. 15 illustrates a typical signal obtained with the accelerometer, allowing the precise determination of the moment of the reaction ignition.

The reproducibility of the ignition time demonstrates that the heating profiles shown in Fig. 13 have reproduced in the actual

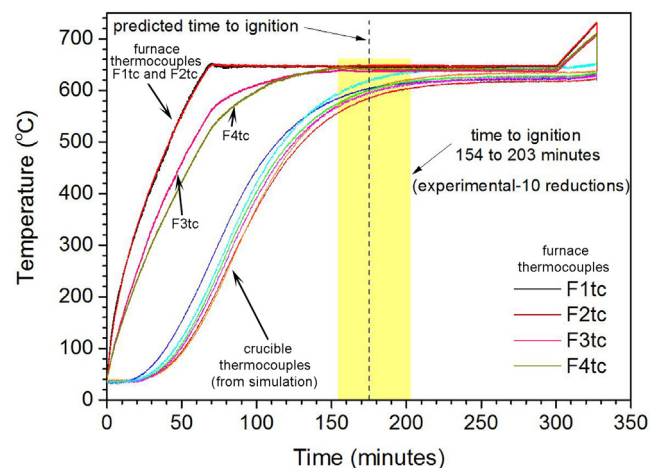


Fig. 14. Time to ignition in actual reduction tests after adjusting the geometry of the system and heating procedure.

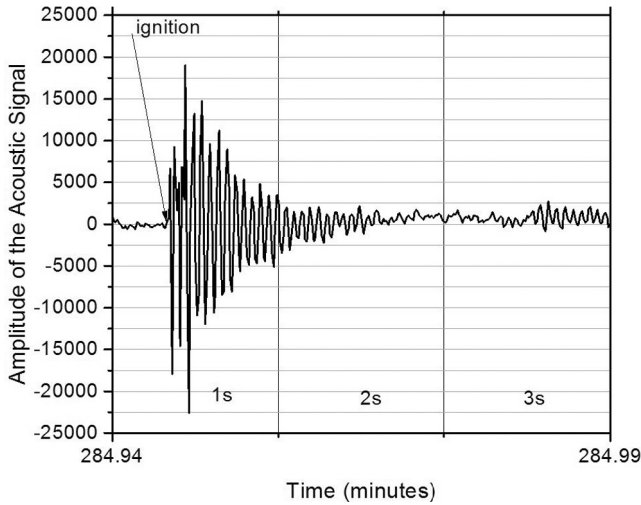


Fig. 15. Typical signal generated by the accelerometer to identify the exact moment of the reaction.

reductions. As a result, the ignition occurred always at the top of the reduction charge and the metal yields stabilized above 80%, as illustrated in Fig. 16.

Once it was demonstrated that the modifications described above stabilized the metallic yield above 80%, reduction programs were started using LEU UF₄. Fifty-nine reduction operations were carried out so far, which confirmed good metallic yields. Fig. 17 shows the yields obtained in the production of enriched uranium metal and summarizes all the results obtained throughout the development of the process to produce uranium metal by magnesiothermic reduction of UF₄.

Very few reductions showed metallic yields slightly below 80%, which was considered acceptable. The limit of 80% for the metallic yield was considered acceptable in view of the unavoidable presence of UO₂F₂ and UO₂ in UF₄. In addition, variations in charge bulk density caused by manual operations and/or fluctuations in the

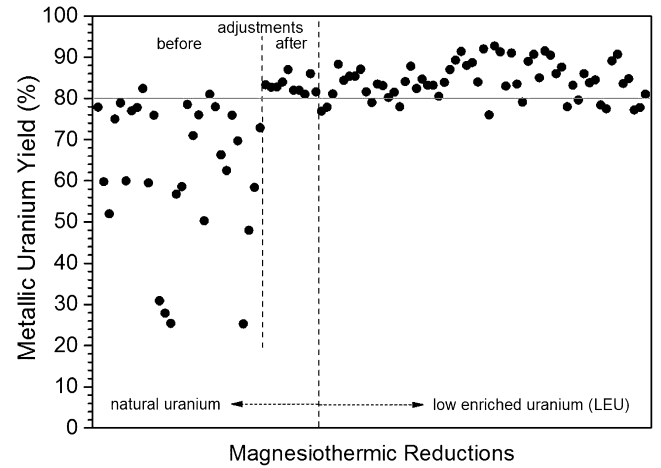


Fig. 17. Metallic yields from operations with low enriched uranium and information on the history of reductions.

physical characteristics of UF₄ powder are also unavoidable, which causes unavoidable fluctuations in the metallic yield. However, for this minimum yield to be considered acceptable in a routine production process, the uranium contained in the slag (around 20 wt %) should necessarily be recovered to return to the process.

3.2. Uranium recovery from slag

After the reduction reaction, about 20% of the produced uranium metal is irreversibly trapped in the MgF₂ slag generated in the reaction, in the form of small solidified droplets. In order to recover this uranium, the slag was first calcined to oxidize the uranium metal to U₃O₈. This was done to facilitate leaching.

The slag calcination condition was set at 600 °C for 3 h. Under these conditions, the formation of U₃O₈ is guaranteed, as illustrated by the diffractogram shown in Fig. 18. The heat treatment under air atmosphere converts all the uranium present in the slag

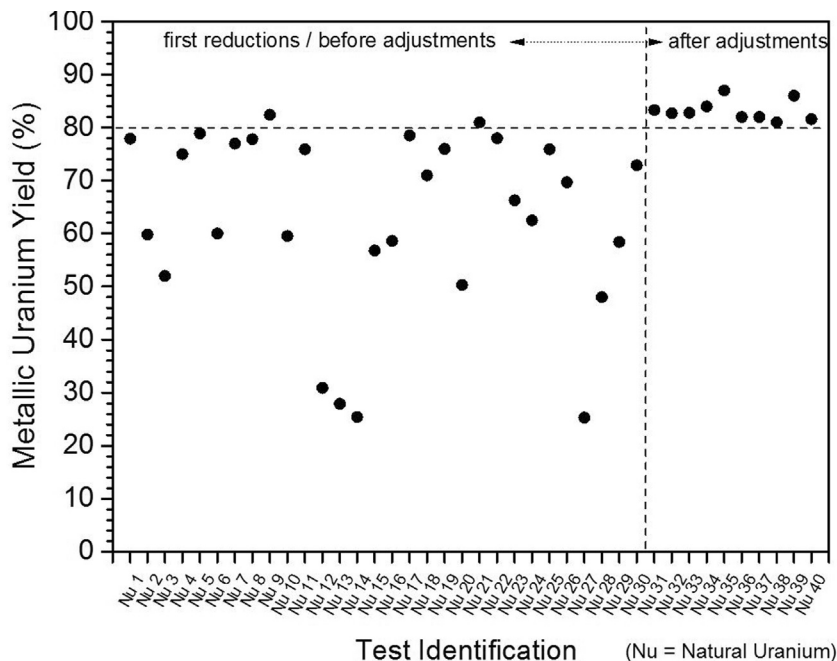


Fig. 16. Stabilization of metallic yield above 80% after thermal profile and geometry adjustments.

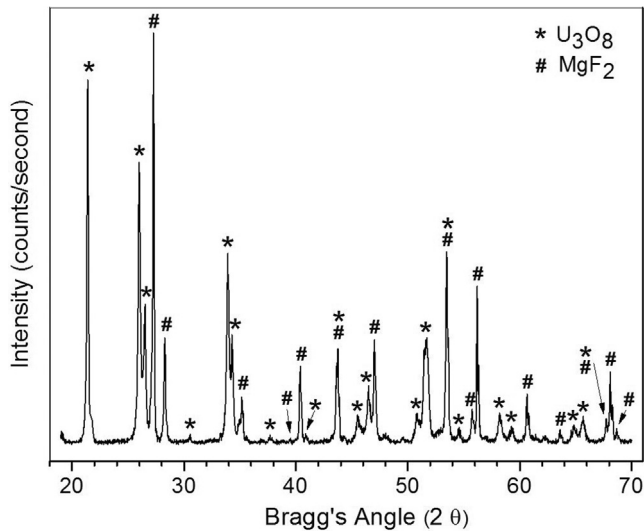


Fig. 18. Diffractogram showing the presence of U_3O_8 after calcination.

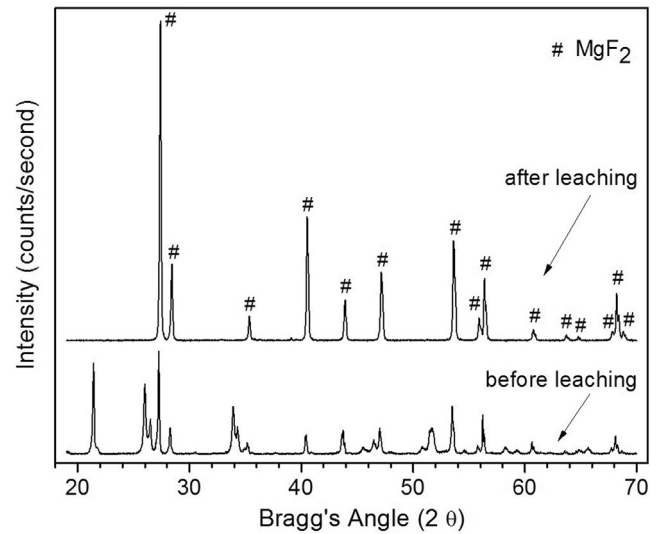


Fig. 20. Diffractogram showing the absence of U_3O_8 after nitric leaching (see Fig. 18).

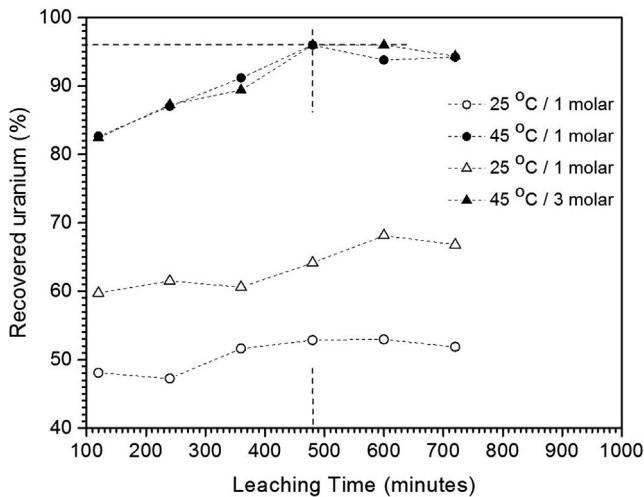


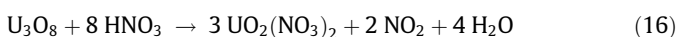
Fig. 19. Recovered uranium as a function of nitric leaching time.

Table 1
Results in nitric leaching of calcined slags after 12 h of leaching.

Leaching Temperature (°C)	HNO ₃ Concentration (molar)	Recovered Uranium (%)	Fluoride (g/L)	Free Acidity (molar)
25	1.0	53	0.002	0.01
25	3.0	77	0.002	1.00
45	1.0	96	0.002	1.00
45	3.0	95	0.006	1.00

into U_3O_8 . The diffraction peaks that do not agree with pure U_3O_8 correspond to crystalline MgF_2 .

Nitrate leaching was found to be adequate to recover the uranium present in the slag produced by this uranium metal production route. The dissolution of uranium (as U_3O_8) from the calcined slag with HNO_3 results in a solution of uranyl nitrate ($UO_2(NO_3)_2$) which is widely used in the nuclear fuel cycle. The main chemical reaction for nitric leaching the calcined slag is represented by:



According to this reaction, the nitric acid consumption is 0.011 mol for each gram of uranium. However, the nitric acid consumption should be higher than the stoichiometric amount due to the presence of fluorides in the slag, such as MgF_2 and CaF_2 , which are poorly soluble. Therefore, in order to guarantee the total leaching of the calcined slag, the consumption of nitric acid was fixed at 0.025 mol/g of uranium, which is an excess of 120% of the stoichiometry of nitric acid. The leaching tests were made at 25 °C and 45 °C, using nitric acid concentrations of 1 and 3 molar. The leaching tests were carried out in batches of 300 g of calcined slag, previously classified in a size smaller than 150 μm . During leaching, samples were collected at intervals of 120 min and analyzed to determine the uranium concentration in solution, fluoride concentration and free acidity of leached solution. The yield in terms of uranium removal from the slag was calculated based on the initial uranium concentration in the slag and the uranium concentration in the leached solution. The results are shown in Fig. 19 and Table 1.

The results presented in Fig. 19 and Table 1 show that the best conditions for leaching would be using temperature at 45 °C and HNO_3 concentration in the range of 1–3 mol/L. After 12 h, the nitric leaching reached 96% of yield in the uranium extraction from slag with a minor residual fluoride content, which was only 0.002 g/L. The HNO_3 concentration at 1 mol/L was chosen since it provided the lowest solubility of fluoride present in the slag. It also provided better economy in terms of acid consumption and less acidic nuclear residues. Leaching time of 480 min was enough to achieve the maximum yield for uranium recovery from the slag. Fig. 20 shows the diffractogram of the slag after leaching. From this X-ray diffractogram, no U_3O_8 is present, since its characteristic peaks are absent. Only MgF_2 is present.

The leaching at low temperature (45 °C) with low nitric concentration (1 mol/L) is favorable since the Mg and Ca fluorides have poor solubility, besides avoiding the corrosion effect caused by fluoride ions. These conditions ensure a stable and more secure leaching from an operational routine standpoint.

The leaching with nitric excess of 120%, i.e., molar ratio of 0.025 HNO_3 per gram of uranium, resulted in an impure solution of $UO_2(NO_3)_2$ with free acidity in the range of 1 mol/L, which is very suitable for direct purification using solvent extraction in the last phase of the uranium recovery.

4. Conclusions

A suitable route to producing low enriched uranium metal by magnesiothermic reduction of UF₄ was studied. The process was shown to be very sensitive to the temperature distribution within the reduction charge at the sparking of spontaneous ignition. The main factor limiting the uranium metallic yield is shown to be the position in the charge where the ignition occurs. If the ignition occurs at the top of the charge, the front of the exothermic reaction shifts from the top downwards, providing the heat needed to ensure efficient separation of the uranium metal from the slag. Otherwise, if ignition occurs at the bottom of the crucible, the reaction occurs but the separation is impaired as the slag is thrown to the top of the crucible, solidifying and trapping the uranium metal inside.

After making the needed modifications to adjust the temperature profiles inside the reduction charge, the process provided reproducible metallic yields around 80%. The remaining uranium in the slag could be recovered by nitric leaching at the yield level of 96%.

The enriched uranium metal produced has been used to manufacture routine fuel elements for the IEA-R1 research reactor (Durazzo and Riella, 2015). The natural uranium metal has been used for research work in the field of high uranium loaded fuel (Leal Neto et al., 2014; Durazzo et al., 2014) and target development (Durazzo et al., 2016).

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