



METALLIC URANIUM PRODUCTION FOR IRRADIATION TARGET ALLOYS

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ABSTRACT

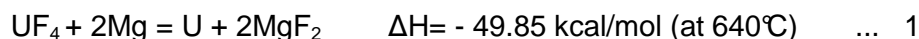
Nuclear medicine radiodiagnosis requires production of ^{99}Mo - $^{99\text{m}}\text{Tc}$ irradiation targets made either using pure uranium foil or using UAl_x alloy produced from metallic uranium. There are several possibilities to produce metallic uranium. Magnesiothermic reduction of UF_4 is known process since early 1940's. IPEN decided to use this route in 1970's for production of natural uranium up to 100kg ingots. LEU U-production, due to possible criticality hazards, it is necessary to handle safe mass (<2.2kgU). IPEN presently produces around of 1000g ingots via magnesiothermic process and in future may produce 2000g or more. This range of U-weight is rather small if compared to big productions of natural uranium. Metallic uranium is reported to be produced in hundreds of kilograms ingots with metallic yield reaching levels of 94%. The magnesiothermic process downscaling to produce LEU has small possibilities to achieve this higher metallic yield, which in IPEN routine is around 85%. This is due to the design of small crucibles, with relatively high proportion of surrounding area to the reaction body, which is prone to withdraw more evolved heat from the exothermic reaction during uranium reduction. In this work, in order to understand better the metallic yield loss, two possible causes are analyzed: (a) less reactivity by UF_4 powder contaminated with unreduced UO_2F_2 and for UF_4 tapped density variation; (b) entrapment of uranium and UF_4 in slag projected (MgF_2) on crucible wall or during slag deposition above the ingot. The projected uranium over the wall happens due to magnesiothermic reaction blast that lasts around 800ms.

1. Introduction

The irradiation targets to produce radioisotopes for nuclear medicine are made with either pure uranium or by using UAl_x alloy produced from metallic uranium. 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 100kg 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 2000g or more. This range of LEU U weight is rather small if compared to big productions of natural uranium. Metallic uranium is reported (5) 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 compared to smaller amount of -49.85 kcal/mol using magnesium as the reducer (6). 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 (7).

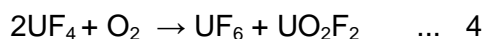
The magnesiothermic reaction is given by:



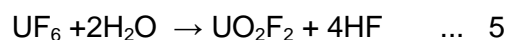
As magnesium thermodynamics is less prompt to ignite than calcium, the batch reactor is heated up to the temperature around 640°C . The routine shows that this ignition normally happens some degrees below this temperature (5). Nevertheless, several reactions may occur during heating of the $\text{UF}_4 + \text{Mg}$ load. Moisture is normally present in the charge, either caught during UF_4 handling after drying or during crucible charging. During heating, as the temperature crosses the water boiling point ($>100^\circ\text{C}$), all moisture becomes water vapor. This vapor not only bores its passage through the load but easily oxidize the reactants in this pathway by the following reactions (1):



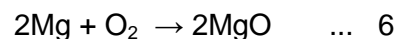
As the loading of the charge is not fully sealed to avoid atmosphere contact, some O_2 is entrapped in the system, leading also to reactants oxidation by:



Producing some UF_6 that transforms into UO_2F_2 by the following reaction:



and magnesium oxidation (very fast above 620°C) by:



The presence of the UO_2 and UO_2F_2 in the produced UF_4 accumulates with previous oxidized ones during the dehydration. All these compounds formation worsens the metallic yield of uranium production.

In this work, it is discussed the effect of LEU UF_4 precipitated via hydrolyzed UF_6 and its potential variability in reactivity. The chemical UO_2F_2 residual content in dried UF_4 is also analyzed for its potential relevance in the uranium production. The tapped density of dehydrated and loaded UF_4 is also commented as affecting the reactivity process of uranium production. The magnesiothermic ignition is also analyzed since the heating time of the charge may affect the reactivity of the load. The reaction sequence after ignition is theoretically proposed as a possible sequence of chemical and physical events. The evidences in the slag solidification on crucible wall, during the reaction process to reduce UF_4 towards U^0 , is very enlightening to guide towards the interpretation of the reaction blast.

2. Experimental and Results

IPEN's UF_4 production is made through a wet route (8). In the period 2008-2010, 32 batches of LEU UF_4 precipitation were made under HF hydrolysis using SnCl_2 as reducing agent, with a strict precipitation temperature at $92 \pm 3^\circ\text{C}$. This lot is considered the experimental basis for uranium production analysis in this article.

For the hydrolysis of UF_6 , the UO_2F_2 solution was kept constant in volume at 37L with additions of 2.7kg SnCl_2 , 6L HF (50%) and complementary water to 50L. This arrangement produces around 3kg of UF_4 precipitate in each batch. The precipitate is

then collected in the bottom of the reactor after 24h. The precipitated mass is filtrated, washed and dehydrated at 400°C for 1h under argon a tmosphere. After dehydration, the UF₄ powder, in lots of 1540g, was supplied to produce metallic uranium by UF₄ reduction by magnesiothermic setting (9).

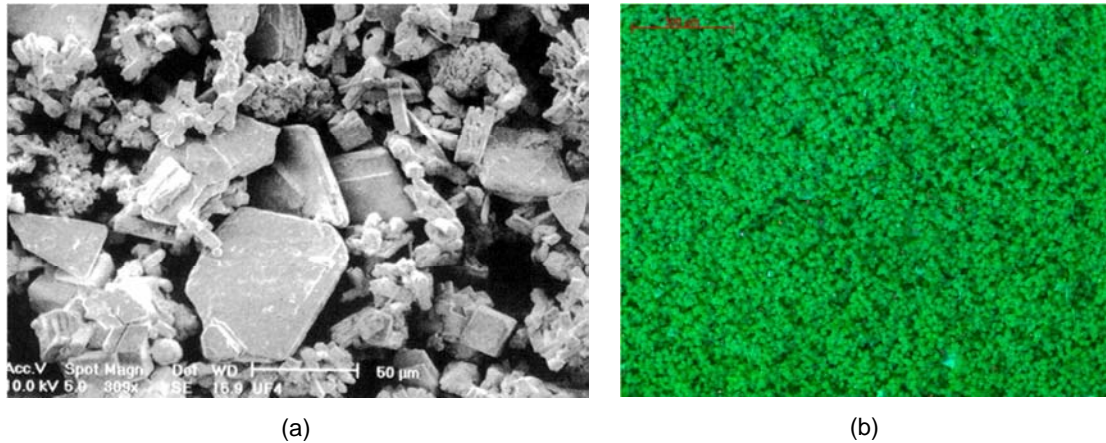


Figure 1- UF₄ produced by IPEN's wet route, using SnCl₂ as precipitation agent. (a) SEM Microstructure; (b) Optical microscopy of UF₄ powder

The microstructure appearance of UF₄ produced is presented in Figure 1 a-b, which is a typical representation of the UF₄ morphology produced by the wet route. As could be noticed in Figure 1a, there are crystallites of different sizes and morphologies.

The IPEN's magnesiothermic reduction process of UF₄ to metallic uranium (in the range of 1000g) could be synthesized as:

1. In preparation for the mass reduction of a single batch, it is used with a standard charge of reactants of $1815 \pm 5\text{g}$ of the mixture Mg + UF₄ ($1540 \pm 1\text{g}$ LEU UF₄) containing 15% excess of stoichiometric Mg content. For purpose of homogenization, the charge of UF₄ + Mg is divided into 10 layers, which are tapped one by one inside the crucible. All this operation is carried out inside a glovebox to prevent nuclear contamination. This sequence is illustrated in Figure 2.
2. After placing the reactants inside the graphite crucible, a variable amount of CaF₂ is tapped over the UF₄+Mg load in the crucible to fully complete the reaction volume. This amount is dependent on tapped density and UF₄+Mg blending, which varies in function to UF₄ fabrication. The crucible is made of fully machined graphite volume with enough resistance to produce safe nuclear uranium amount around 1000g. 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.
3. After closed with the top cover, the crucible is inserted inside a stainless steel cylindrical reactor vessel, made of ABNT/ANSI 310, which allows argon fluxing during batch processing (1 L/min with 2 kgf/cm² of pressure). As shown in Figure 3 (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.

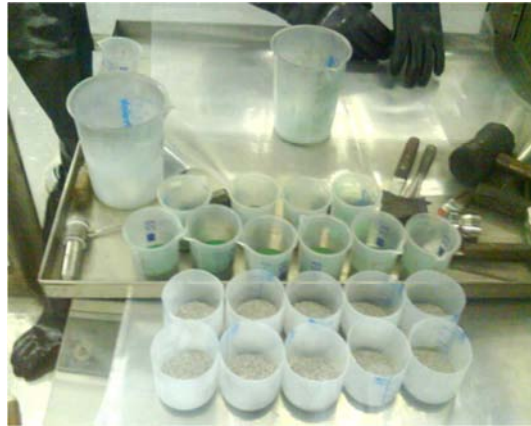
4. The reaction vessel is set up to heated up to 620°C. At this level, the reaction ignition is expected. The total heating time and waiting for ignition is about 180 minutes from heat time to temperature setting point.

5. The reaction of UF_4 with Mg produces an intense exothermic heat release inside the crucible. It is considered as an adiabatic reaction. 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 products project over the crucible wall.

6. This full reaction happens in an noticeable time between 800-1200ms from ignition to final deposit. This control is measured by sound waves, using an accelerometer.

7. After the reaction, 10 minutes is awaited for full solidification of reaction products inside the furnace. Then the furnace is turned off and the reactor vessel is lifted out of the furnace. There is a 16 hours for cooling before its opening. This avoids firing of metallic uranium in contact with atmosphere.

8. The unassembling of reduction set is performed inside a glove box. The top and bottom covers of the crucible are removed. By means of rubber soft hammering, it is able to withdraw the uranium ingot. The MgF_2 slag is removed by mechanical cleaning. The metallic uranium is pickled in nitric acid 65%vol and the final mass of metallic uranium is measured and its density evaluated by Archimedes' method.



(a)

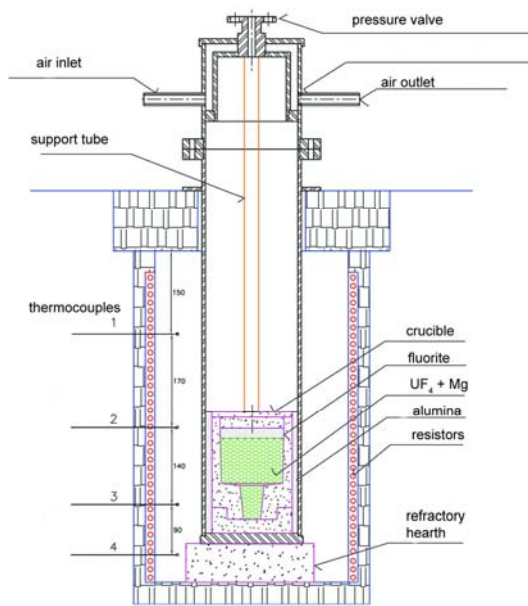


(b)



(c)

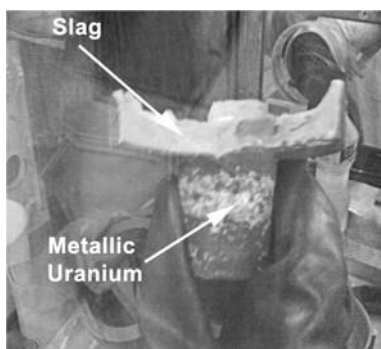
Figure 2 – Sequence of UF_4+Mg charging in IPEN's magnesiothermic method to produce metallic uranium. (a) 10 layer preparation of UF_4 (green) and Mg (metallic bright); (b) blending of material; (c) full charge after tapping the 10 layers.



(a)



(b)



(c)



(d)

Figure 3 – (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 4a-d, there are four graphs displaying relevant variables of UF_4 fabrication and U-reduction reaction. It is considered in these graphs the relation of the variables against the metallic uranium yield, since this is the main indicator of magnesiothermic reaction accomplishment.

The metallic uranium yield data were categorized in subsets of dependent variable containing the mean and the sample standard error inside the box, with whiskers representing the non-outliers range. In the graphs, there are dotted arrows giving indication of trend of averages, which should not be understood as a correlation law, since the range of standard error around the average for some clusters are especially big for a significant statistical regression.

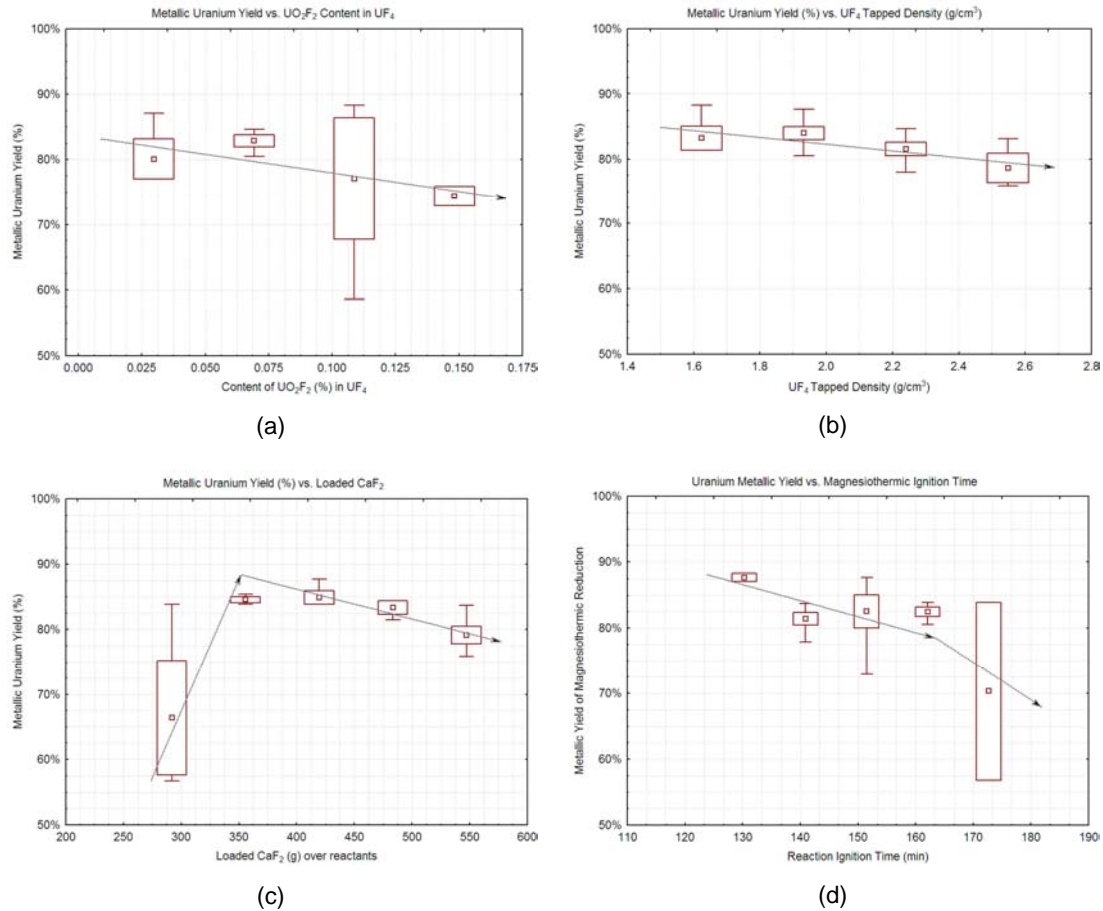


Figure 4 – UF_4 and U production variables versus metallothermic metallic yield: (a) UO_2F_2 content in dried UF_4 , (b) tapped density of dehydrated UF_4 , (c) loaded CaF_2 over the reactants inside the crucible (d) reaction ignition time.

In Figure 4a, the UO_2F_2 content in dried UF_4 reveals the main source of oxidized products that would not be reduced by magnesiothermic reaction, so it is one of the potential sources of metallic yield loss. UO_2 presence was also identified by chemical analysis, but it was very dispersed in content (0.02-0.2%), giving unrelated statistical indication for metallic uranium yield. Probably, the UO_2 formation did not originate only from the UF_4 precipitation but by unpredicted air contact during drying treatment and handling.

In Figure 4b-c, the tapped density of dehydrated UF_4 and the amount of complementary loading of CaF_2 inside the crucible give an indication of reaction volume variability inside the crucible terms of UF_4+Mg blending with a constant weight. Indirectly, these two parameters reveal the importance of physical nearness of the reactants and their reactivity during magnesiothermic reaction.

In Figure 4d, the ignition time is presented. This variable is important since the reactants reactivity is linked to it. The longer is the heating time, the lesser is the reaction promptness.

3. Discussions

The UF_4 microstructure, shown in Figure 1, displayed several crystallites structures. As this figure represents the most prevalent microstructure of produced UF_4 , it may be deduced that the variation of tapped density may be correlated with this structural evidence.

The experimental batches of $UF_6 \rightarrow UO_2F_2 \rightarrow UF_4$ precipitation under HF hydrolysis, using $SnCl_2$ as reduction agent, could not be said as strictly reproducible process.

From Figure 4a, it is noticeable that UO_2F_2 presence in dehydrated UF_4 seems to be relevant in magnesiothermic reaction, since it leads to have less U-production caused by no reactivity of U-oxides and Mg in this reaction process. This evidence impacts directly in the metallic yield performance. Probably, previous precipitation UO_2F_2 crystals will be also anchors, which may help nucleation to form more UO_2F_2 and UO_2 during magnesiothermic heating when moisture (at $100^\circ C$) and crystallization water ($> 400^\circ C$) evolves. Reactions 2 to 6 show that this oxidation is very prone to happen under moisture presence with high temperature (around $600^\circ C$) with relative long time residence (around 180 min) inside a confined vessel. These indications, in Figure 4a, leads to evidence that the higher is the amount of previous UO_2F_2 content in the charge, the lower is the metallic yield.

It was noticeable that UF_4 powder density variation occurred in several UF_4 precipitation batches and influenced the final magnesiothermic result, as accounted in Figure 4b-c. These results in the graphs had a clear indication that tapped density of UF_4+Mg loadings and indirectly by CaF_2 charged as complementary load in reaction chamber tend to decrease the yield.

As shown in Figure 4d, the magnesiothermic metallic yield is strictly linked to heating time to ignite the reactants $UF_4 + Mg$. The longer is the time, the lower is the yield. This ignition time is not a controlled variable itself, but it is dependent on the reactivity of the system. Once kept setting up the magnesiothermic parameters in constant way, the main dependence and yield variability come from UF_4 precipitation and drying conditions, which lead to a non-constant production of different morphologies of UF_4 , associated with issues of potential oxidation.

The reaction moment (ignition), as a closed and not directly manageable event, brings important issues, as far as metallic yield is concerned. There is a practical limitation of improving performance since great amount of finely and not fully reacted uranium is lost inside the projected slag against the walls. These slag and metal mass freeze at this region during the very tiny moment after ignition starts.

The experimental mixtures used $UF_4+15\%$ excess Mg. They are manually blended, segmented in 10 fractions before charging. Each fraction is carefully charged and tapped inside the crucible with roughly constant pressure forming a load volume with 10 homogeneous layers. This practice tries to avoid segregation of UF_4 (heavier) from Mg (lighter). Nevertheless, the production routine showed that the load density varies from batch to batch, probably due to morphology variations in UF_4 particles, which leads to variations in blending and aliquot charging.

At the top of the load, the complementary amount of CaF_2 fills completely the whole reaction chamber in the magnesiothermic crucible. Nevertheless, when charging in big amounts it is also a point of concern. The CaF_2 loading affects not only the compression of reactants, but it is chemically a charge of inert component that will also withdraw heat from the exothermic reaction of UF_4 reduction towards metallic uranium.

An important consideration, normally cited in the literature, is that the more compressed are the reactants, the better would be the yield. This did not presented as fully reliable in this work, since, as shown in Figure 4b-c, the reactivity of charge ran in the opposite direction. It may be speculated that, in small scale magnesiothermic reactor, the efficiency of magnesium vapor to reach the reaction spot with the UF_4 crystallites is more efficient than in a denser charge. Very loose contact also goes in the worst yield as suggested by Figure 4c when lower charging of CaF_2 ($<350g$) represents a quite big fall of yield. In this case, it is thought that magnesium vapor would draw it trail between the UF_4 crystallites towards the top of reaction chamber without reacting properly with them.

Magnesiothermic process, following the present route of IPEN, gave 80-85% of metallic uranium yield, although the potential improvements in UF₄ morphology, better blending with Mg and more reactivity, it is a novelty for this chemical-metallurgical way to produce LEU metallic uranium in small 1000 g batches.

4. Conclusions

It was developed a suitable route to produce UF₄ by chemical reduction and precipitation from hydrolyzed solution of UF₆, in the form of UO₂F₂, using reducing agent SnCl₂ and fluoridric acid addition. This chemical process produces UO₂F₂ contaminations to UF₄ to be used as raw material to magnesiothermic reaction. This contamination tends to decrease metallic uranium yield in a significant way. The UO₂ presence in UF₄ chemical analysis did not indicate the same trend.

There was variation of tapped density of produced UF₄ and CaF₂ amount charged over the UF₄+Mg to complement the reaction chamber. Both variables indicated that higher is the amount of these two variables, the lower is the yield. The ignition time indirectly showed the global reactivity of system and revealed that the longer the ignition time to happen the lower would be the metallic yield.

Magnesiothermic process gave 80-85% range for metallic yield, which is a novelty of this chemical-metallurgical way to produce LEU metallic uranium in 1000 g batches.

5. Acknowledgements

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