



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:



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

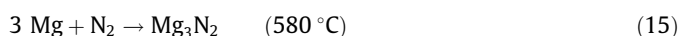
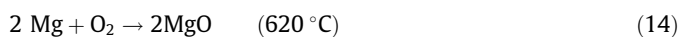
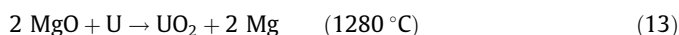
The reaction products utilize the resulting exothermic heat and melt to form the uranium ingot at the bottom of the crucible and the slag. The supernatant slag, which is formed essentially by MgF₂, solidifies at the top of the ingot. Considering the calculations of Rand and Kubaschewski (1963), the sum 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

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