

# Research Reactor Fuel Fabrication to Produce Radioisotopes

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## 1. Introduction

This chapter describes the manufacturing technology of fuel used in research reactors that produce radioisotopes. Besides this production, the research reactors are also used for materials testing. The most common type of research reactors is called "MTR" - Materials Testing Reactor. The MTR fuel elements use fuel plates, which are quite common around the world. There was a historic development in that fuel type over the years to reach the current state-of-art in this technology.

The basic MTR fuel element is an assembled set of aluminum fuel plates. It consists of regularly spaced plates forming a fuel assembly. These spaces allow a stream flow of water that serves as coolant and also as moderator to nuclear reaction. The fuel plates have a meat containing the fissile material, which is entirely covered with aluminum. They are manufactured by adopting the traditional assembling technique of dispersion fuel briquette inserted in a frame covered by aluminum plates, which are welded with subsequent rolling. This technique is known internationally under the name "picture-frame technique". Powder metallurgy techniques are used in the manufacture of the fuel plate meats, making briquettes using ceramic or metallic composites. The briquette is made with powdered nuclear material and pure aluminum powder, which is the structural material matrix of the briquette.

Using  $UF_6$  in the chemical plant, it is able to produce several intermediate compounds of uranium. One of these compounds is  $UF_4$ , which is the main raw material to produce metallic uranium. It could be made by several routes. The production of metallic uranium uses the  $UF_4$  reduction through calcio- and magnesiothermic reaction. The metallic uranium is alloyed with Al, Si or Mo. Previously, stable uranium oxides were used as MTR fuels, but they had very small densities to accomplish a good operational performance of the reactors. The fuel material candidate mostly prone to be used in nuclear research reactors is based on alloys carrying more U-density toward the fuel meat. In present state, the U-Mo alloys are good candidates, but it would not be subject of the present chapter since it on its path to be certified to future use in research reactors. Currently, the most used material is  $U_3Si_2$  LEU, which is low enriched uranium enriched up to 20% of  $^{235}U$  isotope, which is the nuclear fissile material.

The production procedures of  $U_3Si_2$  fuel fabrication will be discussed in this chapter, starting from  $U_3Si_2$  fabrication and powder manufacture. This powder is mixed with aluminum powder and pressed, resulting in a solid briquette with good mechanical strength. After quality inspection, the briquette becomes the fuel plate meat.

The fuel plate manufacturing procedures will be described according to the picture frame technique. This technique includes the assembling of the briquette inside the frame sandwiched with cover plates. The assembly is welded and hot and cold rolled to get the fuel plate, where the fuel meat is completely sealed inside aluminum. All the process and quality control during fabrication will be commented ahead.

Once the plates having been fabricated, the fuel assembly is finally made by fixing the fuel plates and the other mechanical components, such as nozzle, handle and screws. This finishing process to produce the element is also commented in this chapter.

The characteristics of the fuel plates must meet specifications of each particular research reactor characteristics. Inspections and qualifications are carried out in various stages of fuel plate manufacture.

As this chapter describes nuclear fuel manufacturing for research reactors, the sub-items of fabrication process can be divided into the following topics: evolution of nuclear fuel materials for MTR fuel; production of uranium hexafluoride ( $UF_6$ ); production of uranium tetrafluoride ( $UF_4$ ); production of metallic uranium;  $U_3Si_2$  production; production of fuel cores from  $U_3Si_2$  powder and aluminum; production of fuel plates with  $U_3Si_2$ -Al dispersion briquettes; assembling of fuel elements; recovery of uranium; effluent treatment; quality control.

In this chapter, the experience of IPEN/CNEN-SP (Energy and Nuclear Research Institute of Brazilian Commission of Nuclear Energy, São Paulo, Brazil) will be given as a productive route to produce MTR nuclear fuels for research reactors, since this is the main expertise of all the authors of this chapter.

## 2. Evolution of nuclear materials for research reactors fuel

The use of radioisotopes in medicine is certainly one of the most important social uses of nuclear energy. Radiopharmaceuticals are radioactive substances that help doctors to make important decisions for treatments in oncology, cardiology, neurology, among other areas. For patients, the diagnoses represent safety and pain relief, as in the case of samarium-153 use, which is employed to relieve bone pain caused by metastatic tumors.

Nuclear medicine is a medical specialty that uses radioactive material for diagnostic tests and therapeutic purposes. Although it is often confused with radiotherapy, the last application has a lot of different procedures and applications. The main distinction between the two specialties is the way both use the radioactive material. While radiotherapy (radiation therapy) uses sealed sources (or closed), which emit radiation outside the patient, nuclear medicine uses open sources of radiation, administered in vivo (oral or intravenous). If, in radiotherapy, radiation is directed toward the point to be discussed, in nuclear medicine is the body own metabolism of the patient who is in charge of carrying radioactive material into the organ to be examined or treated.

The success of nuclear medicine in diagnosis is due to its ability to show the functioning of various body organs, avoiding the use of invasive techniques such as biopsy and catheterization. The use of ultrapure iodine-123 to examine thyroid function is one example. By scintigraphy, a diagnostic imaging technique, which has several medical applications,

made possible to measure the uptake of iodine by the thyroid and thereby assess the functioning of the gland. Another radioactive element widely used to study the various functions of the human organism is technetium-99m. This isotope can be chemically combined with various organic complexes, which evaluate liver disorders, bone and brain, among others. In bone scintigraphy, the radioactivity of technetium reveals the existence of tumors from six to eight months before they have reached sufficient size to be picked up by X-ray examinations. With this, it is possible to start treatment much earlier with greater cure perspective.

Nuclear reactors that produce radioisotopes are called research reactors. This type of reactor is also used to perform tests on materials and nuclear fuels in the development phase. The modern research reactors are designed with both purposes, radioisotope production and testing of materials, and for this reason are called Multipurpose Reactors.

Unlike power reactors, which are well known and are intended to generate heat for electricity generation, the research reactors or the modern multipurpose reactors aim to generate neutrons used for radioisotopes production or for testing materials in terms of verify their performance under irradiation. Unlike power reactors, research reactors operating with much higher power density, which is necessary to get high neutron fluxes. For this reason its fuel is usually in the form of a metal plate, usually covered by aluminum. They are very different from the fuel rod with ceramic pellets ( $\text{UO}_2$ ) as used in the fuel for power reactors.

The research reactors moderated and cooled with light water and using plate-type fuel elements has been named MTR type reactors (Materials Testing Reactor). After the construction of the first MTR, a joint venture of ORNL (Oak Ridge National Laboratory) and ANL (Argonne National Laboratory) operated it since March 31, 1952. Many research reactors around the world uses MTR type fuel elements, which are formed by assembling fuel plates fabricated by a well-known and established technique of assembling a core, commonly named fuel meat, which incorporates the fissile material, a frame plate and two cladding plates, with subsequent deformation by hot and cold-rolling (picture frame technique) (1) (2).

Initially, the fuel plates usually used as the core material an uranium-aluminum alloy (U-Al) containing 18 wt% of highly enriched uranium (93 wt%  $^{235}\text{U}$ ) (1) (3). Even in the 50's, with the concern about nuclear weapons non-proliferation, the research reactors began to use fuels containing low-enriched uranium (20 wt%  $^{235}\text{U}$ ) (4). With enrichment lowering, in order to maintain the reactivity and lifetime of the reactor cores, it became necessary to increase the amount of uranium in each fuel plate. In the U-Al alloy, the uranium concentration had to be increased to 45 wt% to compensate the decrease in the enrichment level.

Fuel plates containing the meat based on the U-Al alloy with 18 wt% of highly enriched uranium were easily fabricated. However, difficulties arise in fabricating fuel plates with meats of U-Al alloy containing 45 wt% of low-enriched uranium, because of the fragility and propensity for segregation of this alloy (4) (5) (6). An alternative to overcome this problem was the use of cores manufactured by powder metallurgy, which used dispersions of uranium compounds in aluminum and could incorporate quantities of low-enriched uranium significantly greater. For instance, the Argonauta reactor (10 MW), in Rio de Janeiro, Brazil, started its operation in 1956 and was developed by the Argonne National Laboratory, USA. This pioneer Brazilian research reactor used fuel plates with the meat based on an  $\text{U}_3\text{O}_8$ -Al dispersion containing 39 wt% of  $\text{U}_3\text{O}_8$  with low enrichment (7).

Efforts were made to increase the concentration of uranium in this type of dispersion fuel, getting 65 wt% of  $U_3O_8$  in the fuel fabricated for the Puerto Rico Research Reactor of the Puerto Rico Nuclear Center to the end of the 70's (8).

Aiming at obtaining more and more high neutron fluxes, the development of research reactors with higher power required a continuous production of fuels, which used highly enriched uranium (93 wt%  $^{235}U$ ), yielding higher specific reactivity and economics, since these fuels could stay longer in the reactor core (long life). The 100 MW HFIR (High Flux Isotope Reactor) used dispersion  $U_3O_8$ -Al with 40 wt%  $U_3O_8$  (9) and the ATR (Advanced Test Reactor), with 250 MW, used the same type of dispersion with 34 wt% highly enriched  $U_3O_8$  (10). In addition to the  $U_3O_8$ -Al dispersions,  $UAl_x$ -Al dispersions were commonly used ( $x$  is approximately 3), all these fuels systems still using highly enriched uranium. At this time, in late 70's, the highest uranium density obtained inside the fuel was 1.7 gU/cm<sup>3</sup>, which was quite well qualified.

Since highly enriched uranium was easily obtainable in the 70's, the commercial reactors that were using the low-enriched uranium started gradually to convert their cores to highly enriched fuel. Thus, it reached a total of approximately 156 research reactors in 34 countries using highly enriched uranium, resulting in an annual circulation of approximately 5000 kg of this material (11). In 1977, arose again the concern about the proliferation risk associated with loss of fuel during manufacture, transport and storage, leading to restriction by the U.S. government's sale of uranium with high enrichment (above 90 wt%  $^{235}U$ ) and producing an impact on the availability and use of the highly enriched fuel for research reactors.

From 1978 programs, it was established for the enrichment reduction, aimed at developing the technology base for replacement of highly enriched uranium by low-enriched uranium (less than 20 wt%  $^{235}U$ ) in research reactors. The main program, still active today, is the *RERTR Program* (Reduced Enrichment for Research and Test Reactors), which aims to develop the technology necessary to convert the reactors that use highly enriched uranium (= or > 20%  $^{235}U$ ) by low-enriched uranium (less than 20%  $^{235}U$ ). During the existence of this program more than 40 research reactors have been converted. At this time, the decrease of enrichment has demanded an effort bigger than previously, because, in most high power research reactors, which are designed to operate in extremes, this substitution involved the development and qualification of new fuels with maximum possible concentration of uranium, which limits are imposed for manufacturability and performance under severe and prolonged irradiation.

In this context, the developments were based initially on increasing the concentration of uranium in the fuel currently used at the beginning of RERTR program, until the practical limit of 2.3 gU/cm<sup>3</sup> in the case of  $UAl_x$ -Al and 3.2 gU/cm<sup>3</sup> in the case of  $U_3O_8$ -Al. Also, an effort was made in developing new fuels that would allow obtaining uranium densities of 6-7 gU/cm<sup>3</sup>, well above the density that can be achieved with the  $UAl_x$ -Al and  $U_3O_8$ -Al fuel. The development of new fuels would allow the conversion to low enriched from virtually all existing research reactors.

High density of uranium in the dispersion can only be achieved by using the dispersion of fissile compounds with high uranium content. Figure 1 shows the potential of various uranium compounds. The technological limit for the use of dispersions is 45% by volume of fissile material dispersed, since it must be kept a solid aluminum matrix as dispersant. The uranium silicides and  $U_6Fe$  compounds were initially considered promising.

The problem encountered in using these intermetallics with high concentrations of uranium as fissile material in the form of dispersions in aluminum is related to its dimensional stability during operation, leading to swelling of the fuel plates and therefore the problems that compromise the thermohydraulic security of the reactor. In mid-1988, based on results from irradiation tests (12) (13), the  $U_3Si_2$ -Al based dispersion fuel was qualified by the U.S. Nuclear Regulatory Commission and released for sale with uranium densities up to  $4.8 \text{ gU/cm}^3$ , with a swelling consistent with the commonly used dispersions (14).

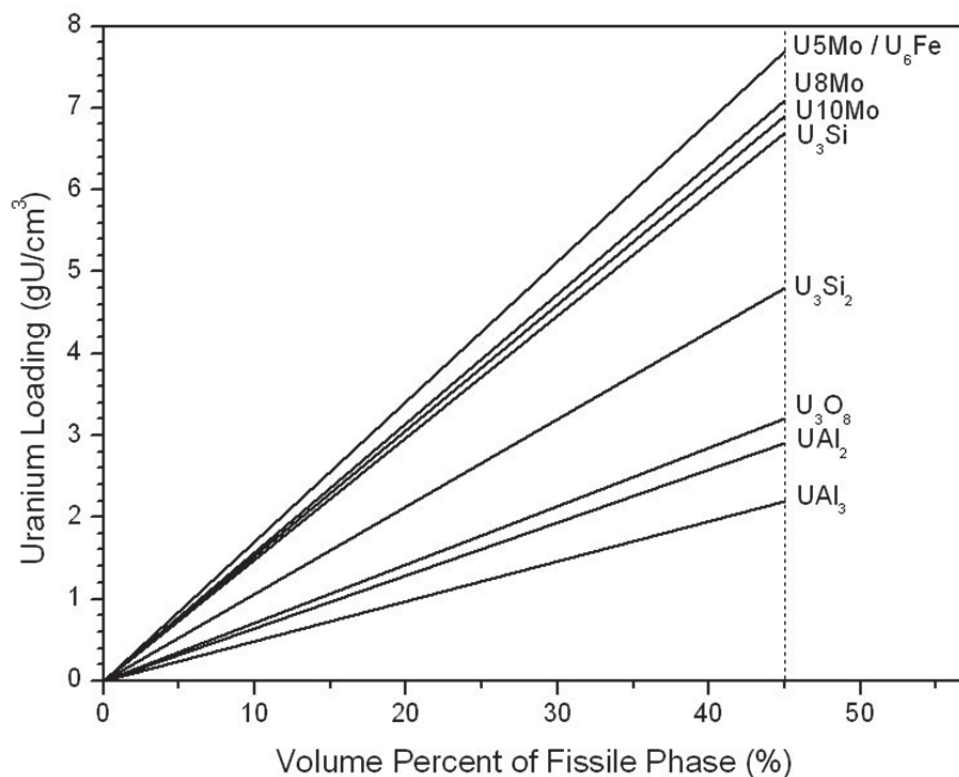


Fig. 1. Density of uranium in terms of concentration of dispersed phase for different fissile uranium compounds.

Research continued aiming at the use of intermetallic with even higher concentrations of uranium, such as  $U_3Si$ ,  $U_3SiAl$  and  $U_6Fe$  as fissile material in the form of dispersions in aluminum. However, results of irradiation tests showed an unacceptable dimensional stability of these new fuels. Due to its high concentration of uranium (96 wt%) the  $U_6Fe$  was mainly considered (15), and the research was virtually abandoned in 1986 due to high swelling observed in irradiation tests, coupled with the promising results obtained with the  $U_3Si_2$ -Al dispersion, being considered a viable alternative (16).

Only through the use of  $U_3Si_2$  as fissile material in the dispersion with aluminum was not possible to convert all research reactors. Many research reactors are awaiting a high-

performance technology solution finale, needing a uranium density of 6-9 gU/cm<sup>3</sup>. In an effort to convert these reactors, other high density fuels has been studied, including dispersions based on U-Mo, U<sub>3</sub>SiCu, U<sub>3</sub>Si<sub>1.5</sub>, U<sub>3</sub>Si<sub>1.6</sub>, U<sub>75</sub>Ga<sub>15</sub>Ge<sub>10</sub>, U<sub>75</sub>Ga<sub>10</sub>Si<sub>15</sub> and uranium nitrides. Still, innovative manufacturing techniques has been investigated, which are based on hot isostatic compaction (HIP - Hot Isostatic Pressing) or increasing the volume fraction of U<sub>3</sub>Si<sub>2</sub> beyond 50% (the limit currently accepted for this technology is 45%) or using wires of U<sub>3</sub>Si and/or U<sub>75</sub>Ga<sub>10</sub>Si<sub>15</sub> and/or U<sub>75</sub>Ga<sub>15</sub>Ge<sub>10</sub> metallurgically bonded with aluminum in a geometry such that result in plates with a density close to 9 gU/cm<sup>3</sup> in the fuel core. The nearest alternative to be commercially deployed is the UMo alloy dispersion in aluminum, which enables to achieve the density near to 8 gU/cm<sup>3</sup>. The performance under irradiation of this type of fuel is being tested with promising results. However, it is not a commercial fuel yet.

Thus, currently the most advanced manufacturing technology commercially available for the MTR type fuel plates is based on the U<sub>3</sub>Si<sub>2</sub>-Al dispersion, with a concentration of U<sub>3</sub>Si<sub>2</sub> resulting in a uranium density into the fuel meat of 4.8 gU/cm<sup>3</sup>. The next commercially available technology will probably use a dispersion of UMo alloy with 7-10 wt% Mo, resulting in a uranium density of between 6 and 8 gU/cm<sup>3</sup>.

Each type of MTR fuel element is produced in accordance with a manufacturing specification and a set of manufacturing drawings agreed between the fabricator and the reactor operator or his representative. The specification sets down the scope and general conditions, the requirements of manufacturing method, together with the inspection requirements and acceptance criteria. In addition to the specification, an inspection schedule is normally produced which includes all of the supporting documentation such as the inspection and record sheet and certification (17; 18; 19; 20; 21).

### 3. Production of uranium tetrafluoride

The UF<sub>4</sub> has a specific role in nuclear fuel technology. It is an important intermediate product, being the basic substance to produce either uranium as metal (U<sup>0</sup>) or uranium hexafluoride (UF<sub>6</sub>) (17).

Uranium tetrafluoride (UF<sub>4</sub>) is a green crystalline solid that melts at about 96°C and has an insignificant vapor pressure. It is slightly soluble in water. UF<sub>4</sub> is less stable than uranium oxides and produces hydrofluoric acid in reaction with water; thus it is a less favorable form for long-term disposal. The bulk density of UF<sub>4</sub> varies from about 2.0 g/cm<sup>3</sup> to about 4.5 g/cm<sup>3</sup> depending on the production process and the properties of the starting uranium compounds. Uranium tetrafluoride (UF<sub>4</sub>) reacts slowly with moisture at room temperature, forming UO<sub>2</sub> and HF, which are very corrosive.

In principle, several other compounds may also be used for the production of metal and hexafluoride uranium, however, the use of UF<sub>4</sub> is prescribed by technological and economic considerations. It is considerably easier to obtain metallic uranium from UF<sub>4</sub>, due to the reactivity of UF<sub>4</sub> mixture with reducing agent (mainly Ca and Mg) with large thermal outcome, which makes easy the production of uranium ingot.

According to the production process, the UF<sub>4</sub> must have certain specifications in regard to its purity. The content of uranium oxides and uranyl fluoride (UO<sub>2</sub>F<sub>2</sub>) may vary and also its density and its granulometric composition. The major technical requirement for tetrafluoride is observed during metallic uranium fabrication. It must contain at least 96% of tetrafluoride, virtually free of impurities. It should be anhydrous and having sufficiently high density.

When the reduction process to produce metallic uranium is performed at higher pressures and lower temperatures, normal tolerances up to 4% of  $\text{UO}_2 + \text{UO}_2\text{F}_2$  should be reduced. It is recommended that the tapped density of loose  $\text{UF}_4$  should be greater than  $1 \text{ g.cm}^{-3}$ . The good quality of the metallic uranium to be produced should have the  $\text{UF}_4$  specification as displayed in Table 1.

Elements	Al	B	Cd	C	Co	Cr	Cu	Fe	Mn	Ni	Si
% in mass	70	0,2	0,1	150	5	25	40	75	15	40	30

Table 1. Specification of the limits for main impurities in  $\text{UF}_4$

In the case the oxide content is high, there would be larger losses of metal with the slag. As the reaction develops high amount of heat, it should be avoided evolution of tetrafluoride volatile components such as water and ammonia. During smelting, the metal is slightly contaminated with impurities from reducing agent and crucible. For this reason,  $\text{UF}_4$  should be pure enough to allow slight contamination degree during this process. It must also be sufficiently dense. The load consists of blending of  $\text{UF}_4$  powder and chips of calcium or magnesium tetrafluoride. The higher the density of  $\text{UF}_4$ , the greater the density of the load, and the greater the amount of heat involved per unit volume of the furnace (17).

The production of uranium tetrafluoride can be made by several processes which are divided into two groups, namely dry (fluorination of uranium oxide or hexafluoride reduction) and aqueous (preparation of  $\text{UF}_4$  from  $\text{U}^{+6}$  salt) pathway (18) (19) (20) (21) (22).

The first task of obtaining  $\text{UF}_4$  were carried through water (22) (23) by the end of the 19<sup>th</sup> century, and from an industrial standpoint that prevailed till the beginning of 20<sup>th</sup> century. The process essentially comprises the steps of reducing the uranium contained in uranyl fluoride solutions, uranyl chloride or uranyl sulfate up to its tetravalent state, followed by  $\text{UF}_4$  precipitation by adding hydrofluoric acid.

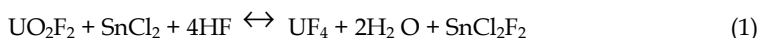
With the development of dry processes, the aqueous processes were abandoned because they had difficulties in filtration, washing and drying, in spite of their simplicity and safety. Nowadays, the production via aqueous route is only used in plants to produce  $\text{UF}_4$  for small quantities, which is the present experience of IPEN in producing LEU  $\text{UF}_4$ . Nevertheless, IPEN also developed the Brazilian technology for dry route.

### 3.1 Procedures for obtaining $\text{UF}_4$ via wet process

#### 3.1.1 Preparation of $\text{UF}_4$ from salts $\text{U}^{+6}$

The  $\text{UF}_4$  preparation methods through water have been developed mostly by the British and its modifications were based on work done by Bolton in 1866 (24; 25)

Essentially, the process consists in reducing the uranium, contained in solutions of uranyl fluoride, uranyl chloride and uranyl sulfate to the tetravalent state and the precipitation of uranium tetrafluoride by adding hydrofluoric acid. Several compounds of uranium have been used as starting materials and various reducing agents have been used. An overview of the process can be obtained from the reaction of uranyl fluoride with stannous chloride and sodium hyposulphide.



An alternative to this process is the replacement of the electrolytic reduction by reducing agents that prevents the possible contamination with the reducing agent. This process has been adopted in countries like USA, Spain, Australia, Japan, Canada, England, South Africa and India (26; 27; 28; 29; 30; 31; 32). For the production of  $UF_4$  with nuclear purity from  $UO_2F_2$  acids solutions, some fundamental stages are required such as obtaining the solution, reduction to uranium valence and precipitation of the formed  $U^{+4}$ . These stages are shown in Figure 2, as schematized operations.

### 3.1.2 Obtaining $UO_2F_2$ solutions

Uranium hexafluoride is a crystalline substance at normal pressure and temperature conditions. At the temperature of 900C under a pressure of 3kgf/cm<sup>2</sup>,  $UF_6$  becomes gas and when it is injected into water, it hydrolyzes immediately according to the following:

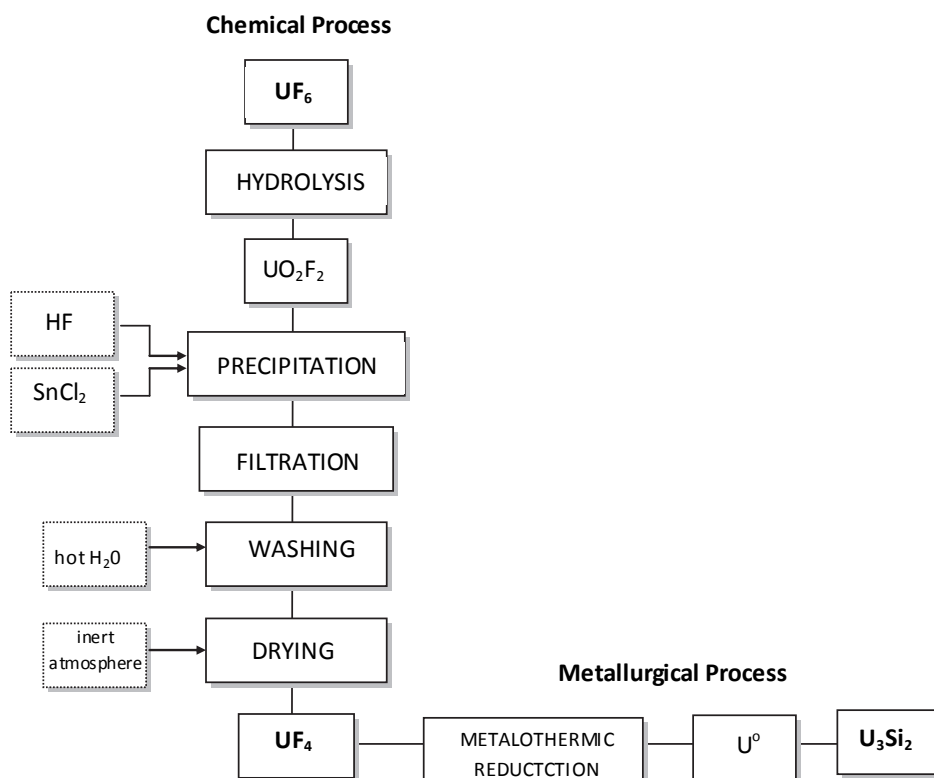


Fig. 2. Wet Process to produce  $UF_4$



Table 2 shows the chemical characteristics of  $\text{UO}_2\text{F}_2$  solution obtained from  $\text{UF}_6$  hydrolysis.

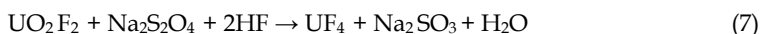
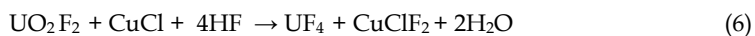
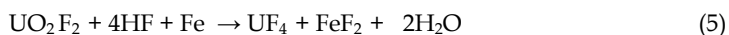
Uranium (g/L) 60									
Fluoride (g/L) 17									
Metallic impurities ( g/mL)									
Cd	B	P	Fe	Cr	Ni	Mo	Zn	Si	Al
<0.1	0.2	<100	1500	100	40	<2	100	300	40
Mn	Mg	Pb	Sn	Bi	V	Cu	Ba	Co	
10	15	<2	<2	<2	<3	3	1	<10	

Table 2. Chemical characteristics of  $\text{UO}_2\text{F}_2$  solution

### 3.1.3 Chemical reduction of $\text{UF}_6$ to $\text{UF}_4$

Uranium in its tetravalent state is very important in different technological processes. Essentially, the preparation process (aqueous way) from solutions containing uranyl ion (hexavalent) involves the reduction towards tetravalent state, and later precipitation as  $\text{UF}_4$  using HF solution. In aqueous solutions, these reductions can be carried out by chemical, electrochemical or photochemical methods.

All the trials for the preparation of  $\text{UF}_4$  using chemical reduction have been carried out using  $\text{UO}_2\text{F}_2$  solution inside a stainless steel reactor, coated with Teflon. The solution has been heated under continuous stirring to reach a temperature set, and the reducing agent has been added. Next, the precipitating agent solution is slowly added to  $\text{UO}_2\text{F}_2$  in solution with hydrofluoric acid (HF). Tests have been carried out using some reducing agents, such as  $\text{SnCl}_2$ ,  $\text{CuCl}$ ,  $\text{FeCl}_2$ ,  $\text{Na}_2\text{S}_2\text{O}_4$ .



Upon  $\text{UF}_4$  precipitation the suspension is left in rest up to reaching room temperature. After over 12 hours, it was performed the solid/liquid separation by vacuum filtration, washing and drying in a muffle kiln. The salts obtained were all identified as being uranium tetrafluoride. According to the results shown in Figure 3, it is evident that, from all used reducing agents, only  $\text{SnCl}_2$  and  $\text{FeCl}_2$  have shown significant results in regards of getting  $\text{UF}_4$ . Nevertheless,  $\text{SnCl}_2$  is more consistent reducing agent at higher temperature of process.

The influence of the temperature upon  $\text{UO}_2\text{F}_2$  and  $\text{UO}_2$  contents in obtained  $\text{UF}_4$  is shown in Figure 4. It was employed  $\text{SnCl}_2$  as the reducing agent in this study to precipitate  $\text{UO}_2\text{F}_2$  solution. The residual moisture is dried at  $130^\circ\text{C}$ . The tin content in all obtained  $\text{UF}_4$  has shown to be in the range of 0.15 - 0.15%.

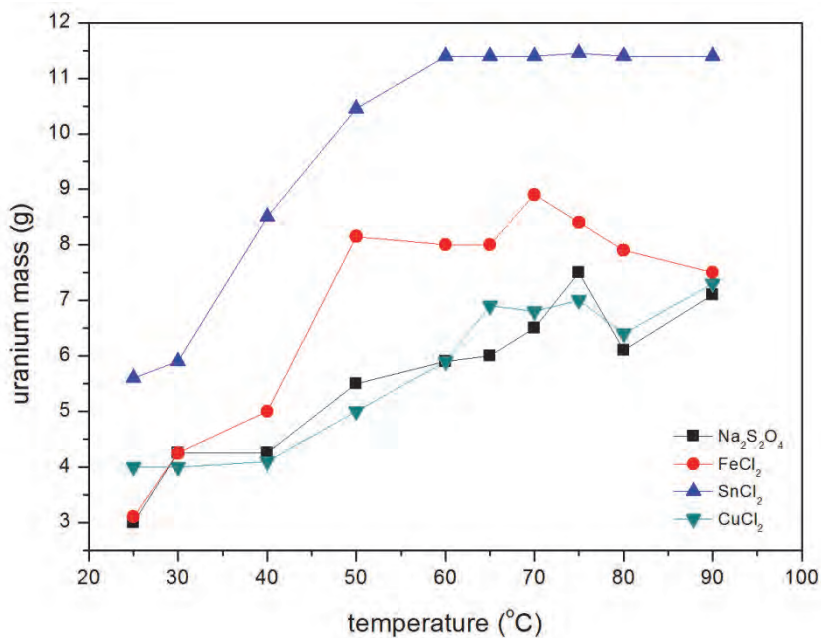


Fig. 3. Influence of reducing agent as a function of obtaining UF<sub>4</sub>

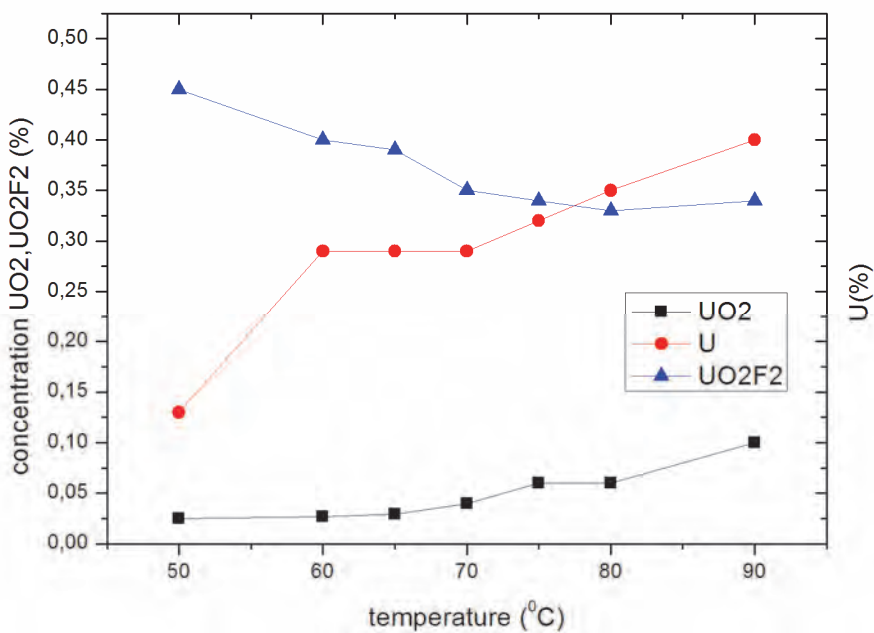
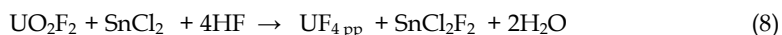


Fig. 4. Influence of the temperature as a function of the contents of UO<sub>2</sub> F<sub>2</sub> and UO<sub>2</sub> in UF<sub>4</sub>

### 3.1.4 Obtaining UF<sub>4</sub>

As shown previously, the process for obtaining UF<sub>4</sub> by reduction precipitation using SnCl<sub>2</sub> had the best results and achieved an yield of 98% of UF<sub>4</sub> precipitation. The precipitation with HF solution is relatively slow and tends to accelerate as the temperature rises (17; 18). This is important, since it avoids excessive precipitate hydration and facilitates the sedimentation, filtration and drying operations. The full reaction is represented by:



During the uranium processing stages, the goal is to achieve an end product with high purity and showing physical and chemical characteristics appropriate for the preparation of nuclear fuel.

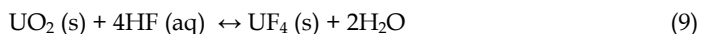
Table 3 lists the suitable chemical and physical characteristics of UF<sub>4</sub> for a later reduction to obtain metallic uranium.

	at 130°C				inert atmosphere at 400°C				
Uranium (%)	74.20				75.0				
Fluoride (%)	24.60				27.90				
UF <sub>4</sub> (%)	97.50				99.85				
UO <sub>2</sub> F <sub>2</sub> (%)	0.29				0.34				
UO <sub>2</sub> (%)	0.06				0.29				
HF(%)	0.23				0.12				
Moisture (%)	0.33				<0.03				
Crystallization H <sub>2</sub> O	4.50				<100				
Met. Impurities (µg/g)	Fe <20	Cr <10	Ni <10	Mo <5	Al <10	Mn <5	Cu <5	Sn 0,1	
Density (g/cm <sup>3</sup> )	6.70								
Granulometry (m)	15.0								
Specific Surface (m <sup>2</sup> /g)	0.21								

Table 3. Chemical and Physical Properties of UF<sub>4</sub> produced by an aqueous route

### 3.1.5 Preparation of UF<sub>4</sub> from UO<sub>2</sub>

The UF<sub>4</sub> obtained by reaction with UO<sub>2</sub> with hydrofluoric acid is easily made. The reaction can be summarized as follows:



This process has some advantages over the other processes. Since the reaction occurs at low temperatures, the reactor can be constructed using materials as polyethylene, polypropylene or carbon steel with plastic coating, while other processes require equipment built with metal (monel, inconel, nickel) which increases the cost of a plant.

In Figure 5, the x-ray diffractogram spectra are presented for UF<sub>4</sub> produced by the method via NH<sub>4</sub>HF<sub>2</sub> (bifluoride route) and by aqueous route. Typical SEM image of precipitated UF<sub>4</sub> is presented in Figure 6. It displays a granular structure with relevant amount of porosity.

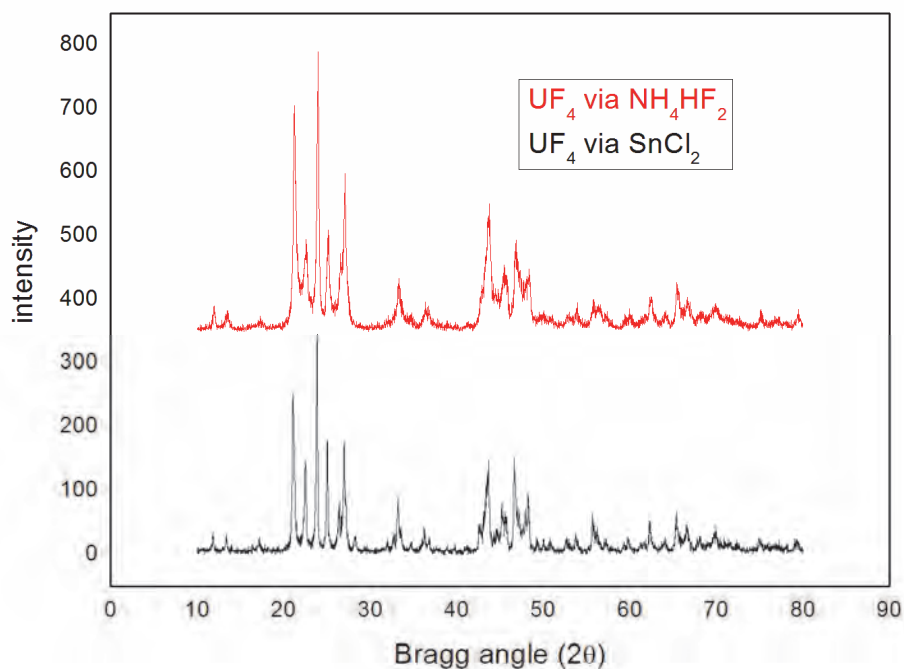


Fig. 5. X-ray diffraction pattern of  $\text{UF}_4$  produced by the bifluoride route and from the aqueous route.

The  $\text{UF}_4$  fabrication using fluorination media with ammonium bifluoride is perfectly feasible. The ammonium bifluoride is a by-product effluent generated during the  $\text{UF}_6$  conversion to AUC<sup>1</sup>.  $\text{UF}_4$  obtained by this route has the same crystalline structure presented by the aqueous process, as demonstrated by the x-ray spectrum. Besides, it has the correct chemical and physical characteristics for metallothermic production of metallic uranium. Even presenting a lower relative tapped density; this property will not be a problem, because this is an alternative process that has as main goals the recovery of uranium, ammonium and the fluorides of the liquid effluents generated in the process of  $\text{UF}_6$  reconversion. This  $\text{UF}_4$  will be lately diluted in the  $\text{UF}_4$  charges produced by the aqueous route. The development of this process (bifluoride route) not only provides an efficient process for uranium recovery from secondary sources, as also eliminates the environmental pollution by discarding the bifluoride. It also provides a chemical compound with chemical and physical characteristics very similar to the aqueous route ( $\text{SnCl}_2$ ).

<sup>1</sup> Ammonium uranyl carbonate ( $\text{UO}_2\text{CO}_3 \cdot 2(\text{NH}_4)_2\text{CO}_3$ ) is known in the uranium processing industry as AUC and is also called uranyl ammonium carbonate. Ammonium uranyl carbonate is one of the many forms called yellowcake in this case it is the product obtained by the heap leach process. This compound is important as a component in the conversion process of uranium hexafluoride ( $\text{UF}_6$ ) to uranium dioxide ( $\text{UO}_2$ ). In aqueous process uranyl nitrate is treated with ammonium bicarbonate to form ammonium uranyl carbonate as a solid precipitate and ammonium bifluoride as by-product (41).

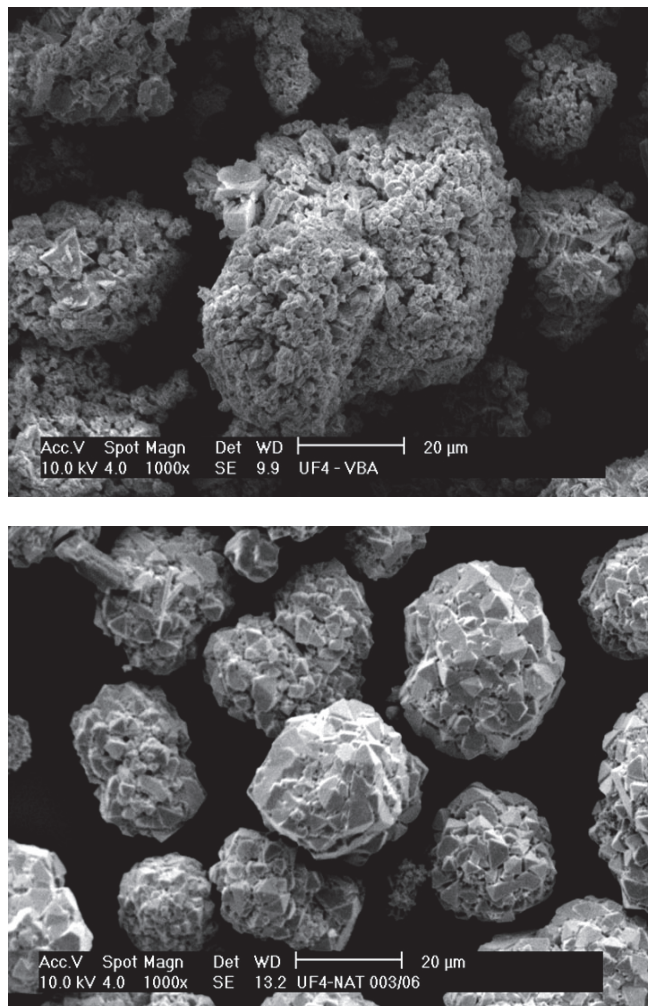


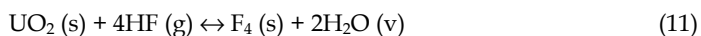
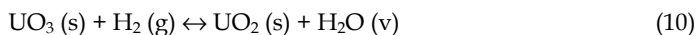
Fig. 6. SEM image of some UF<sub>4</sub> particles, produced by the bifluoride(a) route e via SnCl<sub>2</sub> (b).

### 3.2 Procedures for obtaining UF<sub>4</sub> by dry process

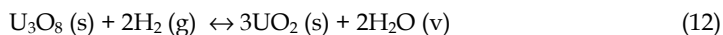
#### 3.2.1 Preparation of UF<sub>4</sub> by fluorination of UO<sub>2</sub>

The achievement of UF<sub>4</sub> by this process was adopted in Canada, France, the former Czechoslovakia, South Africa, United States, Portugal, Brazil, Germany and Sweden (17; 21; 23).

The sequence of operations is to reduce UO<sub>3</sub> by hydrogen, followed by treatment with HF resulting UO<sub>2</sub> anhydrous at atmospheric pressure.



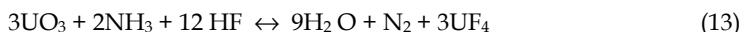
The reduction of  $\text{UO}_2$  is performed at temperatures of 500-700°C. Another alternative is the reduction of  $\text{U}_3\text{O}_8$  recommended when you have storage problems  $\text{UO}_3$ , being extremely hygroscopic.



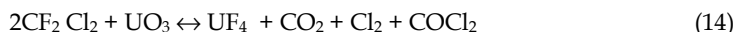
In such a process is commonly used the moving bed or fluidized bed reactor type.

Preparation of  $\text{UF}_4$  by reaction of the  $\text{UO}_3$  with  $\text{NH}_3$  and  $\text{HF}$  gaseous

The process consists of only one step to produce  $\text{UF}_4$ . The mixture consisting of  $\text{NH}_3$  and  $\text{HF}$  is treated with  $\text{UO}_3$  at 500-700°C. This reaction is fast and produces high purity  $\text{UF}_4$ :



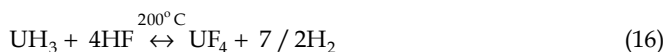
The  $\text{UF}_4$  fabrication by the reaction of uranium oxides with fluorinated hydrocarbons (freon) is as follows:



The literature shows results of reactions of different freons with uranium oxides  $\text{UO}_2$ ,  $\text{U}_3\text{O}_8$  and  $\text{UO}_3$  (27; 29; 33). The reactors used in this process cannot be constructed using nickel, copper, platinum and stainless steel, since they undergo chemical attack of reagents, besides this reaction promotes pyrolysis under carbon presence. The reactors are constructed with graphite or calcium fluoride, which may cause contamination to the obtained  $\text{UF}_4$ . The advantages of this method are equipment simplicity and the possibility of applying this reaction to all the uranium oxides.

### 3.2.2 Preparation of $\text{UF}_4$ from metallic uranium or uranium hydride ( $\text{UH}_3$ )

By fluoridation at high temperatures uranium metal can be quickly converted into uranium tetrafluoride by the reaction below:

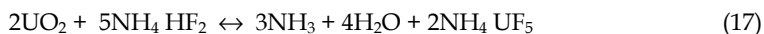


Uranium metal is industrially manufactured from  $\text{UF}_4$ . In the absence of advantage in obtaining first elemental uranium and transform it into  $\text{UH}_3$ , then get to  $\text{UF}_4$ .

### 3.2.3 Procedures for obtaining $\text{UF}_4$ by dry ammonium bifluoride with ( $\text{NH}_4\text{HF}_2$ )

The fluorination of  $\text{UO}_2$  is made with  $\text{NH}_4\text{HF}_2$ , a white solid; it has low vapor pressure and can be operated freely since it is non-toxic. Initially,  $\text{UO}_2$  is mixed with bifluoride, 20% above the stoichiometric amount. The bifluoride crystal is easily crushed and the mixture of  $\text{UO}_2 + \text{NH}_4\text{HF}_2$  is made in a monel 400 container to prevent contamination.

The conversion of bifluoride at room temperature occurs after approximately 24 hours, although under such conditions the water formed in the reduction may be retained in the precipitate. The elimination of  $\text{NH}_3$  and water is facilitated by the reaction of  $\text{UO}_2$  and  $\text{NH}_4\text{HF}_2$  at 150°C:



At this temperature, only 8 hours are necessary to promote the fluorination. The material is loaded into an aluminum container with calcium fluoride and heated inside a furnace. The furnace is fitted with a condensing tube with a relief valve, which releases the water and ammonia from the fluorination reaction to a reservoir and retains the excess of sublimed bifluoride.

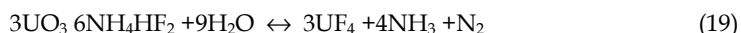
During the fluorination and/or decomposition, the formation of  $\text{UO}_2\text{F}_2$  probably occurs. This is a significant happening, since it may reduce the efficiency of reduction in the next step.

In a second step of the process, under vacuum distillation,  $\text{NH}_4\text{UF}_5$  is decomposed in  $\text{UF}_4$  with the  $\text{NH}_4\text{F}$  by this reaction:



### 3.2.4. Preparation of $\text{UF}_4$ by the reaction of ammonium bifluoride with $\text{UO}_3$

The  $\text{UF}_4$  can be prepared by reaction of ammonium fluoride or bifluoride with  $\text{UO}_3$  according to the equation:

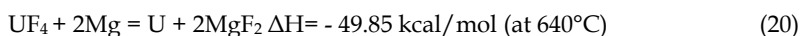


Although the United States have been among the first to study the process (34) Canada is the country that developed this process (35; 36)

## 4. Production of metallic uranium

There are several possibilities to produce metallic uranium (41; 26; 42). Magnesiothermic reduction of  $\text{UF}_4$  is one of them and it is a known process since early 1940's (7; 8). The IPEN technology uses 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 uranium weight is rather small if compared to big productions of natural uranium. Metallic uranium is reported (9) 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  $\text{UF}_4$  is preferred worldwide, since the exothermic heat is higher (-109.7 kcal/mol) compared to smaller amount of -49.85 kcal/mol using magnesium as the reducer (10). 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 there are virtually insignificant LEU uranium is lost (23).

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  $640^\circ\text{C}$ . The routine shows that this ignition normally

happens some degrees below this temperature (9). Nevertheless, several reactions may occur during heating of the  $UF_4+Mg$  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 ( $>100^\circ C$ ), 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 (30):



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 also occurring magnesium oxidation (very fast above  $620^\circ C$ ) by:



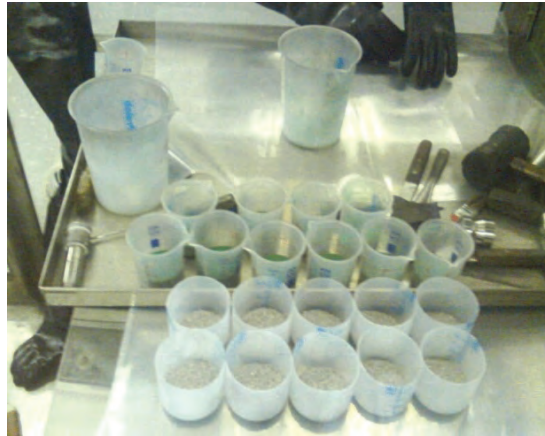
The presence of the  $UO_2$  and  $UO_2F_2$  in the produced  $UF_4$  accumulates with previous oxidized ones during the dehydration. All these compounds formation worsens the metallic yield of uranium production.

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  $U^\circ$ , is very enlightening to guide towards the interpretation of the reaction blast.

The IPEN's magnesiothermic reduction process of  $UF_4$  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  $1815 \pm 5g$  of the mixture  $Mg + UF_4$  ( $1540 \pm 1g$  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, 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 7.
2. After placing the reactants inside the graphite crucible, 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. 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.





(a)



(b)



(c)

Fig. 7. Sequence of  $\text{UF}_4 + \text{Mg}$  charging in IPEN's magnesiothermic method to produce metallic uranium. (a) 10 layer preparation of  $\text{UF}_4$  (green) and Mg (metallic bright); (b) blending of material; (c) full charge after tapping the 10 layers.

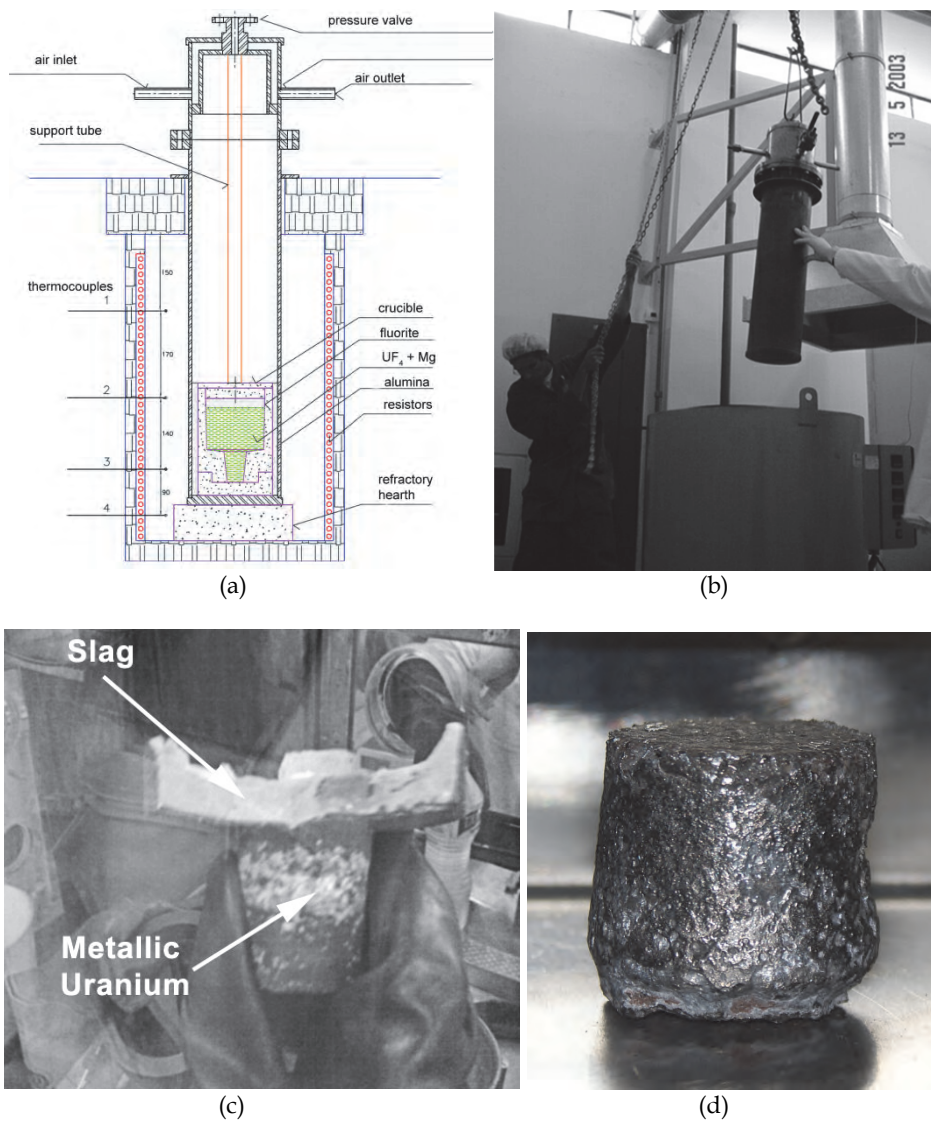
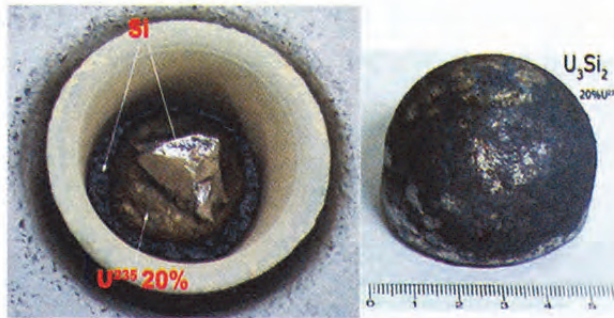


Fig. 8. (a) Schematic drawing of pit furnace, reactor vessel and crucible; (b) Charging of the reactor vessel inside the pit furnace; (c) Raw metallic uranium and upper deposited slag after removing from the crucible; (d) Metallic uranium after cleaning.

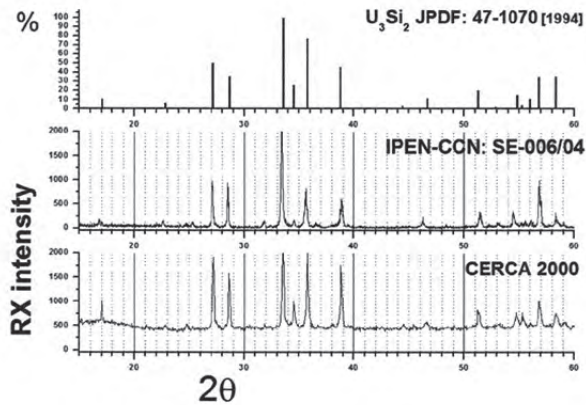
3. After closed with the top cover, the crucible is inserted inside a stainless steel cylindrical reactor vessel, made of ANSI 310, which allows argon fluxing during batch processing (1 L/min with 2 kgf/cm<sup>2</sup> of pressure). As shown in Fig. 8 (a-b), the whole crucible + reactor are placed in resistor pit furnace with four programmable zones having the possibility of raising the temperature up to 1200°C.
4. The reaction vessel is set to heat 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<sub>4</sub> with Mg produces an intense exothermic heat release inside the crucible. It is considered as an adiabatic reaction. It produces metallic uranium and MgF<sub>2</sub> 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 and freeze there.
6. This full reaction happens in a noticeable time between 800 and 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 disassembling 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<sub>2</sub> 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.

## 5. Production of uranium silicide

The intermetallic U<sub>3</sub>Si<sub>2</sub> is produced from metallic uranium (47). This alloy is produced from a uranium ingot and hyperstoichiometric silicon addition (7.9% Si). The induction furnace (15 kW) should be submitted to 2.10<sup>-3</sup> mbar vacuum and flushed with argon-atmosphere. Then the melting is carried out. The blend is molten inside an induction furnace using zirconia crucible reaching more than 1750°C, as this intermetallic requests this level of temperature to be properly homogenized before solidification. No other crucibles, than a zirconia one could bear the aggressive environment created by uranium attack on linings. The load arrangement of uranium and silicon, as shown in Fig. 9, is then charged inside the crucible. It was planned to help the sequence of melting during the several stages that passes the alloy formation until reaching the final intermetallic composition. The quality of this intermetallic produced in this way normally meets the requirements as nuclear material. The X-ray diffractogram (Fig. 9) confirms the necessary proportion of phases presents in the produced powder of this alloy, which should be more than 80wt% of crystalline phases. As rule of thumb, the chemical amounts of boron, cadmium, cobalt, lithium should be less than 10µg/g individually. The other may reach hundreds of µg/g up 1000 µg/g. Carbon could reach up to 2000 µg/g. Isotopic concentration of <sup>235</sup>U is 19.75±0.20wt%. The required density is 11.7g/cm<sup>3</sup>.



**Assembling of  $U_3Si_2$  crucible load**



**X-ray diffractogram of  $U_3Si_2$  produced in Ipen compared**

Fig. 9. Crucible arrangement of before melting to produce the intermetallic.  $U_3Si_2$  product and its x-ray diffractogram results compared to CERCA product and JPDF 47-1070 for pure  $U_3Si_2$ .

### 6. Production of MTR nuclear fuel

The reference industrial process to produce plate-type fuel involves roll-milling together the fissile core, or fuel meat (a blend of an uranium compound and aluminum powders), and the cladding (aluminum alloy plates). This process can draw on considerable feedback from experience, since nearly all research reactors use this type of fuel. The process has seen large-scale implementation with NUKEM, in Germany, UKAEA, in the United Kingdom, CERCA, in France, and Babcock, in the United States.

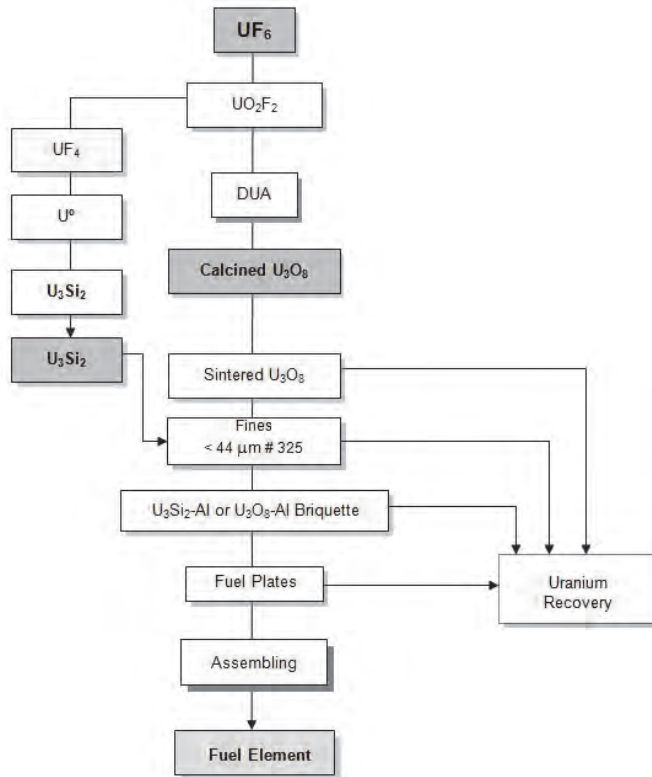


Fig. 10. Fabrication process of silicide fuel elements.

In general, the MTR type fuel element fabrication process using silicide ( $U_3Si_2$ ) can be divided into the following main steps: hydrolysis of  $UF_6$  through its reaction with water; production of uranium tetrafluoride ( $UF_4$ ); production of metallic uranium;  $U_3Si_2$  powder production from uranium metal; production of fuel cores from  $U_3Si_2$  and aluminum powders; production of fuel plates with  $U_3Si_2$ -Al dispersion; assembling of fuel elements; recovery of uranium; effluent treatment; quality control.

The simplified block diagram of the fabrication process for silicide fuel elements is shown in Figure 10. The manufacturing process of the fuel begins with the  $UF_6$  processing. The  $UF_6$  is enriched to 19,75 wt%  $^{235}U$ , a enrichment level that categorize the fuel as LEU (low enriched uranium). Below the main stages of manufacture of such fuel are discussed.

### 6.1 Fuel cores production from $U_3Si_2$ and aluminum powders

The  $U_3Si_2$  ingot produced in the previous step is transferred to a glove box with inert atmosphere of argon, since the  $U_3Si_2$  is pyrophoric. Inside the glove box, the ingot is subjected to a preliminary grinding, resulting in granules less than 4 mm in size with the smallest fraction of fines ( $< 44 \mu m$ ) possible. This operation is performed with the aid of a manual crusher. After doing the preliminary grinding, the material is placed directly on a set of sieves, and then sieved by hand. The sieve set comprises a coarse sieve with 4 mm opening, a fine sieve with  $150 \mu m$  opening and a background compartment. The granules with a diameter greater than 4 mm are crushed again. The granules with size between 4 mm and  $150 \mu m$  are collected for final grinding and particles smaller than  $150 \mu m$  are collected separately for particle size classification.

The  $U_3Si_2$  obtained after the preliminary grinding is manually milled again. The material collected during the preliminary grinding (between 4 mm and  $150 \mu m$ ) is processed in this step. The grind is done carefully, with intermediate sieving, to classify the powder in the range from 150 to  $44 \mu m$ . The specification allows 20 wt% fines fraction (below  $44 \mu m$ ) as maximum. The fraction above the specification ( $150 \mu m$ ) is sent back to the final grinding system. The fraction inside the specified range (between  $150 \mu m$  and  $44 \mu m$ ) is collected and stored. The fraction of fines ( $< 44 \mu m$ ) is collected and stored separately. The glove box contains a vibrating screening machine, which performs the separation of three size fractions of silicide powder, above  $150 \mu m$ , between 150 and  $44 \mu m$  and below  $44 \mu m$ . The batch  $U_3Si_2$  powder composition is adjusted to have maximum fines content in the level of 20 wt%, as specified.

The next process step is the fabrication of the fuel cores, which will form the core of the fuel plates, or fuel meats. The core of the fuel plate contains  $U_3Si_2$  as the fissile material. This core is fabricated by means of powder metallurgy techniques and is normally called briquette or fuel compact. Initially, the mass and composition of the briquette are calculated based on the analyzed values of total uranium and isotope enrichment of the  $U_3Si_2$  powder. The criterion for calculating the briquette mass is the amount of the isotope  $^{235}U$  specified for the fuel and the dimensions of the briquette. Based on the calculated mass of the briquette, the silicide Al powders mass are determined separately and mixed together to ensure that the specified  $^{235}U$  amount is uniformly distributed. These charges are cold pressed to form the fuel compacts, and the briquettes are measured and weighed. The final dimensions of the fuel meat in the finished fuel plate are set by specification and the volume of the briquette is calculated from these data by their values of thickness, width and length. The thickness of the briquette is obtained by multiplying the specified thickness of the fuel meat by the deformation dimension resulted after rolling operation, assuming zero enlargement. The core content of voids depends only on the volume fraction of fuel powder content. To optimize the final geometry of the rolled core, the briquette has rounded corners, and the volume of the corners is included in the calculation of volume.

The difference between the volume of the briquette, obtained as described above, and the volume of the fuel powder, as determined by the division between the mass of the powder and its density, determines the amount of aluminum powder to be added to the mass of the briquette. As the theoretical density of the system cannot be achieved during the compaction of the briquette, the volume of aluminum is reduced by the amount of pores that remain after pressing. The total mass of the briquette is given by the calculated mass of fissile material powder added to the calculated mass of aluminum powder.

According to the calculation for the masses of  $U_3Si_2$  and aluminum powders, the charges for pressing are weighed separately. The weighing is carried out in glass bottles specially designed for installation in a homogenizer. Once the powders are weighed, the charge is mixed inside a glove box with inert atmosphere. This blending ensures that the specified amount of  $^{235}U$  is homogeneously distributed throughout the briquette to be pressed. The weighing operation is performed carefully and, after homogenization, the cautious handling of the charge is critical to avoid segregation.

The homogenization operation is performed using a special homogenizer with a capacity for simultaneous mixing of eight charges. The duration of homogenization is 120 minutes under rotation of 36 rpm and angle of  $45^\circ$ . To prepare the briquettes, the homogenized charges are pressed at room temperature using a hydraulic press with capacity for 700 tons, which is placed in a glove box. The pressing pressure is adjusted to get the desired thickness, keeping the residual porosity from 5 to 7% by volume. The bottle containing the homogenized charge is transferred from the glove box used for homogenization to the glove box used for pressing. Within this glove box, the charge of a briquette is emptied into the die cavity with the inferior puncture initially raised. The powder is placed in layers with the aid of a special smoother to prevent segregation and to minimize the variation of the thickness of the briquette, lowering the punch inferior gradually until all the charge is loaded, when the punch is fully lowered to its position during the pressing. Then, the superior punch is inserted and pressure is applied and maintained for 15 seconds. The entire array is then opened to eject the briquette and the punch superior, which is manually removed. The thickness of the briquette is defined based on final specifications valid for the fuel meat. This thickness is theoretically calculated and then adjusted through manufacturing tests.

Immediately prior to the transfer of the briquettes to be used in the manufacture of fuel plates, they are vacuum degassed at  $2 \times 10^{-3}$  torr in a retort. The temperature is  $250^\circ C$  kept for 1 hour. After remaining inside the degassing retort for the time and temperature specified, the briquette is removed for cooling, keeping the vacuum system working until the room temperature is reached. Thus, the briquettes that will compose the cores of the fuel plates are used in the new phase of processing, or assembling the sets for rolling. Figure 11 illustrates the process for preparing the briquettes and the set.

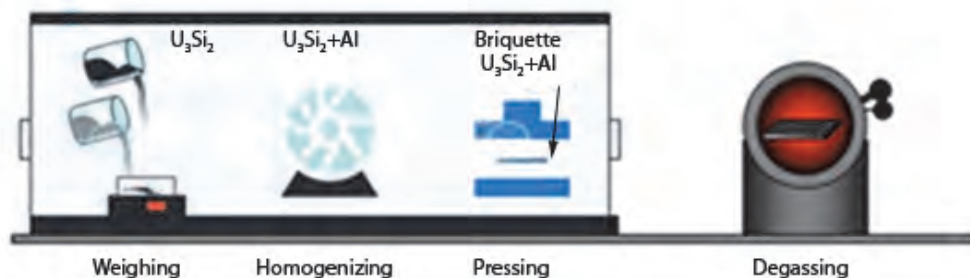


Fig. 11. Process for briquettes preparation and degassing.

## 6.2 Production of fuel plates with $U_3Si_2$ – Al dispersion

The technology of fuel plates manufacture adopts assembling and rolling of a set composed by the fuel meat (briquette), a frame plate and two cladding plates. In this way, after the rolling operation, it is fabricated a fuel plate containing inside the fuel meat totally isolated from the environment, which is done through the perfect metallurgical bonding between the core and frame with the claddings. The frame and cladding plates are made from commercial aluminum Al 6061 alloy (48).

In order to prepare the rolling assemblies, the frame plate is heated in a furnace at 440 °C. The cold briquette is then assembled inside the frame plate. Once cooled the frame, the briquette should be perfectly housed and fixed in the frame cavity by mechanical interference. The other cladding plates are placed above and below the frame plate with the core, completing then the assembling to be rolled. This assembly set is then fixed in a rotating welding bench and welded at its edges. The welding is TIG type protected with argon. A continuous welding bead is done on the four corners of the assembly, leaving the ends free in order to allow air to be exhausted in the first rolling pass. Figure 12 illustrates the procedure of preparing the assemblies for rolling.

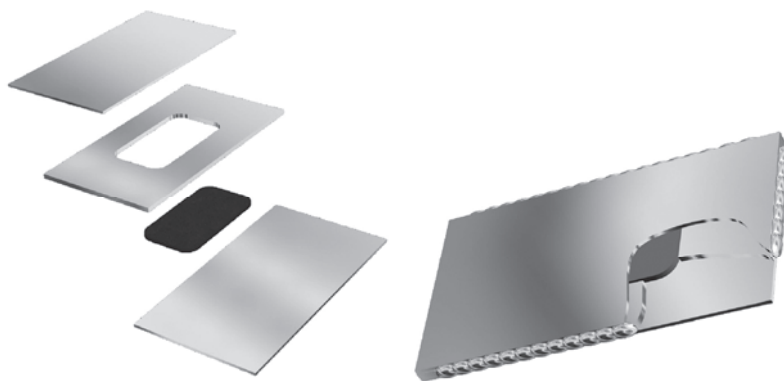


Fig. 12. Diagram illustrating the assembling of the set core-frame-claddings.

The welded assemblies are properly identified and inserted in a furnace for 60 minutes at a temperature of 440 °C. The hot rolling is performed in several passes following a well-established rolling schedule. The rolling schedule defines thickness reduction per pass in order to control the end defects and the final dimensions of the fuel meat. The rolling schedule is determined by theoretical calculations and empirical data from manufacturing tests and must guarantee the metallurgical bonding and the control and reproducibility of the fuel meat deformation. The rolling mill usually has an accuracy of 0.025 mm and is equipped with rolling cylinders coated with a chrome layer. It is important the perfect lubrication of the rolling cylinders. Between each pass, the assemblies are reheated for 15 minutes. After the final hot-rolling pass, the fuel plates are identified again in the same position of the initial identification in a region outside the fuel meat, using mechanical marker.

After hot rolling, a blister test is performed to test the metallurgical quality of bonding between meat-frame-claddings. The hot rolled plates are heated at 440 °C for 1 hour. After



removal from the furnace, the fuel plates are visually inspected for observation and recording of bubbles (47; 48). Fuel plates that present bubbles are registered as reject and forwarded for chemically recover of uranium.

The cold rolling operation is performed in the same rolling mill used in the hot rolling. In this operation the specified thickness is achieved with precision. The total cold reduction is approximately 10% in thickness and is applied in one or two passes. During cold rolling, the length of the fuel meat is checked, ensuring the fulfillment of the specification for the minimum core length and for the thickness of the fuel plate.

After cold rolling, the fuel plates are pre-cut for facilitate handling during the subsequent fabrication operations, as flattening, radiography and final cut. The fuel plates obtained in cold rolling have their surfaces still undulating, requiring a flattening operation. This operation is performed using a roll-flattener, which is basically consisted with a group of flattener cylinders controlled by a position adjustment system to keep the cylinders in a flat position. Only one pass is enough to flatten the fuel plates.

The next step is the final cut of the fuel plate to reach the specified dimensions. This cut is made using a guillotine cutter machine and is oriented by x-ray radiography. This radiography is obtained by using an industrial system set, where the fuel meat can be perfectly positioned inside the fuel plate and, then, the plate receives line tracing to guide the final cut. Next, the fuel plates are degreased in acetone and pickled in a solution of NaOH 10wt% for 1 minute at 60 °C. Then, they are washed in water for 1 minute, neutralized in cold 40wt% HNO<sub>3</sub> for 1 minute, rinsed again in running demineralized water for 5 minutes (spray), washed by immersion in hot demineralized water and dried manually with the aid of hot air blast. Figure 13 shows a drawing of the fuel plate, illustrating its fuel meat. Figure 14 shows the sequence of operations performed to manufacture the fuel plates.

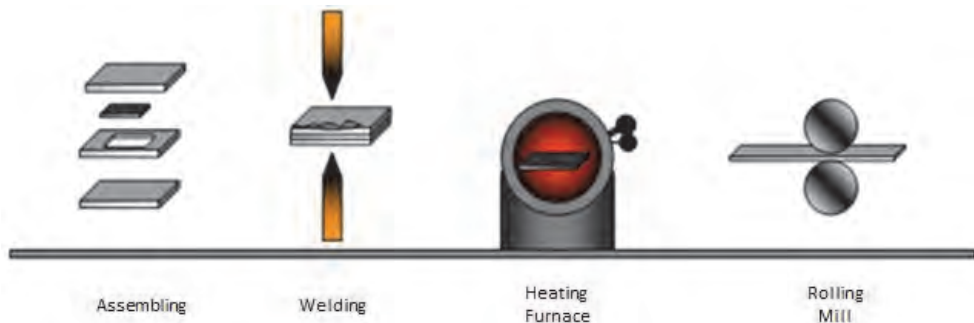


Fig. 13. Illustration of the process for preparing the assemblies and rolling

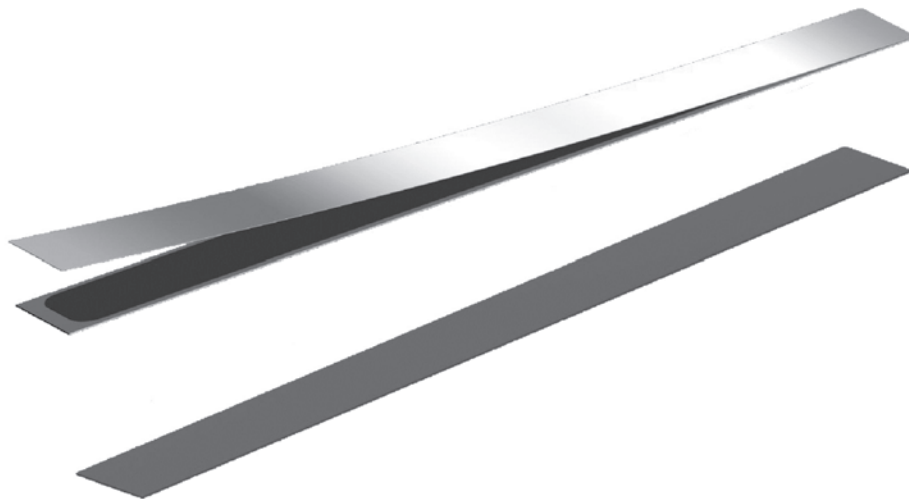


Fig. 14. The schematic illustration of the finished fuel plate (after rolling).

The finished fuel plates are characterized dimensionally, measuring in its length, width and thickness. Fuel plates that do not meet the dimensional specifications are rejected and sent for uranium recovery.

After the final cut, two new radiographs are obtained. The first one aims at checking the position of the fuel meat inside the fuel plate, as well as to verify its dimension, length and width. The second radiography aims to check the uranium distribution homogeneity in the fuel meat and also its integrity, as well as the possible presence of "white spots" and fissile particles outside the fuel meat zone.

To check the reproducibility and stability of the manufacturing process of fuel plates, the residual porosity of the fuel meat of all fuel plates produced are determined using the Archimedes principle.

Every 24 fuel plates produced, one fuel plate is separated to characterize the end defects in the fuel meat, which are basically the cladding thickness reduction in the area of the "dog-boning", inspection of the "diffuse zone" (end of the fuel meat) for studying the "fish tail" defect and to do the final geometry inspection of the fuel meat. This analysis is performed destructively to allow metallographic image analysis. In the case of fuel plate production routine, the quality analysis samples is randomly made (1:20) over all produced plates to check possible defects that do not meet specifications. In case, the sample is rejected then a second fuel plate is randomly taken from the batch and is destroyed to be examined. If this second sampled plate also proves defective then the entire batch is rejected. This metallographic analysis is performed using standard metallographic techniques and specific equipment for this purpose. All fuel plates rejected are forwarded for uranium chemical recovery.

The metallurgical bonding quality of the assembled plates set, after rolling, is checked by means of bending tests. This test is performed at two occasions, after pre-cutting and after the final cut. This test is performed in the leftover material from the cutting operations. The material is extensively bent in an angle of  $180^\circ$  and in reverse. In case of bonding failure, which is easily detected by visual inspection, the fuel plate is rejected and sent to uranium chemical recovery.

### 6.3 Assembling of fuel elements

In IPEN, two types of fuel elements are manufactured. The standard fuel element consists of 18 fuel plates, 2 side plates (right and left), a nozzle, a handling pin and 8 screws. The control fuel element is composed of 12 fuel plates, two side plates (right and left), two guide plates, a nozzle, a dashpot and 12 screws. The dimensional characteristics of the fuel elements are specified. All structural components of the fuel element are manufactured according to designs that are part of the specifications.

The process begins with the assembling of fuel plates to form a case that is the structural body of the fuel element. The plates are fixed to the side plates (left and right) by mechanical clamping. Subsequently, the nozzle is fixed. For the standard fuel element, the handling pin is fixed on the side opposite to the nozzle. In the case of the control fuel element, the dashpot is fixed on the side opposite to the nozzle. After cleaning and inspection, the fuel element is packed and stored until transportation to the reactor. Figure 15 illustrates the steps for the fuel elements assembling process.

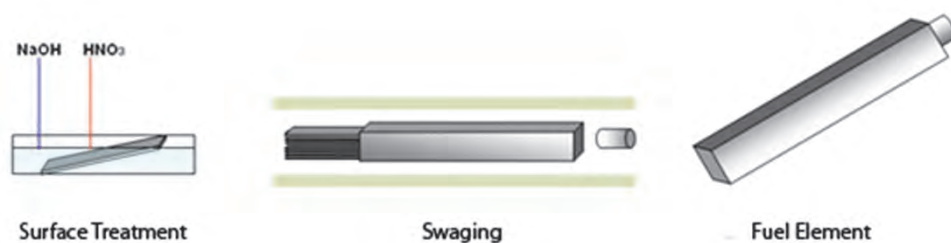


Fig. 15. The process of assembling the fuel elements.

After fixing the fuel plates in the side plates to form the main case, the next component to be installed is the nozzle. The nozzle is used to fix the fuel elements in the reactor core. It is fixed by screws at the lower end of the main case. The nozzle is aligned with the case of fuel element through an adjustment operation by using precision measuring instruments. The holes in the nozzle that are used to fix the side plates are already machined. The holes to hold the external fuel plates at the nozzle are machined with the nozzle already fixed in the side plates, with the aid of a milling machine. The screws used are made with aluminum and are already qualified and properly cleaned before use. The final tightening is done after a previous dimensional characterization, once verified the alignment of the nozzle in the main case. If alignment does not meet the specification, it is adjusted. In the case of the control fuel element, the procedure for fixing the nozzle and dashpot is the same as described above.

The handling pin is used to handle the standard fuel element inside the reactor pool. It is installed at the upper end of the main case, which contains two holes where the handling pin is fixed by clinching. In this operation, the ends of the handling pin, which have cavities, are deformed by pressure with the aid of a drilling machine. In the case of the control fuel element, this pin is replaced by the dashpot, which is aimed at damping the control or security bars that operates within this type of fuel elements. Figure 16 illustrates the standard fuel element and its components.



Fig. 16. Schematic illustration of the fuel element produced at IPEN.

Once qualified, the fuel element is washed in a bath of ethyl alcohol and dried manually with the aid of a jet of hot air. After this cleaning, a visual inspection is conducted, especially inside the cooling channels (the channels between the fuel plates), trying to detect possible obstructions caused by chips or foreign material. After washing and inspection, the fuel element is transferred to the reactor.

## 7. Uranium recovery and effluent treatment

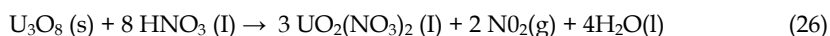
A great variety of uranium residues must be recovered by chemical means. A major source of such residues is uranium remaining in crucibles after melting and pouring. The recovery of solid or liquid uranium residues is vital because quantities are generated in every step of the process and this is a valuable material that must be recovered for reuse. Figure 17 displays a schematic diagram of the process showing the flow of products and residues.

The first step of the chemical recovery process is usually acid leaching to solubilize the uranium content. Any of several purification steps may then be employed to separate impurities such as iron, chromium, nickel, silicon, boron, etc. The end product of chemical recovery process is  $UF_4$  which can be reduced to metal and then recycled. A typical sequence of chemical processing steps to recover uranium compounds from leach liquor is solvent extraction with tributyl phosphate, dinitration of purified uranyl nitrate solution to produce uranium trioxide ( $UO_3$ ), and hydrogen reduction and hydrofluorination of  $UO_2$  to  $UF_4$ . The technology of these operations is similar to that used in processing normal uranium.

Since chemical recovery will usually involve aqueous mixtures of uranium compounds, nuclear safety limits the critical dimensions of process equipment and imposes bath quantities within safe limits. If these factors are properly provided for chemical recovery unit design, the process operating costs will not be substantially raised by nuclear safety requirements.

The aggregate amount of scrap recycled via chemical recovery may reach 10% or more of finished fuel material weight. Chemical recovery is naturally more costly than direct recycle of metallic scrap to remelt. These considerations justify various expedients to by-pass chemical recovery by recycling metallic scrap. However, particular emphasis is given to the recovery of all residues solids and liquids because of the higher intrinsic value of the enriched material.

As an example, the IPEN process to produce  $U_3Si_2$  involves metallic uranium as an intermediate product, through magnesiothermic reduction which produces slags containing uranium. The recovery process consists on slag lixivium of calcined by-products from metallic uranium reduction. The results from researching this process confirmed that this method could be integrated in treatment and recovery routines of uranium. The chemical route avoids dealing with metallic uranium since this material is unstable, pyroforic and extremely reactive. On the other hand,  $U_3O_8$  is a stable oxide with low chemical reactivity, and it justifies the slags calcination of metallic uranium reduction by-products. This calcination occurs under oxidizing atmosphere and transforms the metallic uranium into  $U_3O_8$ . Some experiments have been carried out using diferente nitric molar concentrations, acid excess contents and temperature control of the lixivium process. The nitric lixivium main chemical reaction for calcined metallic uranium slags is represented by the equation:



The adopted process has the following parameters:

- Temperature and time: calcination of metallic uranium slag at 600°C during 3h;
- Granulometric control: sieving and segmentation of calcined slag in the range of 100-200 mesh;
- Concentration: lixivium adjustment of  $HNO_3$  at 1 molar;  $HNO_3$  excess (120%);
- Lixivium temperature: 40 - 50°C;
- Agitation: 300 rpm, turbine stem type (45° inclination).

As results, the full lixivium took 9 hours; the fluoride concentration in lixivium was 0,002g/L. Lixivium made at lower temperatures and lower nitric concentrations reduced both the magnesium and calcium fluorides solubility and the corrosion effect caused bifluoride ions was not prominent. This ensured a stable and secure lixivium from the operational point of view. The nitric dissolution of metallic uranium slags produced uranyl nitrate solution, which has been reused as a feed-in compound for uranium purification system made by solvent extraction method, using diluted n-tributylphosphate. The purified uranium product was then precipitated as ammonium diuranate (ADU) at 60°C, by injecting ammonium gas diluted with air. Aiming at returning the recovered product to the fuel fabrication cycle with nuclear quality level, the purified ADU was converted into uranium tetrafluoride ( $UF_4$ ) by  $U_3O_8$  route. The final yield in U content was 94%, proving the viability of IPEN's slag recovering from uranium magnesiothermic reduction.

## 8. Acknowledgements

Thanks are due to IPEN for providing generously the technology of Nuclear Fuel Center, fully exemplified in this chapter, providing so nuclear know-how to a more peaceful, safer and healthy world. We are especially thankful to our colleagues who provided lots of information shown here, mainly Mr. Davilson Gomes da Silva who made many of the illustrations to qualify better this text.

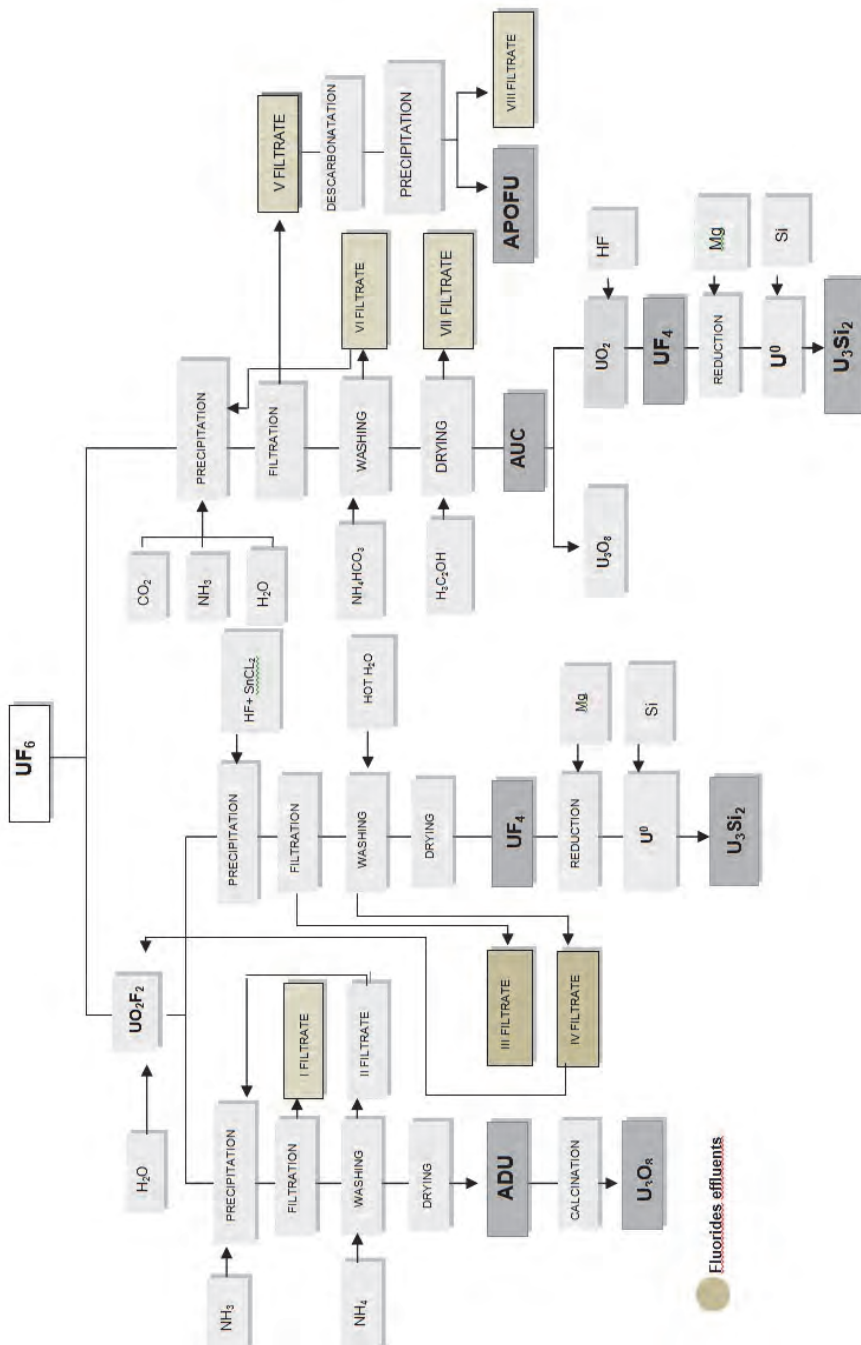


Fig. 17. Flowsheet MTR fuel processing (products and residues solid, liquids) (55; 54)

## 9. Conclusions

This chapter gave a general idea of the MTR fuel elements production for multipurpose and researching reactors that are producing radioisotopes throughout the world. Nowadays, the level of uranium enrichment is envisaged to be 20% (LEU), according to ruling requests of RERTR program. The given example of this production derived from IPEN/CNEN-São Paulo-Brazil, which produces through a well established routine to fabricate its own MTR fuel elements. Nevertheless, the technique to produce such elements has many variants, which are applied diversely from plant to plant.

As a final consideration, the future of fuel elements material, based on RERTR request, should also supply many high performance research reactors needing higher core densities of 6 to 9 gU/cm<sup>3</sup>. This demand is not possible with U<sub>3</sub>Si<sub>2</sub> elements, since its operational upper limit is less than 5 gU/cm<sup>3</sup>. So, the presently envisaged product to reach this request is based on U-Mo alloy. Nevertheless, this product is not ready yet. Future prognosis are very confident that alloys U + 7 to 10wt%Mo should meet up this ability. This alloy production is still in experimental-pilot level, by this moment (2011), but with very consistent and pertinent results. For those willing to follow the development of this research, we indicate the transaction pages of RERTR and RRFM<sup>2</sup>, where all papers and results are displayed freely.

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<sup>2</sup>RERTR - Reduced Enrichment for Research and Test Reactors Program]: <http://www.rertr.anl.gov/>  
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