OBTAINING OF THE NUCLEAR GRADE ZIRCONIUM TETRACHLORIDE BY THE CHLORINATION PROCESS

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ABSTRACT

The nuclear grade tetrachloride zirconium ($ZrCl_4$) is an important chemical reagent for obtaining of the metallic zirconium sponge for the manufacture of the fuel rods of the fuel element, used in nuclear reactors. The zirconium oxide (ZrO_2) pellets are fed into the alumina reactor located inside of the chlorination furnace, which reacts with the chlorine gas, condensing to form the $ZrCl_4$. The study to the chlorination process of the ZrO_2 pellets allowed the obtaining of the $ZrCl_4$ in favorable conditions for production of this material in laboratory scale, aiming for obtaining of the zirconium sponge by the reduction process.

Key words: tetrachloride zirconium, ZrO_2 pellets, metallic zirconium sponge, nuclear reactors

INTRODUCTION

Metal chlorides are raw materials of fundamental importance, both economic and strategic, for the electronics, telecommunications, metallurgical, nuclear industries, and in areas related to advanced ceramics, chemicals, and automobiles. Among the metallic chlorides, zirconium tetrachloride ($ZrCl_4$) is one of the starting materials for the production of zirconium metal via the Kroll process [1, 2]. Zirconium metal or zirconium-based alloys are used in structural material for nuclear power reactors, in vacuum tubes of electronic instruments, in pyrotechnics, manufacture of munitions, in chemical plant equipment and production of steels and nonferrous metal alloys [1]. In special, the zirconium metal and zirconium-based alloys used in nuclear industry as a structural material is explained by its low thermal neutron capture cross section (about 0,2 barn), its high resistance to corrosion and favorable mechanical properties [1].

According to Landsberg, Hoatson and Block [3], the chlorination process is important step in the large scale, commercial production of zirconium metal. Zirconium tetrachloride ($ZrCl_4$) may be obtained by chlorination of three raw materials: zircon concentrates, zirconium oxide, and zirconium carbide. In this present article, the $ZrCl_4$ was prepared by chlorination of reactor grade zirconium oxide in presence reducing agent at high temperatures. The $ZrCl_4$ which sublimes at 331^{o}C is recovered in water cooled condensers which are discharged into glass recipients.

The objective of this work is to present the development of the chlorination process directing for obtaining of the nuclear grade zirconium tetrachloride. The raw materials such as porous pellets were characterized by X-ray diffractometry (XRD), scanning electron microscopy (SEM), porosity, compression test and drop test, aiming microstructural and physical characteristics suitable for the process, and the $ZrCl_4$ product was characterized by inductively coupled plasma optical emission spectrometry (ICP-OES) for verification of the impurities contained in the product.

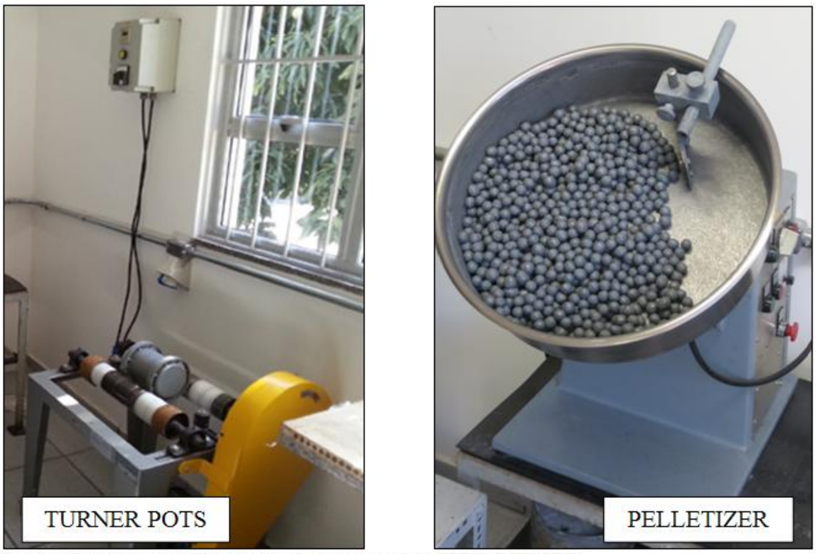
EXPERIMENTAL

Zirconium oxide pellets preparation

The powders of nuclear grade zirconium oxide (77.7% in weight) were mixed with graphite (9.8% in weight) and sugar (12.5% in weight) turner pots, after these powders were dried in an oven, and were pelletized using the following operational conditions [4]:

- inclination of the pelletizing plate = 45°
- inclination of the scaper = 45°
- initial rotational speed of the pelletizing plate = 26 rpm
- final rotational speed of the pelletizing plate = 52 rpm

The **Fig 1** shows turner pots and pelletizer with pellets utilized our experiments.



Source: Reduction and Chlorination Laboratory of the IPEN-CCTM-P7

Fig 1 Turner pots and pelletizer equipments.

The pellets obtained were dried in an oven at 80-100 °C to remove humidity. Subsequently, the green pellets were stabilized at 600 °C to increase their strength sufficient to withstand handling in the chlorination stage. The stabilized pellets were classified according to their diameters, between 9.5 and 15.9 mm for chlorination process [5]. The green pellets and stabilized pellets are show in **Fig 2**.

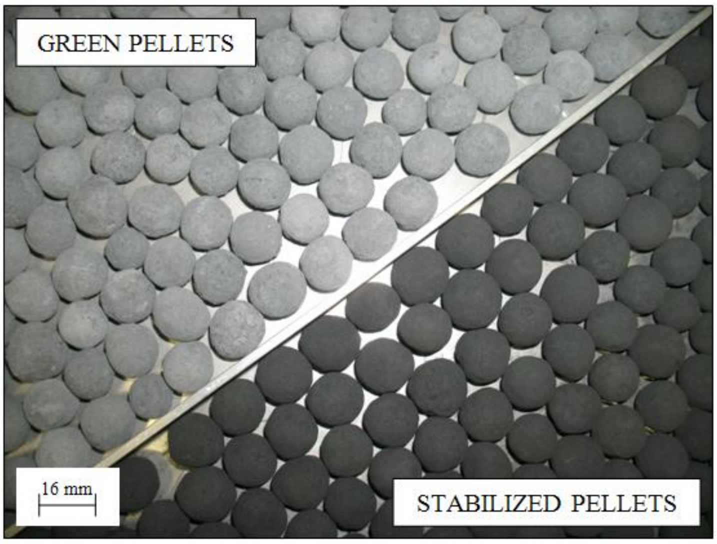


Fig 2 The green and stabilized pellets.

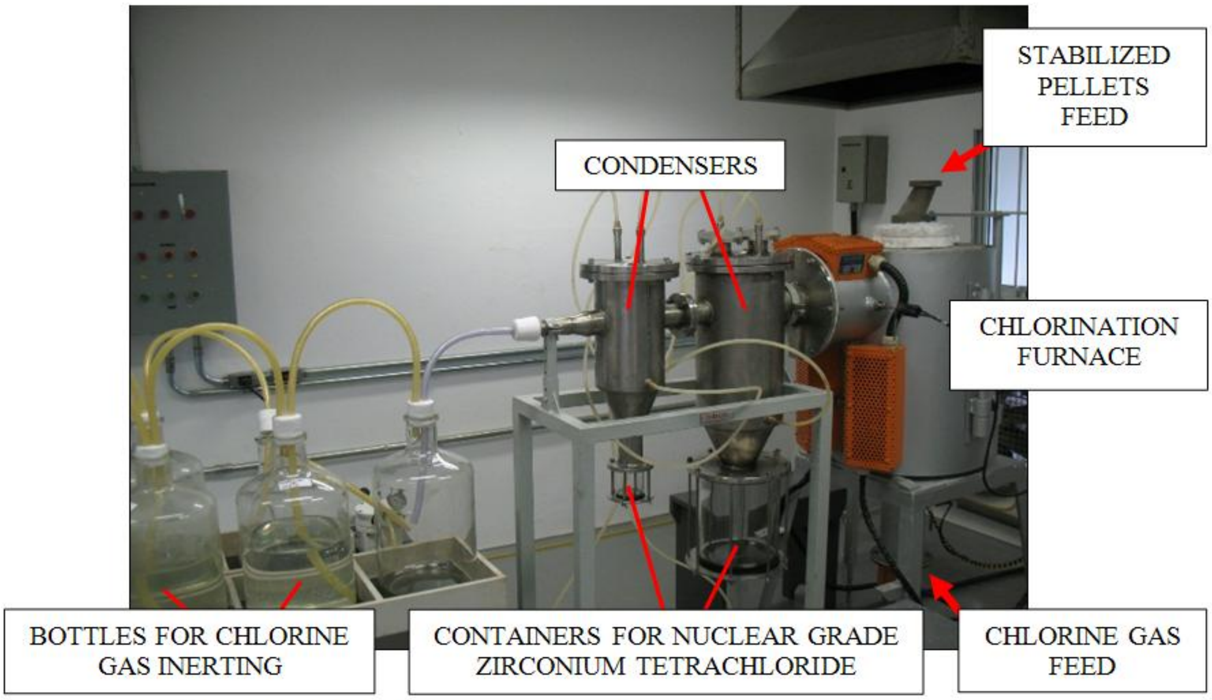
The chemical composition of the ZrO_2 obtained by x-ray fluorescence is shown in **Table 1**. The specific mass (density) of the ZrO_2 as determined by helium gas picnometry was de 5.750 ± 0.001 g/cm^3, and found to be quite close to the theoretical value (5.68 g/cm^3) .The average particle size of the ZrO_2 within the grain size range was 16.71 µm, as obtained by sieve analysis.

Table 1 Chemical composition of the ZrO_2

Chemical compound	**Content (%)**
ZrO_2	90.902 ± 0.062
SiO_2	7.606 ± 0.036
Al_2O_3	1.477 ± 0.052
HfO_2	0.015 ± 0.005

The chlorinator was constructed, using alumina tube, with inside diameter of 100 mm and height of 1000 mm. A porous graphite disk is positioned in the central part of the reactor.

A vertical bed alumina chlorinator was heated externally by an electric resistance furnace. Nitrogen gas was admitted to eliminate moisture of experimental system. Dry chlorine gas at the desired flowrate was passed through the bed of ZrO_2 pellets kept at a desired temperature. At the end of the experiment the bed ZrO_2 pellets was cooled in nitrogen atmosphere. The product chlorides were collected in two ice cooled condensers and the unreacted Cl_2 was allowed to be absorbed in sodium hydroxide solution and water scrubbers. After chlorinating for the desired period, the weight of the remaing ZrO_2 pellets was determined. A sketch of the chlorination unit is given in **Fig 3**.



Source: Reduction and Chlorination Laboratory of the IPEN-CCTM-P7

Fig 3 The chlorination unit of nuclear grade zirconium oxide.

The nuclear grade zirconium tetrachloride produced is removed from the glass containers and packed in plastic bags and stored in a glass desiccator as shown in **Fig 4**.

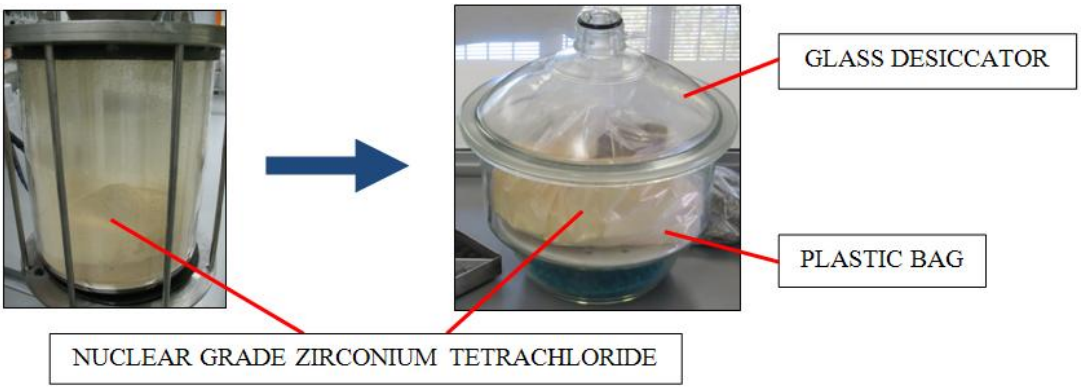


Fig 4 Packaging nuclear grade zirconium tetrachloride product.

The nuclear grade zirconium tetrachloride is used as raw material for the production of nuclear grade metallic zirconium sponge.

RESULTS AND DISCUSSION

The porous pellets fed into the furnace chlorination were characterized by X-ray diffractometry (XRD), scanning electron microscopy (SEM), porosity, compression test and drop test, and the $ZrCl_4$ product was characterized by inductively coupled plasma optical emission spectrometry (ICP-OES).

The analysis by X-ray diffraction, the diffraction of porous pellets is presented in **Fig 5**. The peaks related to ZrO_2 and graphite, were identified using the Crystallographica Search Match (CSM) program. The crystal structure is monoclinic identified as the database PDF N° 37-1484 for ZrO_2 and crystal structure is hexagonal identified as the database PDF N° 41-1487.

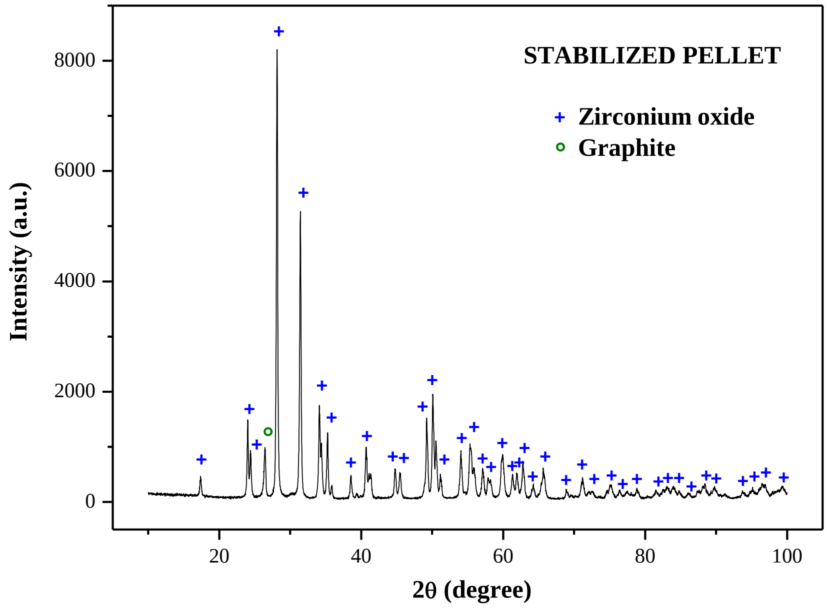


Fig 5 XRD pattern of porous pellets.

The graphite maintained in the stabilized pellets shows that the stabilization process was efficient, where graphite is used as reducing agent in the chlorination process.

The stabilized pellet has porosities as can be seen in SEM micrographs in **Fig 6**, both externally (a) and internally (b). The average value of porosity found in the stabilized pellets was approximately 27%, calculated by the Archimedes method. The porosity is necessary so that the chlorine gas occur more interaction with the zirconium oxide and graphite compound in the stabilized pellets.

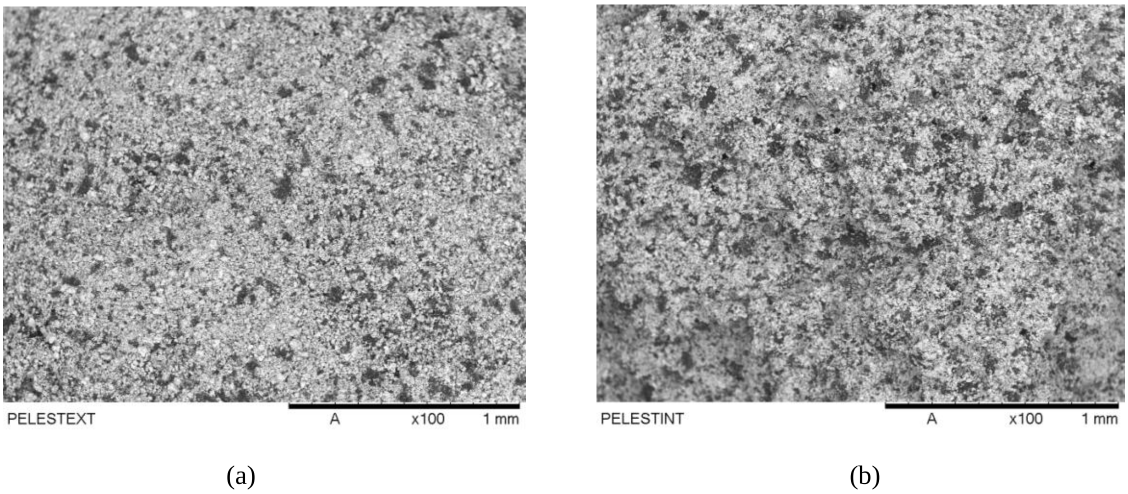


Fig 6 Micrographs of stabilized pellet on the outside (a) and inside (b).

In the compression test, the stabilized pellets in the range of 9.5mm to 15.9mm in diameter showed an average maximum load value of 58.20 kgf of compression, this value, much higher compared with the ceramic grade stabilized pellets produced at IPEN with a value of 3.53 kgf [4].

The drop test of the stabilized pellets was conducted falling directly on a graphite grid, height around 800 mm, to evaluate the fracture. This test was performed due to the stabilized pellets are fed over during the operation in the chlorination process. After the drop test, the stabilized pellets were intact.

The analysis by ICP-OES, the results of nuclear grade zirconium tetrachloride product is presented in the **Table 2**. The impurities contained in the nuclear grade zirconium tetrachloride were aluminum (Al), iron (Fe), hafnium (Hf), silicon (Si) and titanium (Ti).

Table 2 Nuclear grade zirconium tetrachloride produced in laboratory scale

Chemical Elements	Concentration (ppm)
Aluminum	1044 ± 9
Iron	851 ± 16
Hafnium	78 ± 1
Silicon	95 ± 6
Titanium	69 ± 6

These impurities are found in nuclear grade zirconium tetrachloride produced by company ATI Metals [6] as seen in **Table 3**.

Table 3 Nuclear grade zirconium tetrachloride produced by ATI Metals

Chemical Elements	Concentration (ppm)
Aluminum	50-100
Iron	500-1000
Hafnium	50-100
Silicon	<25-100
Titanium	<50-200

The chemical elements Fe, Hf, Si and Ti are according to company data ATI Metals, with the exception of Al, which has a high value. The high concentration value should probably be reacting chlorine gas with alumina reactor located within the chlorination furnace. It’s important to note that the Hf amount is low, meaning that the zirconium tetrachloride produced is nuclear grade.

The yield of the chlorination reaction was approximately 95%, calculated as the difference between the weight of pellets fed and residue discharged at the end of the reaction.

CONCLUSIONS

The forming of porous pellets in the pelletizer was possible with the operating conditions adopted. The stabilized pellets remained the graphite, as observed in X-ray diffractogram and the porosity was confirmed, observed in micrographs and calculation by the Archimedes method.

The drop and compression tests were sufficient to prove that the stabilized pellets are very resistant to support the stacking of pellets in the fixed bed of reactor alumina.

In the experimental unit for the chlorination process was possible to obtain the nuclear grade zirconium tetrachloride with the reaction of zirconium oxide pellets with chlorine gas in proper operating condition.

The yield of the chlorination reaction was 95% approximately.

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