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Drying and characterization of evaporator concentrates coming from PWR

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ABSTRACT

To control the fission, boric acid is added to the water of the primary circuit inside a Pressurized Water Reactor (PWR). After used, this solution is treated in an evaporator to reduce its volume, generating the evaporator concentrate (EC). This concentrate should be solidified for transport and storage. Cementation is one of the available processes to incorporate the concentrate. However, when the evaporator concentrate is cemented there is an increase in the volume of the final product. It is proposed to use an additional process, drying prior be to the cementation. This process is applicable to further reduce the waste volume to be solidified reducing the number of waste packages, consequently decreasing the storage area and all related risks. Two equipment, a lab oven, and a spray dryer were studied to treat the evaporator concentrate. The dried EC was characterized, and the density, the particle size, and the surface area were determined. After drying the evaporator concentrates solution, there was more than 80% weight reduction and initially, the dried product of the spray dryer showed better conditions to be incorporated in the cementitious matrix.

Keywords: **evaporator concentrates, drying, characterization**

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1. INTRODUCTION

In our daily lives the nuclear energy is important, as in medicine for treatments and diagnostics, in agriculture for foods irradiation, in order to eliminate microorganisms and to avoid premature aging, and in the electrical energy production without emitting greenhouse effect gases using nuclear reactors, etc. [1,2].

In the world, the most common nuclear reactor is the Pressurized Water Reactor (PWR). The water has an important role because it is present in all its operational steps. In the primary circuit occurs the fission reactions [2-4]. The boric acid is used to control the reactivity inside of the reactor circuit, due to its high shock section - a measure of the probability of occurrence of neutron absorption by a nucleus [4,5].

This boric acid solution is regenerated in ion exchange columns, but when this treatment is not possible anymore, this solution is sent to the evaporator to reduce its volume. The product of this process is named evaporator concentrate (EC) and it is classified as a radioactive waste [6,7].

The concentration of the boric acid in the primary circuit is function of the reactor, and for Angra 1 reactor this concentration is about 12.5% weight/volume. It is classified as a low and intermediate level radioactive waste (LILW) in accordance with the Brazilian standard CNEN NN 8.01 [7-12].

In addition, CNEN NN 8.02 establishes that for disposal all wastes should be solidified to obtain a monolithic product, in order to reduce the potential for migration or dispersion of radionuclides [13,14].

Because, of high stability, low cost and easy to be handling, cementation is one of the most acceptable methods for LILW solidification [15,16]. However, this process has the disadvantage of increasing the volume of the final product [17].

Drying is the evaporation of volatile materials from the solution, usually water, to produce a solid product. Many industries, such as food, pharmaceutical, and agriculture, use this process because it is efficient for the volume reduction [18]. There are R&D studies of drying processes for liquid sewage waste, as well as evaporator concentrate [19]. In Germany, the FAVORITE® process includes the vacuum drying of evaporator concentrates, resins, among others [20].

As it was mentioned, the cementation increases the final product volume. Then, to solve this issue some studies are being developed aiming at reducing the volume of the evaporator concentrate from drying before its solidification [21,22].

The lab oven uses an electrical resistance to heats the material and the exchange of heat occurs by convection. The work parameter of this equipment is the temperature [23].

The spray dryer atomizes the solution, using three different flows: co-current, countercurrent, and mixed system. In the co-current flow, the liquid is sprayed in the same direction of the hot air inlet. In the countercurrent flow, the liquid is sprayed in the opposite direction of the hot air inlet. The mixed system is the combination of these two types. The parameters of this equipment are entrance and exit temperature, rotation speed, and workflow. The final product of this process is a solid material with an aspect of a powder [18, 24].

It is necessary to characterize the dried product and to establish its physical and chemical properties. The objective of this paper is to summarize the study of volume reduction of evaporator concentrate using drying processes. It was used lab oven and spray dryer, and the dried product properties analyzed were density, particle size, humidity, specific surface area, and morphology.

2. MATERIALS AND METHODS

The methodology was developed according to the steps presented in Figure 1. Step 1 consisted in preparation one solution simulating the evaporator concentrate, in step 2, the evaporator concentrate was dried and in step 3 the dried evaporator concentrate was characterized.

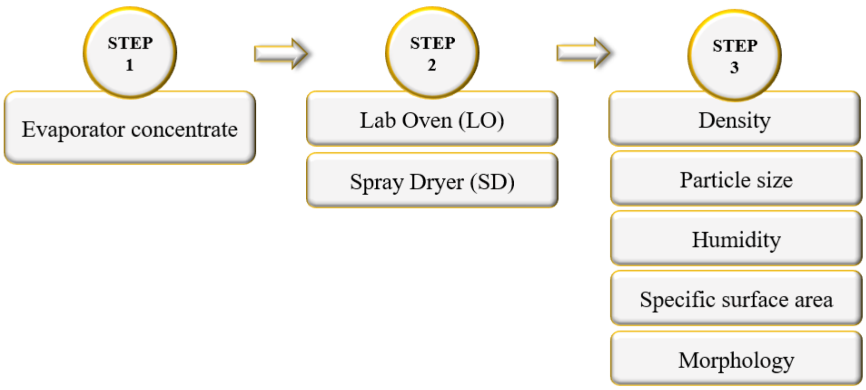

Figure 1: *Methodology steps.*
Source: Author

2.1. Step 1 – Simulated waste (EC)

The reagents and quantity necessaries to prepare the EC simulated are presented in Table 1. These reagents were solubilized in water and it was kept about 80ºC, under agitation [7-8].

Table 1: Reagents used to prepare 3L of simulated waste (EC).

Reagents	**$MgCl_2$**	**SiO_2**	**NaCl**	**Al_2O_3**	**$Ca(NO_3)_2$**	**NaOH (1,023N)**	**H_3BO_3**
Quantity	0.082 g	0.089 g	0.374 g	0.800 g	1.591 g	39.50 ml	369.0 g
% w/v	0.0027	0.003	0.012	0.026	0.053	0.052	12.3

2.2 Step 2 - Drying of the Evaporator Concentrate

The simulated evaporator concentrate (80°C) was dried using a lab oven and a spray dryer. The lab oven was chosen due to its simple use and control. In the order hand, the spray dryer was chosen due to its good performance.

2.2.1 Drying in a Lab Oven

The beaker containing o simulated EC at 80ºC was capped and it was placed in Lab Oven (LO) and the working temperature used was 110ºC. The drying time was determined when the mass of the material stayed constant, resulting in approximately two weeks.

2.2.2 Drying in a Spray dryer

The Spray Dryer (SD) used it belongs to the Drying Laboratory of Engineering Institute (IEN/CNEN), in Rio de Janeiro. One prepared EC solution at 80°C was used for this test. The operation conditions were in inlet temperature at 150 °C, exit temperature about at 80°C, co-current system, speed of rotating disc at 27000 turns/s, air as inlet gas, and the workflow at 66 $mL.min^{-1}$. The drying time was about one hour.

2.3 Step 3 - Characterization of the Dried Evaporator Concentrate

The characterization was realized with the dried evaporator concentrate by lab oven (DEC LO) and by spray dryer (DEC SD). It was characterized regarding their density, particle size, humidity, specific surface area, and morphology.

2.3.1 Density

The density was determined with Quantachrome Instruments Ultrapycnometer 1000™ at Nuclear Fuel Laboratory (LABCON - SENAN/CDTN). For a reliable result, the density was measured 20 times using samples of two grams of DEC LO and DEC SD. A statistical analysis (T-test – Student test) was performed to compare the average density results.

2.3.2 Particle Size

The particle size was measured by the Sieving Method at Cementation Laboratory (SEGRE/CDTN). Fifty grams of DEC LO and DEC SD were sieved for 15 minutes through a series of PRODUTEST sieves. The sieves aperture used to the test were 1.190; 0.850; 0.590; 0.500; 0.297; 0.210; 0.150; 0.106 and 0.075 millimeters. To determine the average particle diameter, it was used the Sauter Diameter equation (Dsauter), as presented in equations 1 and 2.

$$\overline{D}_{sauter} = \frac{1}{\sum_{n=1}^{i} \frac{x_n}{\overline{D}_n}} \tag{1}$$

$$\overline{D}_n = \frac{D_{n-1} + D_n}{2} \tag{2}$$

X_n = fraction of mass retained in the aperture of the n sieve.

D_n = n sieve aperture diameter.

D_{n-1} = aperture diameter of sieve n-1.

2.3.3 Humidity

The humidity was determined by the HG53™ Halogen Moisture Analyzer at Cementation Laboratory (LABCIM - SEGRE/CDTN). It was used ten grams in each test, which was done in triplicate. The test temperature was 105°C. A statistical analysis (T-test – Student test) was performed to compare the average humidity results.

2.3.4 Specific surface area

The specific surface area was determined by the BET method. The analyzes were performed in a Quantachrome™ Enhanced Data Reduction equipment, at Nuclear Fuel laboratory (LABCON - SENAN/CDTN), and the results for the specific surface area were obtained in the NOVADRP™ software.

2.3.5 Morphology

The morphology of the dried material was determined by a Scanning Electron Microscope (SEM) with a Field Emission Gun (SEM-FEG), by secondary electrons. The tests were performed with the equipment SIGMA VP™ at the Microscopy Laboratory (SENAN/CDTN).

3. RESULTS AND DISCUSSION

3.1 Dried Evaporator Concentrate

Figure 2 presents the DEC LO and the DEC SD. In both samples, the dried product is fine powder and white. Additionally, the DEC LO presented agglomerated particles.

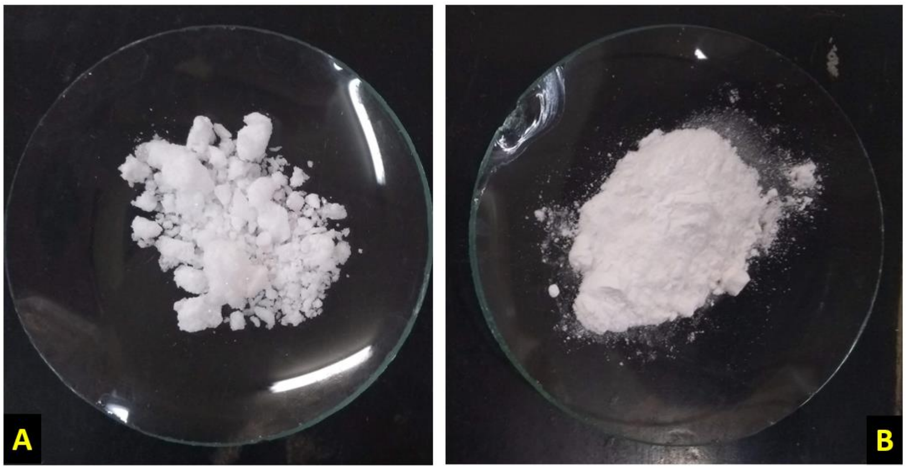

Figure 2: *DEC coming from of the drying lab oven (A) and spray dryer(B).*
Source: Author

In both processes was observed a reduction of more the 80% of the initial mass. The drying time of the LO was about two weeks, although the drying time of the SD was about one hour for the same amount of material. The LO is equipment that has good access, price, and it requires less ability to operate, and the SD is equipment that has good performance. Before defining the best equipment, all parameters involved in the process must be evaluated.

3.2 Characterization of the Dried Evaporator Concentrate

3.2.1 Density

Table 2 presents the average values of the density obtained by the equipment. To evaluate the results was applicated the Student test.

Table 2: Density of the dried products

	DEC LO	**DEC SD**
Densidade (g/cm^3)	1,5291±0,0028	1,6205±0,0547

The Student Test was used with a significance of 95%, to verify if there is a significant difference between these density values. It was observed, from the statistical analysis, that the $t_{calculated}$ (7,2756) is greater than the $t_{critical}$ (2,0244), confirming that values are different. This was also ratified by the calculated p-value (1,045E-08), which is lower than the significance level (0,05). This indicates that the density of the EC dried in the spray dryer is higher.

3.2.2 Particle Size

It was observed that 84,1% of DEC SD and 71,1% of DEC LO passed through the aperture 1.19mm as it is shown in Figure 3, i.e., the dried products have a diameter of less to 1.19mm.

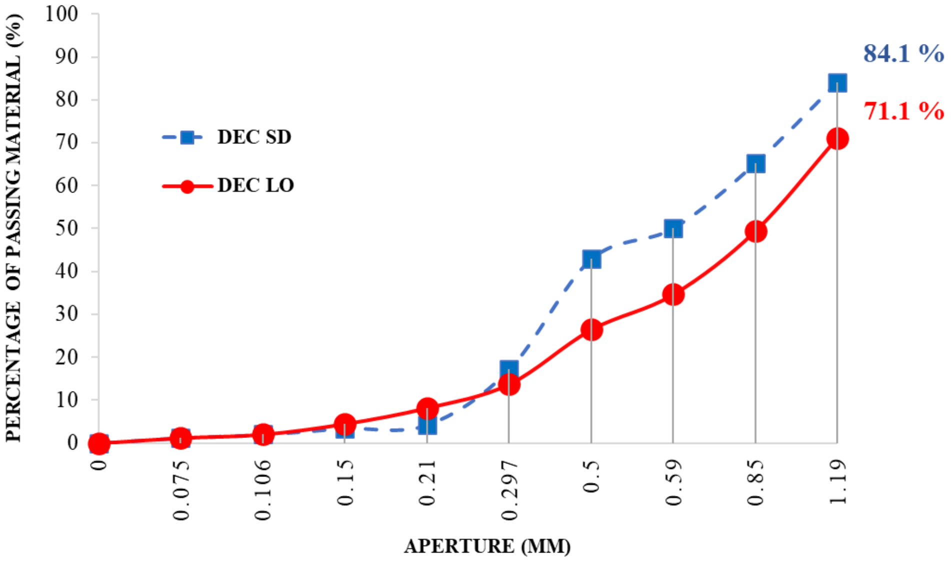

Figure 3: *Granulometric analysis of DEC LO and DEC SD.*
Source: Author

The calculated Sauter diameter was $D_{SauterDECLO}$=0.462mm and $D_{SauterDECSD}$=0.419mm. It is observed that the main diameter of the dried particles by the spray dryer is lower than the lab oven.

3.2.3 Humidity

The average value of humidity of dried evaporator concentrate is shown in Table 3. The Student Test was used with a significance of 95% to verify if there is a significant difference between these humidity values. It was observed, from the statistical analysis that the $t_{calculated}$ (1,938) is smaller than the $t_{critical}$ (2,776), which means that the values are equal. This was also ratified by the calculated p-value (0,124), which is greater than the significance level (0,05). The Student Test signaled that the humidity of DEC LO and DEC SD is significantly equal, i.e., the drying process did not affect the final humidity of the material.

Table 3: Humidity value of dried evaporator concentrates in lab oven (DEC LO) and spray dryer (DEC SD)

	DEC LO	**DEC SD**
Humidity (%)	28.66±0,74	29.75±0,66

3.2.4 Specific surface area

The specific surface area, pore volume, and volume of pores average values of DEC LO and DEC SD are presented in Table 4.

Table 4: Results of average specific surface area, pore volume and pore diameter in the dry evaporator concentrate

	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Volume of pore (Å)
DEC LO	1.1636	0.00784	269.36
DEC SD	2.4767	0.01196	193.11

The results indicate that the DEC SD has a higher interaction capacity with other materials because of higher values of the specific surface area and pore volume. These parameters are important for the solidification process, because this necessary that the chemical reactions between EC and cement produce stables products. It is observed also that the average volume of pore for DEC SD is lower than for DEC LO, however, it won't interfere directly with the interaction capacity.

3.2.5 Morphology

To evaluate if the structure was maintained after drying, it was necessary to realize a morphological analysis. The morphology of the boric acid was used as parameter and Figure 5 shown the SEM image with an increase of 1,000 and 10,000 times. It is observed that boric acid can have a lamellar and well-defined structure.

The dried evaporator concentrates in a lab oven has a lamellar structure, like boric acid, i.e., the surface structure was maintained, as showed in Figure 6.

The structure of the dried evaporator concentrates by a spray dryer is different due to the type of drying process. Figure 7 shows the DEC SD images. The DEC SD has hollow spheres with plates on the surfaces.

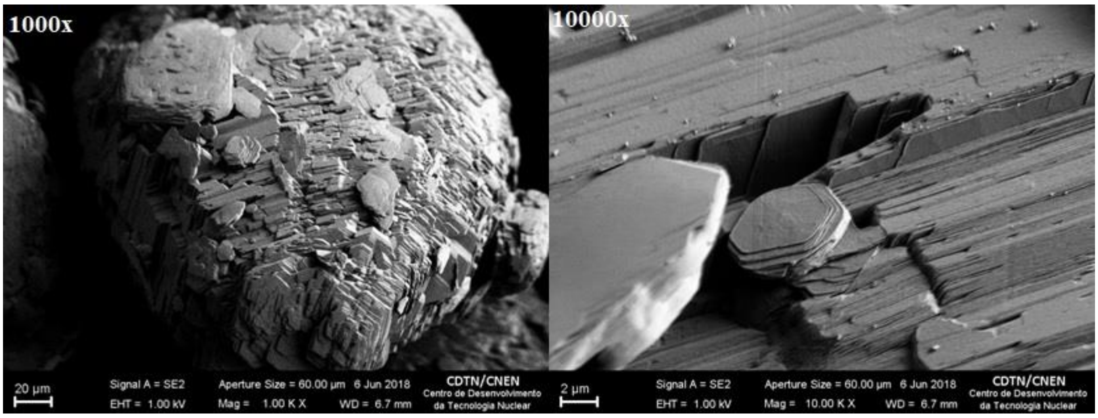

Figure 5: *Boric acid morphology.*
Source: Author

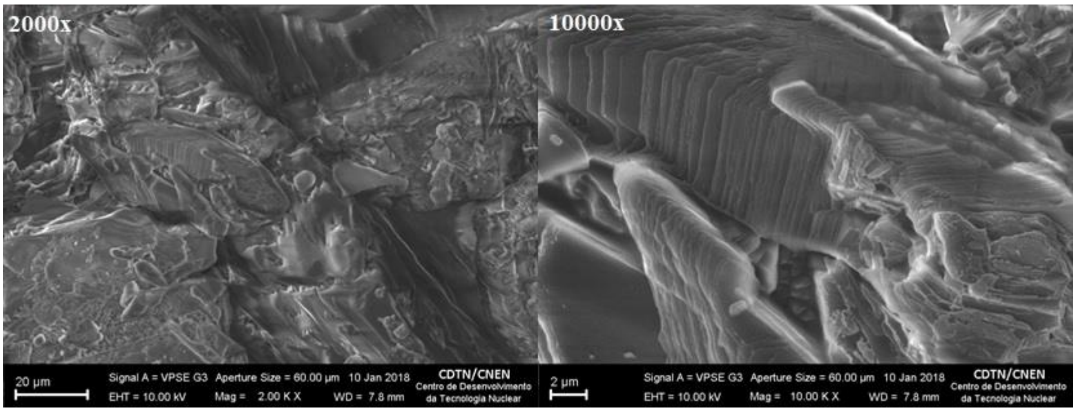

Figure 6: *DEC LO morphology.*
Source: Author

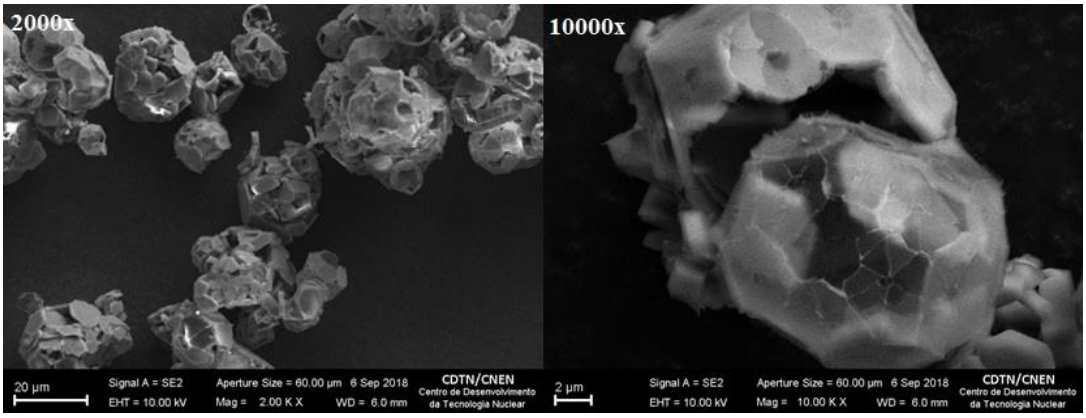

Figure 7: *DEC LO morphology.*
Source: Author

4. CONCLUSION

In this study, a LO and SD were used as drying equipment. The drying time of the evaporator concentrate was larger in the lab oven than in the spray dryer, considering the same mass. In both drying processes there was a reduction in mass above 80%.

The dried evaporator concentrate had the same color, however, the product of spray dryer was finer powder, as verified by the Sieve Test and calculated by Sauter's average diameter.

The DEC SD density was slightly higher than the DEC LO density. The final humidity of the dried evaporator concentrate was statistically equal for both processes, showing that the drying process did not affect this parameter, as demonstrated by the Student test.

The specific surface values and pore volume of the products obtained in the spray dryer indicated that there are more sites available for the interaction with the cement favoring solidification reactions.

In all cases a lamellar structure and plates were observed. However, dried evaporator concentrate by spray dryer showed a spherical and empty surface, which may favor the cementation, due to its large contact area. From these results, the spray dryer seems to have good possibilities to be used to reduce the volume and to produce an appropriate material for cementation. Nevertheless, further experiments are required to confirm this.

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