Synthesis of High Value-added Zeolitic Materials Using Glass Powder Residue as a Silica Source

Alves, J. A. B. L. R.[a], *Dantas, E. R. S.*[b], *Pergher, S. B. C.*[a]*, *Melo, D. M. A.*[a], *Melo, M. A. F.*[b]

[a]*Institute of Chemistry, Federal University of Rio Grande do Norte – UFRN,
Av. Salgado Filho, 3000, Natal, RN, Brazil*
[b]*Chemical Engineering Department, Federal University of Rio Grande do Norte – UFRN,
Av. Salgado Filho, 3000, Natal, RN, Brazil*

In this work, zeolite A was obtained using alkaline fusion followed by a hydrothermal treatment of glass powder residue derived from the manufacturing of glass. The following parameters were evaluated: leaching of the stock material (silica source), mineralizing agent, alumina source, and the alkaline fusion and crystallization temperatures. The synthesized materials were characterized by chemical analysis using energy dispersive X-ray analysis (EDX), X-ray diffraction (XRD) and scanning electron microscopy (SEM). The XRD and SEM results showed that zeolite A was obtained under almost all of the evaluated parameters. The use of pseudoboehmite as an aluminum source led to the formation of zeolite X as a secondary phase and a change in the temperature of fusion, which at 500 °C, there was formation of zeolite A, hydrated sodalite and zeolite X.

Keywords: *glass powder, zeolite A, zeolite X*

1. Introduction

Both society and government authorities are placing increasing pressure on industries to improve the development of processes so that they can be considerably less harmful to the environment[1].

Many methods and processes for remedying or mitigating the damages to the environment caused by anthropogenic actions have been described in the literature. Among these methods, using natural and/or synthetic zeolites as adsorbents for metals in industrial effluents has been of great interest.

Zeolites are hydrated crystalline aluminosilicates composed of pores with molecular dimensions and a regular arrangement of cavities and canals (3-15 Å) that may or may not be interconnected, and these cavities and canals contain the compensating ions (Na, K, Ca, Mg, Sr, and Ba), molecules of water and other adsorbates and salts[2]. Industrial processes for refining, petrochemistry and fine chemicals also use zeolite-based catalysts. The main factors that affect the zeolite structure that is formed are the crystallization temperature and time, silicon/aluminum ratio in the reaction mixture, and types of compensating cations and structure directing agents[3].

The production of zeolites is expensive due to the use of high-purity reagents, such as the sources of silica, alumina and the structure directing agent, in addition to the heat treatment at temperatures greater than 500 °C, which is a process with a high energetic cost. The development of simple methodologies that have good reproducibility and low costs is becoming the focus of several studies. Natural raw materials, such as diatomite, perlite[4], rejects of kaolin[5], other clay minerals[6] and coal ashes[7], are being used in the synthesis of the zeolites, such as sodalite, A, X, Y, ZSM-5, and mordenite, among others[8]. Some studies have investigated the effects of varying the silica source while maintaining the other reaction parameters constant, and they noted that the use of different silica sources significantly influenced the synthesis results, in which products were obtained with different amounts of a zeolite impurity phase, different conversion rates and different particle sizes[9].

During the polishing step of the glass manufacturing process, a solid residue that is rich in silica is obtained, which is essentially composed of glass in powder form. This residue cannot be recycled in the same manner as broken glass because recycling in the presence of this powder causes the appearance of bubbles in the glass, which is an unwanted effect[10]. In the present work, we evaluated the possibility of using the residue derived from the glass manufacturing process as an alternative source of silica for the synthesis of zeolites.

2. Experimental Procedure

The silica source used was the residue derived from the manufacturing of colorless glass by a company that makes glass in the Brazilian State of Rio Grande do Norte. Initially, the residue was macerated and sifted to obtain granulometric fractions between 250-400 mesh. After this procedure, chemical analysis of the residue was performed using energy dispersive X-ray analysis (EDX) with a Shimadzu model EDX-720 instrument to quantify the chemical composition of the material.

*e-mail: sibeleperger@gmail.com

The method for synthesizing zeolite A was adapted from the work of Machado and Miotto[11], in which the molar composition of the gel in the synthesis procedure was $3SiO_2:Al_2O_3:5.7Na_2O:228H_2O$. First, alkaline fusion of the reaction mixture (glass powder residue + sodium hydroxide (NaOH) + aluminum oxide (Al_2O_3)) was performed in a porcelain crucible at 350 °C for 2 h. The molten mass was mixed with deionized water and maintained under vigorous agitation for 30 min to form the gel phase. The obtained gel was placed in a Teflon autoclave coated in stainless steel and aged for 24 h at 100 °C. The generated solid was filtered, washed with deionized water and dried at 100 °C for 15 h.

Some synthesis parameters were evaluated, such as the mineralizing agent (NaOH or $Ca(OH)_2$), aluminum source (alumina or pseudoboehmite), alkaline fusion temperature (250, 350 and 500 °C) and crystallization temperature (100, 135, 152 and 170 °C).

The glass powder residue and the synthesized zeolites were characterized using X-ray diffraction (XRD) with a Siemens model D5000 diffractometer employing a Ni filter and Cu-Kα radiation ($\lambda = 1.54$ Å). These materials were also characterized using scanning electron microscopy (SEM) with a JEOL JSM 6060 scanning electron microscope with an accelerating voltage of 20 kV and different magnifications.

3. Results and Discussion

As shown in Table 1, the chemical composition of the raw glass powder residue shows high levels of silica and calcium oxide and a low level of alumina. The chemical analysis reveals that the glass powder residue is a possible candidate as a silica source for the synthesis of zeolites. The possibility of performing a treatment with 0.1 mol/L HCl to avoid impurities, such as calcium oxide and other metals, that interfere in the synthesis and obtainment of zeolite A was evaluated. A discreet decrease was observed in the amounts of impurities present in the residue after the acid leaching process.

According to the diffractograms presented in Figure 1, following the alkaline fusion of the glass powder residue (raw or purified with HCl) with NaOH and hydrothermal treatment at 100 °C for 24 h, crystallization of silica and

alumina occurred, with a predominant formation of zeolite A (JCPDS card 73-2340) and a secondary phase corresponding to hydrated sodalite (JCPDS 89-9099). These structures belong to the cubic and dodecagonal systems, respectively, in which the compensating cation is the sodium ion, indicating that there was no significant interference of the impurities remaining after the leaching process in obtaining the desired phase.

As shown in the micrographs in Figures 2b and 2c, the formation of more than one phase was observed; the primary phase consisted of crystals with a cubic morphology, typical of zeolite A[12]. Furthermore, small crystals with a round shape, typical of polycrystals such as balls of wool that grow and cluster multiple times, were observed and are typical of sodalite[13].

The subsequent syntheses were performed using the glass powder residue without purification with HCl because the obtained zeolites were not altered after the leaching process, indicating that this pre-treatment is unnecessary, and the zeolites obtained from these syntheses were compared with the zeolite synthesized from the natural glass powder.

With the objective of evaluating the effect of the mineralizing agent and of determining whether changing the inorganic cation and increasing the hydroxide ions has a value superior than NaOH, calcium hydroxide ($Ca(OH)_2$) was used in this synthesis as a mineralizing agent with the following molar composition: $3SiO_2: Al_2O_3:1.7Na_2O:4CaO:228H_2O$. The inorganic cations in the reaction mixture played a role in determining the obtained structure, in influencing the morphology, and in the crystallinity and the conversion rate[14]. The hydroxide ion, in turn, has the function of controlling the degree of polymerization of the silicate and the induction period in the formation of a viable nucleus[15].

X-ray diffraction confirmed that there was no formation of a zeolitic structure using $Ca(OH)_2$, other than the occurrence of crystallization of the silica and of the alumina (Figures 3b and 4). According to Flanigen[16], the structural

Table 1. Chemical analysis of the raw glass powder residue without and with HCl treatment.

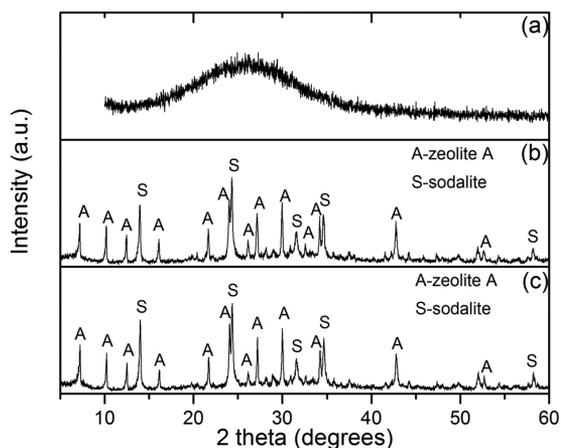| Constituents (%)	Without HCl treatment	With HCl treatment
SiO_2	70.50	76.92
CaO	19.67	14.13
SO_3	4.23	4.06
MgO	3.38	2.52
Al_2O_3	1.23	1.75
Fe_2O_3	0.35	0.26
K_2O	0.38	0.24
CuO	0.03	0.02
SrO	0.01	0.01
Others	0.16	0.08

Figure 1. X-Ray diffraction patterns of the glass powder (a), of zeolite A synthesized with the raw glass powder residue (ZeoPV-raw) (b) and with the residue purified with HCl (ZeoPV-purified) (c).
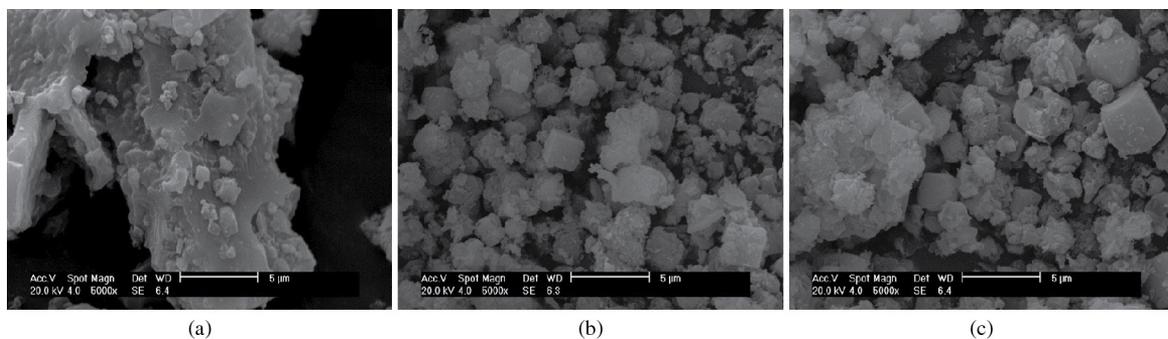
(a)   (b)   (c)

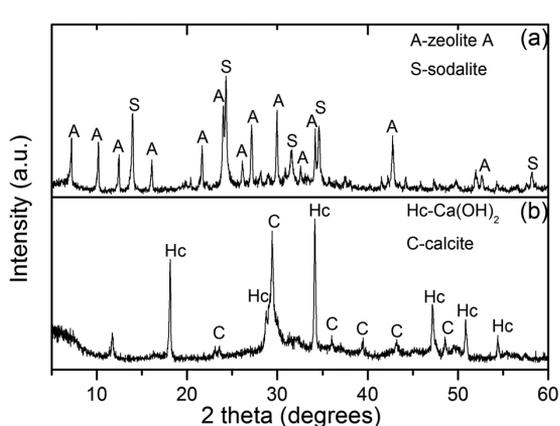**Figure 2.** Micrographs obtained for the glass powder residue (a), ZeoPV-raw (b) and ZeoPV-purified (c).

Figure 3. X-Ray diffraction patterns of ZeoPV-raw (a) and the zeolite synthesized with Ca(OH)$_2$ (ZeoPV-CaO) (b).
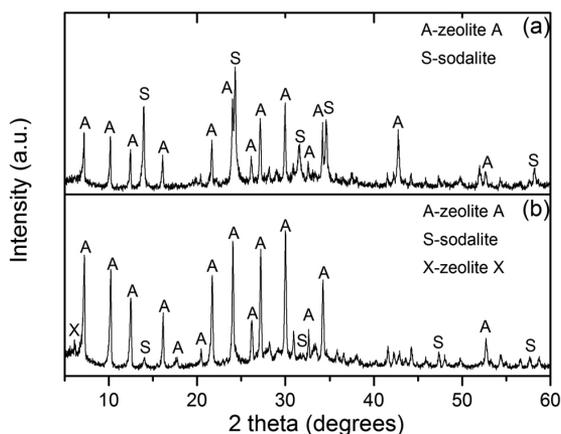

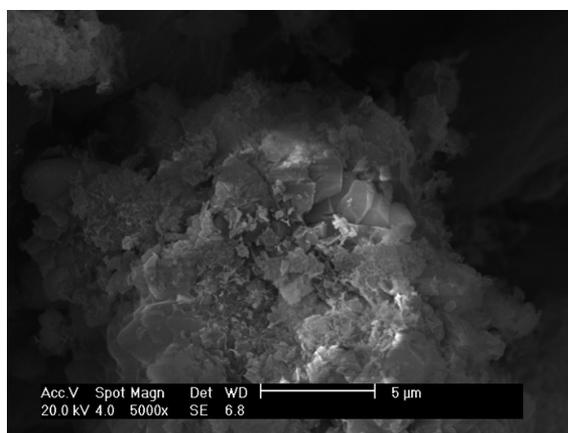**Figure 5.** Schematic of the structures of zeolites A, X and Y.

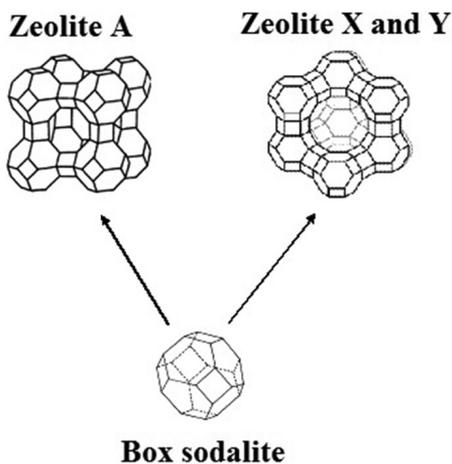**Figure 4.** Micrograph obtained for ZeoPV-CaO (a).

Figure 6. X-Ray diffraction patterns of ZeoPV-raw (a) and ZeoPV-Al (b)

unit that forms the zeolitic unit needs inorganic cations or specific groups of cations to direct the structure. The identification of the phases obtained from ZeoPV-CaO refers to reminiscent Ca(OH)$_2$ (JCPDS 81-2041) and calcite (JCPDS 81-2027). The amorphous strip refers to the silica of the glass powder residue that did not crystallize. The inefficient alkaline fusion temperature and time required to dissolve the calcium hydroxide makes the depolymerization

and/or hydrolysis of the alumina at an adequate rate difficult, preventing the nucleation and growth of crystals[17]. Figure 4 shows a rhombohedral morphology typical of calcite[18], corroborating the XRD pattern.

The possibility of using pseudoboehmite as a source of aluminum was evaluated. Pseudoboehmite is an aluminum hydroxide with a disordered crystal structure and a composition of Al$_2$O$_3$. xH$_2$O (2.0 > x > 1.0). This aluminum

hydroxide is amorphous based on X-ray diffraction, but it is crystalline based on electron diffraction[19].

The use of pseudoboehmite as a source of aluminum led to the formation of zeolite A (JCPDS 73-2340) and hydrated sodalite (JCPDS 89-9099), but with the presence of zeolite X (JCPDS 88-0190), as identified in the diffractogram of Figure 5b. Figure 6, it is observed that the sodalite box can lead to the formation of zeolites A, X or Y depending on the Si/Al ratio, crystallization temperature and aging time[20].
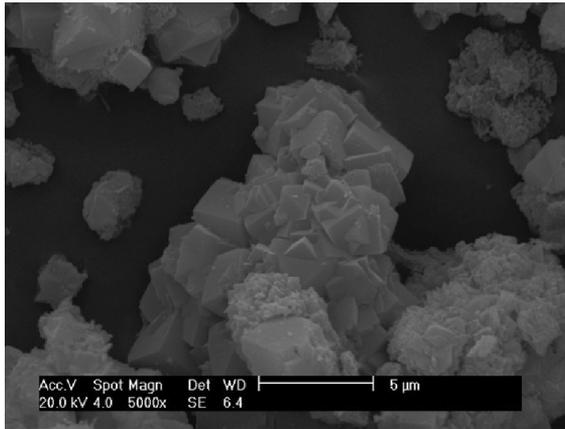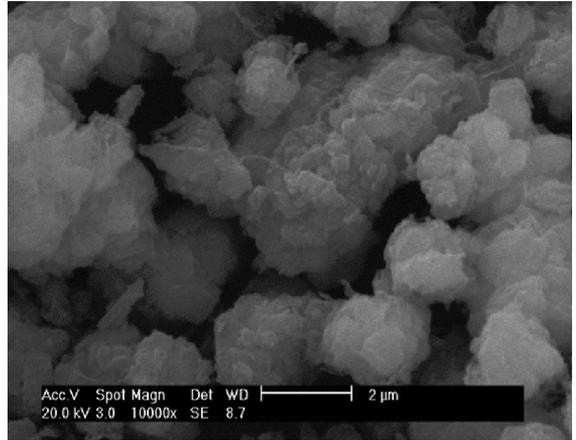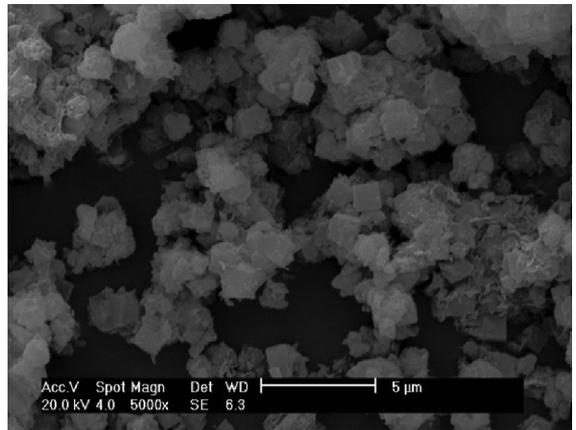

(a)
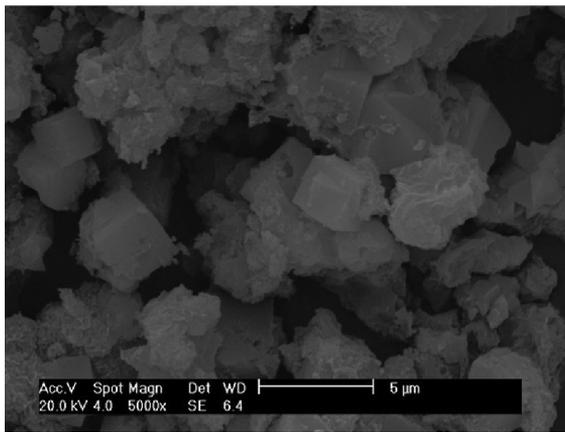
(b)

Figure 7. Micrograph obtained for ZeoPV-Al (a and b).

(a)

(b)

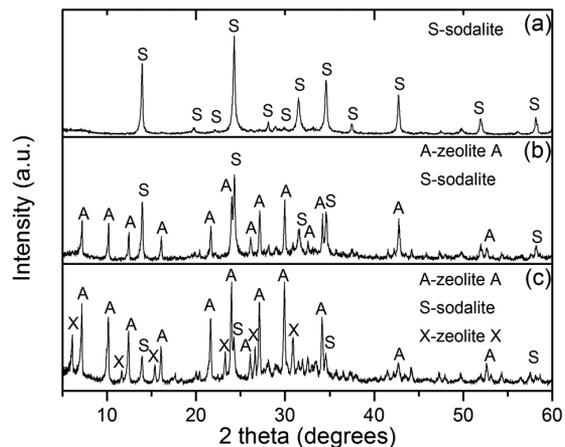**Figure 9.** Micrographs obtained for ZeoPV-250 (a) and ZeoPV-500 (b).

Figure 8. X-Ray diffraction patterns of ZeoPV-250 (a), ZeoPV-raw (b) and ZeoPV-500 (c).
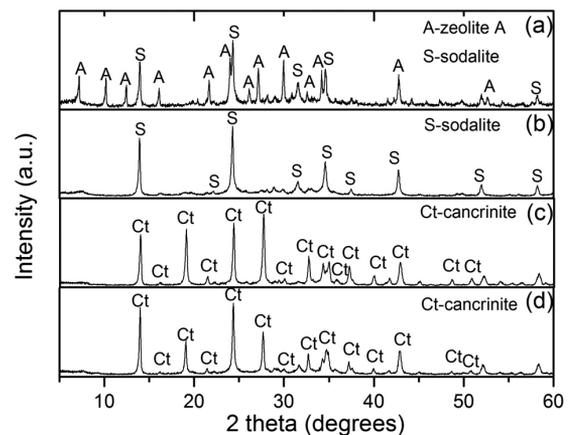

Figure 10. X-Ray diffraction patterns of ZeoPV-raw (a), ZeoPV-en135 (b) ZeoPV-en152 (c) and ZeoPV-en170 (d).
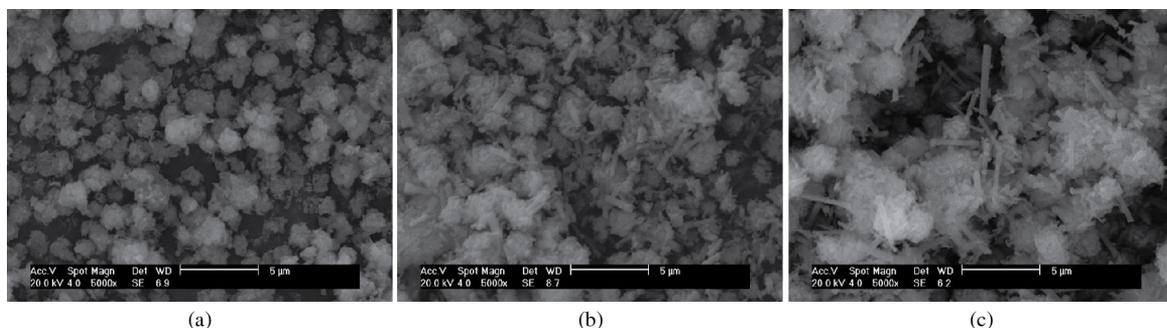
Figure 11. Micrographs obtained for ZeoPV-en135 (a), ZeoPV-en152 (b) and ZeoPV-en170 (c).

According to Janicke[21], pseudoboehmite contains both octahedral and tetrahedral aluminum, whereas in alumina, the aluminum is only tetrahedral. The octahedral aluminum is easier to dissolve with the silica during the alkaline fusion, forming a type of tetrahedral AlO_4^- unit that is part of the zeolite. This caused an increase in the crystallinity of the zeolite synthetized with pseudoboehmite as a source of aluminum when compared to ZeoPV-raw (Figure 2b). In addition, zeolite X appeared as a secondary phase, which must be related to the octahedral aluminum of pseudoboehmite. In Figure 7, the overlap of cubic crystals and other crystals without a defined shape are observed. The cubic crystal is typical morphology of A zeolite. The intercrystalline growth of cubic crystals is related to the simultaneous formation of zeolite A and zeolite X. Others crystals observed with not defined morphology is related probably to sodalite phase.

Several authors have investigated the synthesis of zeolites A, X and Y from the alkaline fusion of the reaction mixture (source of silica + source of aluminum + strong base) at 350 °C for 2 hours[22]. In this study, the alkaline fusion temperature varied from 250-500 °C.

The change in the alkaline fusion temperature altered the phase that was obtained. According to the XRD results (Figure 8), the hydrated sodalite phase is preferentially obtained at 250 °C (JCPDS 89-9099) (Figure 8a and 9a). At 350 °C and 500 °C, there is formation of zeolite A (JCPDS 73-2340) and hydrated sodalite (Figures 8b and 8c). In addition to zeolite A, at 500 °C, there is formation of zeolite X (JCPDS 88-0190). The increase in the alkaline fusion temperature directly interferes with the solubility of the alumina and silica species, increasing their concentration[23], and it also improves the incorporation of the additional source of alumina[7]. The micrographs shown in Figure 9b confirm the formation of zeolite A (presence of cubic crystals), the hydrated sodalite (round-shaped crystals) and zeolite X (intercrystalline growth), as previously discussed.

While evaluating the possibility of varying the crystallization temperature, it was verified that at temperatures of 152 °C and 170 °C, there is formation of cancrinite (JCPDS 73-0540), as indicated by its diffractograms (Figures 10c and 10d) and micrographs, which show crystals in the shape of hexagonal prisms (Figures 11b and 11c)[24]. At a temperature of 135 °C, the formation of sodalite is observed (Figures 10b and 11a). At 100ºC, the formation of the zeolite A is verified (10a and 2b). The crystallization temperature is one of the fundamental factors for the formation of zeolites, and it can change the zeolitic phase that is obtained while it changes its induction time before crystallization; in other words, an increase in the temperature implies a decrease in the induction period[3]. According to Ginter[25], an increase in the crystallization temperature leads to dense phases due to the removal of water molecules, which stabilizes the pores.

4. Conclusion

The study of the synthesis of zeolites while varying the leaching of the stock material (silica source), mineralizing agent, alumina source, alkaline fusion temperature and crystallization temperature showed that a mixture of phases is obtained in all cases, with zeolite A being obtained easily along with secondary phases, such as zeolite X, hydrated sodalite, calcite and cancrinite. Under soft reaction conditions, zeolite A can be obtained using the following conditions: 250 °C for alkaline fusion with NaOH, glass powder residue without treatment with HCl and crystallization temperature of 100 °C.

The use of glass powder residue as an alternative source of silica proved to be efficient in the production of zeolite A using an alkaline fusion process followed by a hydrothermal treatment.

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