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Synthesis of pollucite and analcime zeolites by recovering aluminum from a saline slag

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ABSTRACT

This work describes a valorization procedure for one of the most important wastes generated during aluminum recycling, namely, saline slag. This procedure was divided in two steps: a) recovery of aluminum or its compounds in various fractions, and b) the use of one of those fractions in the synthesis of two zeolites: analcime ($NaAlSi_2O_6 \cdot H_2O$) and pollucite ($CsAlSi_2O_6 \cdot nH_2O$). Saline slag was ground, sieved (1 mm), washed and separated into two fractions of different sizes, one larger and another smaller than 0.4 mm. The fraction smaller than 0.4 mm was treated under reflux conditions with NaOH or CsOH solutions. The extraction liquor contained aluminum and alkali metal cations; after adding the necessary amount of Si, hydrothermal synthesis was carried out, obtaining the zeolitic materials. Characterization of the solids obtained was carried out by powder X-ray diffraction, thermal analysis, FT–IR spectroscopy, element chemical analysis and electron microscopy. The valorization procedure proposed in this work showed that a high percentage of Al (close to 45 wt%) can be recovered from the fraction smaller than 0.4 mm and that the liquors extracted with NaOH or CsOH can be used as a source for the hydrothermal synthesis (200 °C for 24 h) of two zeolites of the analcime family, obtaining in both cases pure and crystalline solids.

1. Introduction

Nowadays aluminum is one of the most used metals around the World. Its properties, such as low density (2.70 g/cm^3), low melting point (660 °C), and corrosion resistance (Sverdlin, 2003) make aluminum an ideal material for many applications. Another interesting property of aluminum is that it can be recycled and reused without losing its properties. The combination of the Bayer and Hall–Héroult processes can produce aluminum at an industrial scale from natural bauxite. The whole process is expensive because the requirement of electric energy is high and various wastes such as *red mud*, are generated (Gil, 2005), with a potentially enormous danger on the environment. Secondary aluminum production is another way to get aluminum and this way is based on recycling of the metal. This second process requires less energy than the combination of the Bayer and Hall–Héroult processes (Gil, 2005), but other wastes are also generated. In this case, the most important waste generated is the so-called *Salt Cake or Saline Slag* (Bruckard and Woodcock, 2007, 2009; Gil, 2005). Saline slag is produced when flux salts (mainly NaCl and KCl) are used for melting aluminum (Gil, 2005). According to the policies of the European Union, saline slag is considered a hazardous waste (Directive 2010/75/EU, 2010), and various ways for managing wastes have been proposed (Gil, 2005; Gil et al., 2014, 2018a, 2018b; Gil and Korili, 2010, 2016; Tsakiridis, 2012; Tsakiridis et al., 2013). Out of the European Union, the policies also tend to recover this waste (Mahinroosta and Allahverdi, 2018). In this way, Bruckard and Woodcock (2007, 2009) proposed to recover metallic aluminum from aluminum dross and Davies et al. (2008) proposed to treat salt cakes by aqueous leaching and Bayer–type digestion. Gil and Korili (2010, 2016) have studied the current situation of managing the wastes, concluding that the best option is to recover metallic aluminum and dispose of the non-metallic fraction in controlled landfills. Gil and co-workers have used saline slags as an adsorbent (Gil et al., 2014, 2018a; Gil and Korili, 2016) or as a precursor of adsorbing materials (Gil et al., 2018b). To use saline slag as a

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precursor of several types of aluminum-containing materials, aluminum existing in the slag must be previously extracted; such extraction may allow to prepare a large variety of Al-containing solids (Gil and Korili, 2016). In these terms, after extraction with sulfuric acid, Das et al. (2007) synthesized η-Al_2O_3 that can be used as a catalyst. Gil and co-workers (Gil et al., 2018b; Santamaría et al., 2020a, 2020b, 2020c) synthesized hydrotalcite (HT) with various divalent metal cations (M^{2+}) and Al^{3+} as the trivalent cation, (Co, Fe, Mg, Ni, Zn, Ti)Al−HT. Galindo and co-workers (2014, 2015) synthesized MgAl hydrotalcites by the co-precipitation method from the extraction liquor of tertiary aluminum wates; Abd-El-Raoof et al. (2019) prepared hydrotalcite and hydrocalumite from Al dross; and Murayama et al. synthesized layered double hydroxides, LDH, (2012) and aluminophosphates (2006). Recently, the synthesis of zeolites from industrial wastes has been proposed by various authors (Belviso et al., 2018; Kang et al., 2019; Kuroki et al., 2019; López-Delgado et al., 2020; Sánchez-Hernández et al., 2016, 2017; Sayehi et al., 2020; Yoldi et al., 2020), and has been reviewed by Yoldi et al. (2019a).

Analcime ($NaAlSi_2O_6 \cdot nH_2O$) and pollucite ($CsAlSi_2O_6 \cdot nH_2O$) zeolites belong to the analcime zeolite family. Their structures are similar each other and are based on $(Al,Si)O_4$ tetrahedra sharing corners, which have pores, channels and/or cavities at the molecular level. In pollucite, these channels are formed by six oxygen−containing rings built up by sharing oxygens of the $(Al,Si)O_4$ tetrahedra, with a channel diameter of 2.8 Å (Hou et al., 2019); the ionic diameter of Cs^+ is 3.34 Å (Lide, 1995; Hou et al., 2019) and, for this reason, Cs^+ can be immobilized inside the pollucite structure. However, the ionic diameter of Na^+ is 2.04 Å (Lide, 1995) and it can be exchanged by other cations of suitable size. In addition, Na^+ and Cs^+ can be substituted by each other isomorphically, giving rise to a solid solution (Jing et al., 2017). Therefore, for the preparation of these two pure zeolites, it is essencial that only Na^+ or only Cs^+ are present in the starting solutions, in order to avoid the formation of an analcime−pollucite solid solution.

Raw saline slag is made up of aggregates of different sizes and shapes, ranging from fine powder particles to particles larger than 2 cm. They are greyish in color, due to their composition. These aggregates contain various aluminum species; the major is Al_2O_3 corundum, while others have also been reported as minor or traces, such as metallic Al, $Al(OH)_3$ bayerite and gibbsite, AlN, cryolite and elpasolite (Bruckard and Woodcock, 2009). The objective of this work is to valorize a saline slag derived from aluminum industrial recycling. This slag is considered as a hazardous waste and usually stored in controlled landfills. For its valorization, aluminum should be extracted, and then used in the synthesis of two zeolites with various applications. Metallic aluminum will not be used, assuming that it may be separated beforehand and submitted to the recycling process. Thus, aluminum from the non-metallic fraction of the salt cake should be recovered under reflux conditions, and the resulting liquor will be used to synthesize analcime and pollucite zeolites under hydrothermal conditions (Yoldi et al., 2019b). The novelty and practical applicability of this work consists in the development of a synthesis method that allows the synthesis of pure analcime and pollucite zeolites from an aluminum residue, saline slag. In previous works, sodium analcime has been prepared from aluminum waste, particularly from the finest grain fraction of aluminum slag milling and the so called black dross (López-Delgado et al., 2014, 2020; Sánchez-Hernández et al., 2016; Meshram and Singh, 2018). The synthesis of other types of zeolites (zeolite X, zeolite A and sodalite) has been described from saline slags (Yoldi et al., 2020). The method now proposed allows to extract a high amount of aluminum from the saline slag and successfully obtain the zeolites, also allowing the preparation of pollucite. The presence of Na and Cs in these materials may improve the basic properties of the zeolites and may open possible applications as adsorbents and catalysts.

2. Experimental

2.1. Raw materials

Saline slag was kindly supplied by *IDALSA* (*Ibérica de Aleaciones Ligeras S.L.*, Spain). The saline slag was ground in a ball mill, using an alumina jar and alumina balls, then was sieved with a 1 mm light screen. The fraction smaller than 1 mm was washed with water several times until chloride test was negative, and then air dried in an oven at 70 °C overnight (Bruckard and Woodcock, 2009; Gil and Korili, 2010, 2016). After the washing treatment, the chloride-free salt cake was sieved with a 0.4 mm light screen. The fraction larger than 0.4 mm and the fraction smaller than 0.4 mm were analyzed by powder X-ray diffraction and X-ray microfluorescence. The fraction with a size between 1 and 0.4 mm was named as *intermediate fraction*, while the fraction smaller than 0.4 mm was named as *small fraction*. This was the fraction used in this work. The recovery of aluminum was evaluated by treating portions of 7.5 g of this fraction with 25 mL of aqueous solutions of NaOH or CsOH, with concentrations 1, 2, 3 or 4 M, under reflux conditions, for a time of 2 h.

The reagents used in this work were $CsOH \cdot nH_2O$ (99.5%, Sigma-Aldrich), SiO_2 (high purity grade, 60−100 mesh, Sigma−Aldrich) and NaOH (technical grade, Panreac). All reagents were used as received, without any further purification.

2.2. Synthesis of zeolites

Two samples (7.5 g each) of the non-metallic fraction smaller than 0.4 mm and free of chlorides (small fraction) were treated with 25 mL of 1 M aqueous solution of CsOH or NaOH, respectively, for 2 h using a reflux system, while being magnetically stirred at a speed of 500 rpm. The slurries were separated by filtration, and the liquid made up to a final volume of 50 mL. The amounts of aluminum, sodium, cesium and silicon in the extraction liquor were determined by ICP−OES. The liquor resulting from treating the 7.5 g portion of the *small fraction* with the aqueous NaOH solution was called *Al−Na solution* and the extraction liquor resulting from treating the small fraction portion with aqueous CsOH solution was named *Al−Cs solution*.

The hydrothermal synthesis of both zeolites was carried out following a method adapted from Garney (2016). The extraction solutions were used as a source of aluminum in the synthesis of analcime and pollucite, respectively. The stochiometric amount of Si required to prepare the zeolites was added as SiO_2 dissolved in the smallest possible volume of a basic solution of the corresponding alkaline hydroxide, NaOH or CsOH, at a pH close to 13, resulting in the Si−Na and Si−Cs solutions. Subsequently, in the case of analcime, Al−Na and Si−Na solutions were mixed and placed in a stainless steel reactor lined with Teflon and heated at 200 °C for 24 h. In the case of pollucite, Al−Cs and Si−Cs solutions were mixed and placed in a stainless steel reactor lined with Teflon and heated at 200 °C for 24 h. No templates were used. Finally, the solids were recovered by filtration, washed with distilled water until the pH of the filtrate was lower than 10, de-agglomerated by adding 10 mL of 10% ethanol in water and immersed in an ultrasonic bath for 1 h, and then dried at 100 °C in an oven at open air overnight.

The extraction liquors were named as follows: Name of the reagent (NaOH or CsOH)−concentration of the reagent (M)−time of extraction (h). For instance, for sample NaOH−1M−2h, the extraction was carried out with 1 M NaOH for 2 h. Then, cesium

pollucite zeolite was denoted as POL and sodium analcime zeolite was denoted as ANA.

2.3. Characterization techniques

The powder X–ray diffraction (PXRD) patterns were recorded in a Siemens D–5000 instrument using Cu-Kα radiation (λ = 1.54050 Å) with fixed divergence, from 10° to 80° (2θ) at a scanning rate of 2°(2θ)/min with steps of 0.05° and time per step of 1.5 s. ICDD database was used to identify the crystalline phases (ICDD Database, 2020).

The X–ray micro–fluorescence spectroscopy (XRF) analyses were carried out using a Bruker M4 model micro–fluorescence spectrometer model (Nucleus Research Platform, University of Salamanca, Spain).

The scanning electron microscopy (SEM) analyses were carried out in a Zeiss EVO HD 25 Scanning Electron Microscope, while the Transmission Electron Microscopy (TEM) analyses were performed using a Tecnai Spirit Twin in 120 kV Transmission Electron Microscope, both at the Nucleus Research Platform, University of Salamanca, Spain.

The FT-IR spectra were recorded in a PerkinElmer Spectrum Two instrument with a nominal resolution of 4 cm^{-1} from 400 to 4000 cm^{-1}, using KBr (Merck, grade IR spectroscopy) pressed pellets and averaging 20 scans to improve the signal-to-noise ratio.

Element chemical analyses for different elements were carried out by ICP-OES in a Yobin Ivon Ultima II apparatus (Nucleus Research Platform, University of Salamanca, Spain).

Thermal analyses were performed on a SDT Q600 apparatus (TA Instruments) under a flow of 50 mL/min of oxygen (Air Liquide, 99.999%) and a temperature heating rate of 2 °C/min from room temperature to 900 °C.

3. Results and discussion

3.1. Extraction of aluminum

The chemical compositions of the raw salt cake and the fractions with particle size smaller than 1 mm are given in Table 1.

The chemical analysis (expressed as oxides, except for chlorine) showed the complex composition of the saline slag, with several elements existing in various amounts. In addition, other elements such as V, Cr, Mn, Ni or Pb were present in the range of ppm. The total aluminum content was high, 21.30% expressed as aluminum oxide, although this did not give information about the easiness of its recovering.

Raw saline slag. Its chemical composition agreed with previous data reported for the slag from the same company (Gil and Korili, 2010); the content of metallic aluminum in this waste was below 10 wt% and the content of fluxing salts was between 20 and 80 wt%. In other previous work "black dross" was used in the synthesis of zeolites but in this case the metallic aluminum content was between 7% and 50% (the supplier of the dross was not identified) (López-Delgado et al., 2014). Raw saline slag showed 21.30% of aluminum expressed as Al_2O_3. Chlorine showed the highest percentage, in agreement with the large content of Na and K (given as oxides in the analysis, but mostly existing as chlorides in the sample). Sodium must be removed to avoid interference with zeolite synthesis. The presence of other elements (Mg, Ca, Ti, Fe, Cu, Zn, V, Zr, Si, etc.) and their content vary depending on the aluminum scrap being recycled.

The chemical composition of intermediate fraction is also given in Table 1. Sodium was not detected and the amounts of chlorine and potassium were drastically reduced, confirming that the washing treatment was effective. Consequently, the non-soluble elements showed an important increase in their relative content. Aluminum, expressed as Al_2O_3, represented now 70% of the sample mass. As aluminum may be present in many different phases (Bruckard and Woodcock, 2007, 2009; Das et al., 2007; Tsakiridis, 2012; Tsakiridis et al., 2013), for gaining information on how it was actually in the solid, these fractions were analyzed by X-ray diffraction (Fig. 1). In the case of the intermediate fraction, the most intense peaks corresponded to metallic aluminum (ICDD 4–787).

The chemical composition of the small fraction is also included in Table 1. In this case, the aluminum content was 76.8 wt%, expressed as its oxide. Several phases of aluminum oxides were found by PXRD (see Fig. 1). The most intense peaks corresponded to corundum (ICDD 43–1484), gibbsite (ICDD 33–18), boehmite (ICDD 21–1307), bayerite (ICDD 22–11) and spinel (ICDD 21–1152). The chemical and mineralogical compositions of this fraction also accorded to the literature results (Bruckard and Woodcock, 2007, 2009; Das et al., 2007; Davies et al., 2008; Gil and Korili, 2010; Tsakiridis, 2012; Tsakiridis et al., 2013). Thus, this fraction was chosen as the source of Al for the preparation of the zeolite materials. The aluminum phases identified by PXRD in the intermediate and small fractions are able to be solubilized under the experimental conditions applied here to obtain the liquor, which due to the reducing and amphoteric properties of aluminum allowed its dissolution under these conditions as $[Al(OH)_4]^-$ aluminate anions. However, the intermediate fraction could be re-incorporated into the aluminum recycling process due to its high content of metallic aluminum. According to the composition of the small fraction, it

Table 1
Chemical composition (wt.%) of raw saline slag, intermediate fraction and small fraction.

Component	Raw saline slag	Intermediate fraction	Small fraction
Al_2O_3	21.30	70.00	76.80
Na_2O	18.90	Not detected	Not detected
MgO	1.30	4.50	10.30
SiO_2	2.20	15.00	5.30
SO_3	0.24	0.29	0.50
Cl	33.90	0.90	0.21
K_2O	19.80	1.10	0.45
CaO	0.72	4.10	2.12
TiO_2	0.19	0.70	0.76
Fe_2O_3	0.70	1.40	2.00
CuO	0.34	1.10	0.78
ZnO	0.15	0.60	0.28

Elements with oxide content ≤0.1% are not given.

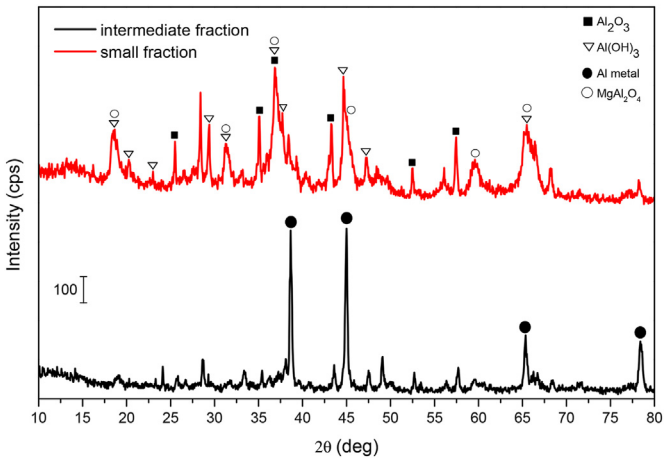

Fig. 1. X-ray patterns of Intermediate and Small fractions.

was essential to avoid the presence of impurities in the extraction liquor. For the synthesis of pollucite, it was essential that there was no sodium in the aluminum precursor solution. In any case, sodium was not detected and the amount of chloride had been drastically decreased. On the other hand, Mg, Ca, Ti, Fe, Cu and Zn were not soluble under the extraction conditions used. However, Al and Si were soluble under these extraction conditions, which allowed to obtain an extraction liquor suitable for zeolite synthesis. The presence of K had no effect on the synthesis of analcime and pollucite.

Once salt had been removed, and taking into account that the Al and Si present in the small fraction can be dissolved in a strongly basic medium, the treatment of the small fraction with NaOH or CsOH was suitable to obtain the precursor solutions (Al–Na and Al–Cs solutions) for the synthesis of analcime and pollucite, respectively.

The percentage of recovered aluminum for various NaOH concentrations is shown in Fig. 2. The reflux time and the ratio small fraction/dissolution volume were kept constant. Under these experimental conditions, an increase in the NaOH concentration produced an increase in the percentage of aluminum recovered. This trend was also observed when using CsOH (Fig. 2). For alkaline hydroxide concentrations of 1 M and 2 M there were not significant differences in percentage of recovered aluminum when using both reagents and in both cases it was close to 10% for 1 M concentration and 24% for 2 M concentration. But for alkaline hydroxide concentrations of 3 and 4 M, the percentage of recovered aluminum was higher for CsOH, reaching a percentage of 44% of recovered aluminum, while for NaOH the highest percentage reached was close to 30%.

The extraction liquors NaOH-1M-2h (Al–Na) and CsOH-1M-2h (Al–Cs) were chosen for the synthesis of ANA and POL zeolites, respectively, but any other liquor could be used as a source of aluminum and alkali metal in the preparation of these zeolitic materials. The chemical compositions of these extraction liquors are included in Table 2. In this case, the results are given in mg/L, and the final volume of both liquors was 50 mL.

Aluminum was more effectively extracted with NaOH 1 M than with CsOH 1 M, although the extraction yield was close to 10% in both cases. This confirmed that most of the existing aluminum phases were hardly soluble, despite strong alkaline conditions were used. An increase in the NaOH or CsOH concentration improved the performance for aluminum extraction.

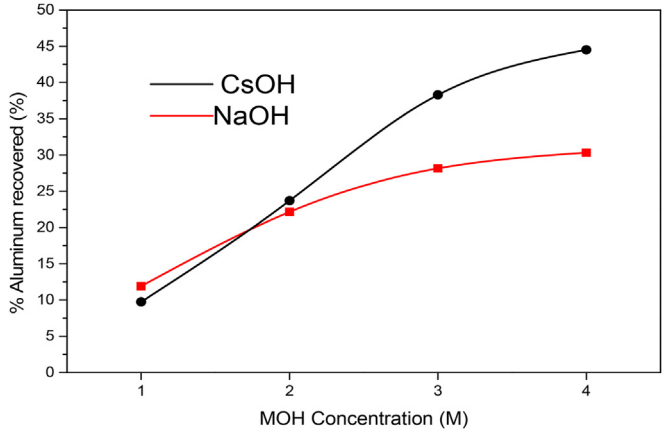

Fig. 2. Percentage of recovered aluminum for different alkaline hydroxide concentrations.

Table 2
Chemical composition of extraction liquors.

	Element				
Sample	Al (mg/L)	Si (mg/L)	Na (mg/L)	K (mg/L)	Cs (mg/L)
CsOH-1M-2h (Al–Cs)	5934	114	545	355	64,081
NaOH-1M-2h (Al–Na)	7159	129	10,230	448	–

3.2. Characterization of the zeolites

The PXRD patterns of both solids prepared are shown in Fig. 3. The diffractograms of the synthesized solids were very similar to those of the reference ICDD patterns, so both ANA (ICDD 41–1478) and POL (ICDD 25–194) were obtained from the extraction liquors with NaOH and CsOH, respectively. Jing et al. (2016) determined that the best crystallization time was 24 h. POL began to be formed merely after 1 h, but with low crystallinity. The same authors studied the effect of the Cs/Al and Si/Al ratios and the crystallization temperature on pollucite formation, finding that the Cs/Al ratio had no significant effect on the crystallinity (Jing et al., 2017). This fact allowed us to explain that the Cs/Al ratio in the extraction liquor was not a limiting parameter for the crystallinity of the final solids synthesized. Jing et al. (2017) also reported that apparently crystalline pollucite could not be obtained with a Si/Al molar ratio lower than 1.5 at temperatures lower than 200 °C. For this reason, in the present study the Si/Al ratio was fixed at 2 and the curing temperature at 200 °C. In the case of analcime, the Si/Al ratio was fixed also at 2. As in the case of pollucite, it was likely that the Na/Al ratio did not have an important influence on the crystallinity of the zeolite (Jing et al., 2017).

The PXRD patterns of analcime and pollucite zeolites were very similar to each other, the main difference being the relative intensities of some diffraction peaks. In both cases, the most intense peak was that due to planes (400), located at 26°(2θ). Then, the second most intense peak for POL was due to planes (321) and for ANA that for planes (211), which were located at 2θ values of 24° and 16°, respectively (Jing et al., 2017). Peaks due to planes (220), (422) and (461) were not detected in the case of POL. ANA and POL are zeolites from the analcime family and have very similar structures. It is possible to find pollucite–analcime solid solutions with different Cs/Na ratios in Nature. The ionic diameter of Cs^+ (3.34 Å) (Lide, 1995; Hou et al., 2019) is larger than that of Na^+ (2.04 Å) (Lide, 1995); for this reason Cs^+ cations cannot occupy sodium positions of ANA. In POL, Cs^+ occupies sites which in ANA are occupied by H_2O molecules (Jing et al., 2017). As a result, the water content in POL was lower than in ANA, as shown by the thermal analyses.

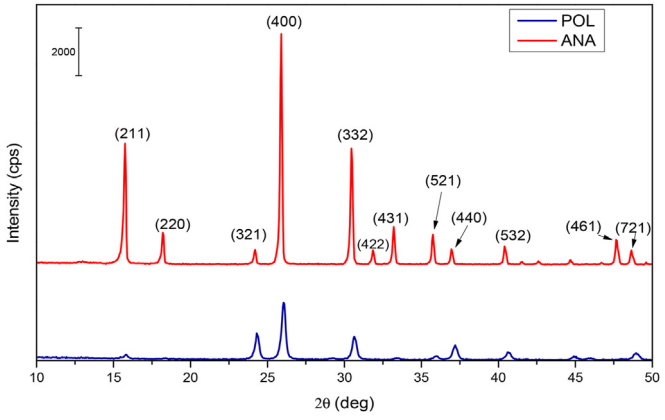

Fig. 3. X-ray pattern of ANA and POL.

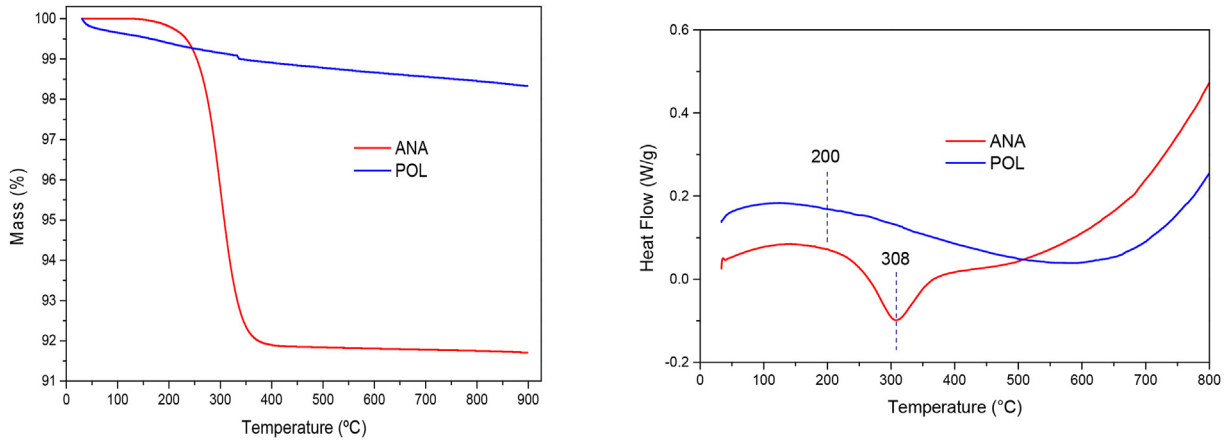

Fig. 4. TG and DSC curves of ANA and POL zeolites.

The TG and DSC curves of both zeolites here synthetized are shown in Fig. 4. The main difference between the curves from both solids was the water content, calculated from the mass loss. In the case of POL, the water content was scarcely around 1.5%, but for ANA it was 8%. This could be explained by the difference in ionic sizes between Na^+ and Cs^+, which implies that Cs^+ in POL occupies positions that in ANA are occupied by water (Fan et al., 2016; Jing et al., 2017). For this reason, the water content in POL was lower than in ANA.

The DSC curves show the dehydration temperature for both solids. In the case of pollucite this happened around 200 °C (Jing et al., 2017) and for ANA around 308 °C. This fact showed that water in POL was held more weakly than in ANA, hence it can be removed at a lower temperature.

The FT–IR spectra of ANA and POL zeolites are shown in Fig. 5. There are few differences between both spectra. In both cases, bands at 3616 and 3436 cm^{-1} were assigned to stretching vibrations of O–H bonds, and the bands at 1641 and 1629 cm^{-1} corresponded to the bending vibration of water (Jing et al., 2016; Pechar and Rykl, 1983).

The bands at 1009 cm^{-1} and 1042 cm^{-1} were assigned to the antisymmetric T–O (where T = Si or Al) stretching vibrations, while bands at 763 and 727 cm^{-1} for pollucite and 740 cm^{-1} for analcime were due to the symmetric T–O stretching vibrations. The bands at 625 and 616 cm^{-1} corresponded to the bending vibration of O–T–O units (Jing et al., 2016; Pechar and Rykl, 1983).

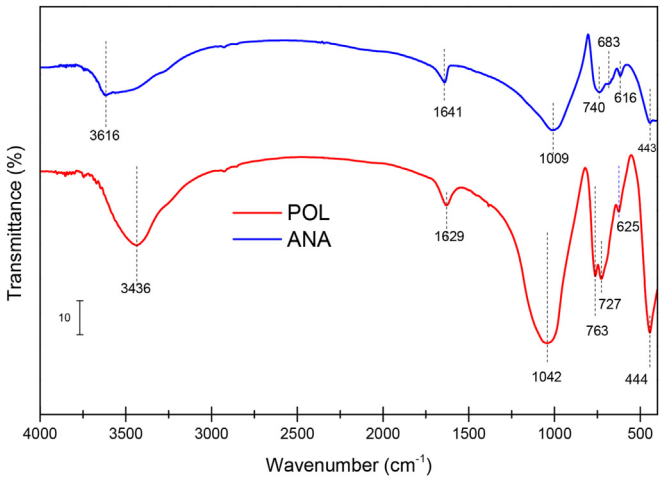

Fig. 5. FT–IR spectra of ANA and POL.

Various SEM micrographs of ANA are shown in Fig. 6. Fig. 6a and b shows the presence of homogeneous and independent roughly spherical particles of diameter lower than 100 μm. The morphology of analcime exhibited trapezohedral crystals (López-Delgado et al., 2014). When the magnification was increased, this zeolite showed pentagonal faces with clearly defined edges (Fig. 6c and d).

Four SEM micrographs of POL are shown in Fig. 7. Fig. 7a shows irregular particles with size lower than 100 μm. If magnification was increased, agglomerates of particles of more or less spherical morphologies with an approximate diameter of 1–2 μm, were observed (Fig. 7b and d). This was confirmed in Fig. 7c, where spheres of different sizes were observed.

Two TEM micrographs of ANA are included in Fig. 8. Fig. 8a shows two types of particles, one of them had a spherical morphology and the other had an irregular morphology, but in both cases, the particles did not seem to be hollow. The diameter of the spherical particles was around 500 nm. Fig. 8b shows clearly differentiated regions, which could be due to the small pentagonal faces existing in the analcime spheres.

Two TEM micrographs of POL sample are shown in Fig. 9. In both cases, Fig. 9a and b shows agglomerates of rounded particles. Particles with different diameters around 30–50 nm were observed; these particles would be pollucite spheres. In this case, the spheres may be hollow.

The mass percentages of Na, Cs, Si and Al in the final solids are included in Table 3. In the case of sample ANA, the Na/Al molar ratio was 1.3, roughly close to the expected value (1.0) in analcime. However, the Si/Al ratio was 3.7, almost twice the value expected for analcime (2.0). The isomorphic substitution of Si^{4+} by Al^{3+} in the SiO_4 tetrahedra was low because the Si/Al ratio was high, and the amount of Na^+ incorporated into the structure was lower than if the Si/Al ratio were lower (Tangkawanit et al., 2005); in this way, the Si/Na ratio was 2.83, greater than the expected value for analcime (2.0).

In the case of sample POL, there was around 1% of sodium, which could be present in the initial slag, being dissolved by the alkaline treatment. The Cs/Al ratio was 0.95 and the (Cs + Na)/Al ratio was 1.08, so it was possible that a small amount of analcime might have been formed (Jing et al., 2017), or that Na^+ isomorphically substituted Cs^+. The Si/Al ratio was 3.8, similar to the obtained value in analcime. Again, the substitution degree of Si^{4+} by Al^{3+} was low. For certain specific potential applications, such as cesium storage, the Si/Al ratio in the final solid would be decreased so that the structure can accommodate a larger amount of cesium.

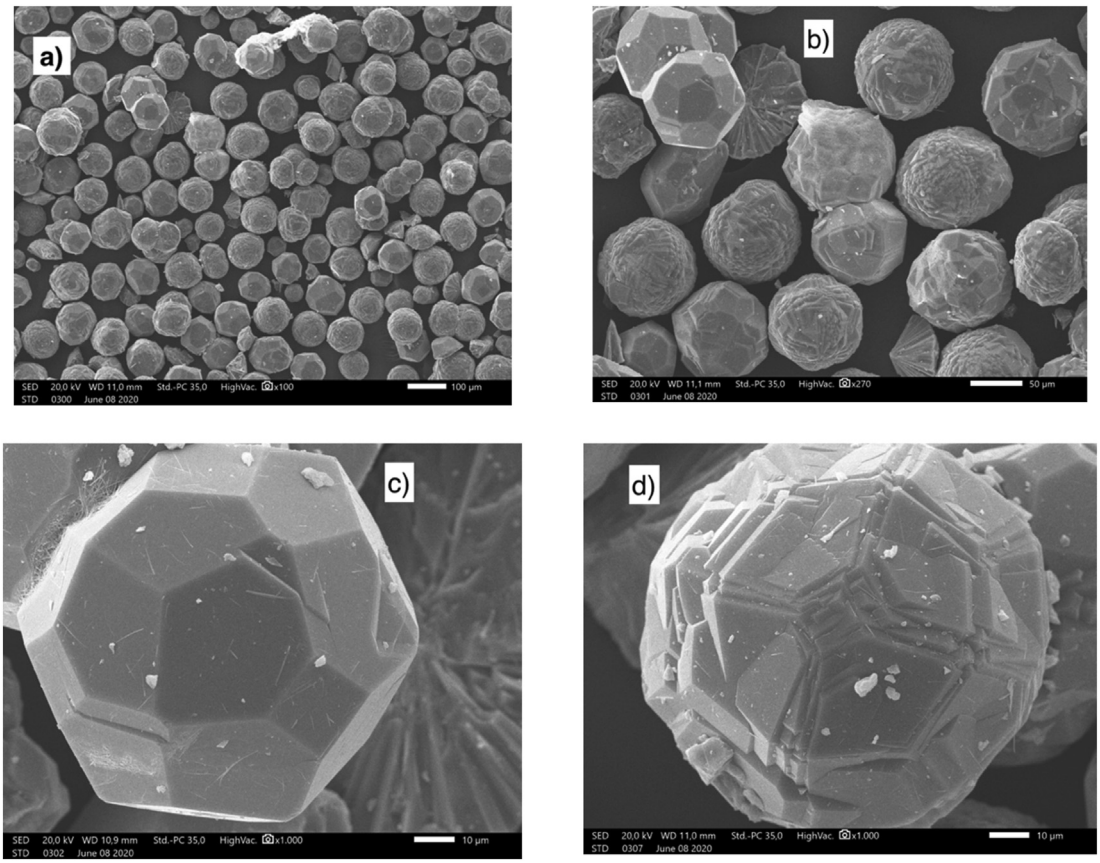

Fig. 6. SEM micrographs of sample ANA; magnifications: a) ×100, b) x270, c) and d) x1000.

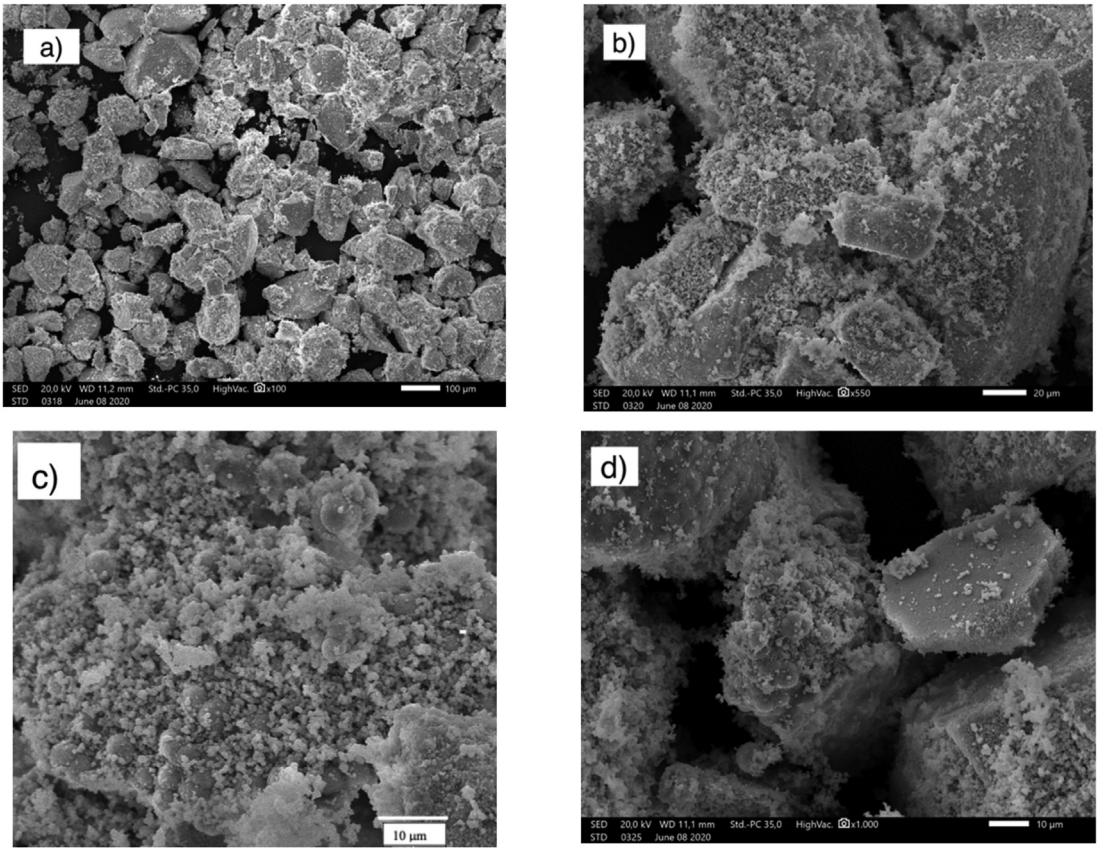

Fig. 7. SEM micrographs of sample POL; magnifications: a) ×100, b) x550, c) x1000 and d) x550.

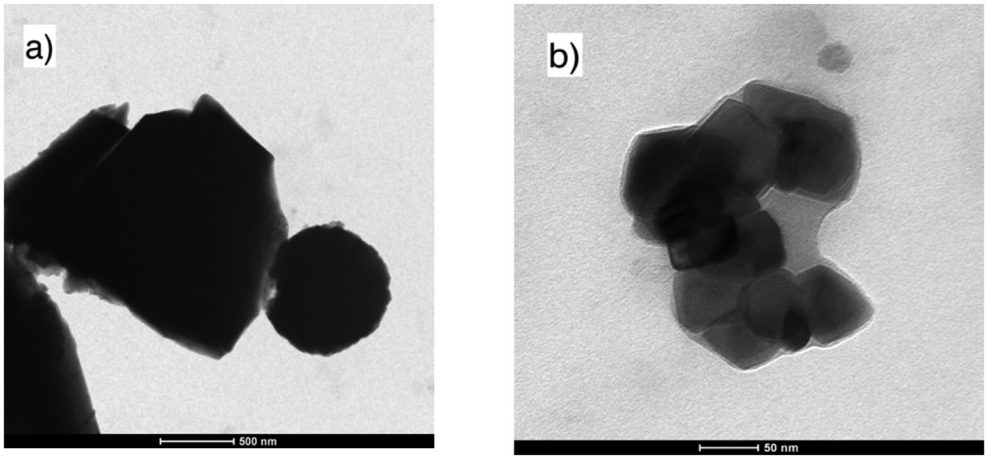

Fig. 8. TEM micrographs of ANA.

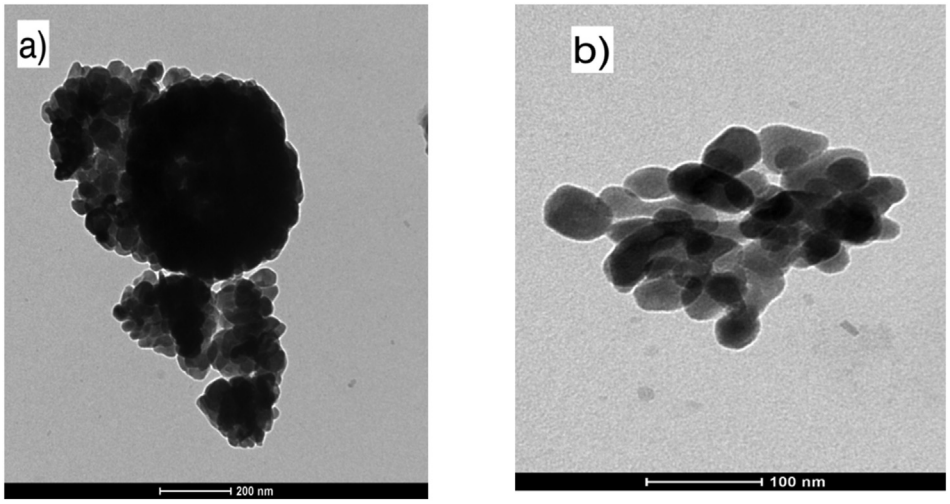

Fig. 9. TEM micrographs of POL.

Table 3
Chemical composition of the solids (wt.%).

	Element			
Sample	Al	Si	Na	Cs
ANA	10.87	42.36	12.22	–
POL	8.34	32.67	0.95	38.99

4. Conclusions

Pollucite and analcime zeolites can be synthesized from aluminum saline slag. First, it was necessary to remove sodium chloride from saline slag and then, the non−metallic fraction was treated under reflux conditions with an alkaline hydroxide. Extraction performance was improved when increasing the alkaline hydroxide concentration, being the best extraction at high concentration of CsOH, keeping time reflux in 2 h and ratio small fraction/dissolution volume constant. The liquor from the extraction was used as a source for Al in the preparation of the zeolitic materials. Both zeolites were synthesized by the hydrothermal method at 200 °C for 24 h. The crystallinity and water content were higher for analcime than for pollucite. Morphological analyses showed that in both cases spherical particles were formed, which are larger for ANA solids with pentagonal or polygonal faces. In the case of pollucite, spheres were smaller and it is possible that they are hollow.

The Si/Al ratios in the final solids were high in both cases, and therefore substitution of Si^{4+} by Al^{3+} was small. To use analcime as ion exchanger or pollucite for cesium storage, the Si/Al ratio should be smaller, to increase the performance of these materials in those applications.

CRediT authorship contribution statement

Alejandro Jiménez: Data curation, Formal analysis, Investigation, Methodology, Validation, Writing − original draft. **Alexander Misol:** Data curation, Investigation, Validation. **Álvaro Morato:** Data curation, Investigation, Validation. **Vicente Rives:** Conceptualization, Data curation, Formal analysis, Methodology, Supervision, Validation, Writing − review & editing. **Miguel A. Vicente:** Conceptualization, Data curation, Formal analysis, Methodology, Project administration, Resources, Supervision, Validation, Writing − review & editing. **Antonio Gil:** Conceptualization, Data curation, Formal analysis, Project administration, Resources, Supervision, Writing − review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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