

Zeolite Synthesis from Aluminum Saline Slag Waste

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Abstract

This work describes the synthetic procedures developed to obtain zeolite X (NaX), zeolite A (LTA) and sodalite (SOD) using aluminum saline slag waste (AISSW) as aluminum source in a two-step hydrothermal method involving alkaline extraction of Al, with separation of the residual waste, and hydrothermal treatment at low temperatures and long reaction times. Use of the mother liquor obtained after filtration and separation of the zeolite is also analyzed in the alkaline extraction of Al. The synthetic parameters that determine the type of zeolite, purity, crystallinity, specific surface area, pore size and pore volume include the Si/Al molar ratio, pH, nucleation temperature and time, and crystallization temperature and time. These critical parameters were studied and determined to synthesize NaX, LTA and SOD as individual phases. The materials obtained were characterized by X-ray diffraction, scanning electron microscopy and N₂ adsorption/desorption measurements at -196 °C. The characteristics of the best zeolites obtained are similar to those of IZA references and the specific surface areas are in the range of commercial ones: NaX ranges from 450 to 500 m²/g and LTA from 250 to 300 m²/g. The results show that it is possible to synthesize zeolites from AISSW, thus allowing these materials to be applied as promising adsorbents and catalysts.

Keywords: industrial waste valorization, high-value-added products, aluminum alkaline extraction, wastes valorization, zeolite synthesis.

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1. Introduction

Zeolites are very versatile porous materials that can be applied in a large number of applications due to their physical properties. Thus, these materials are used in chemical engineering processes as catalysts, molecular sieves, ion exchangers and adsorbents [1]. Recently, they have also been applied in the construction sector due to their pozzolanic character, with the incorporation thereof into cement mixtures and mortars allowing their properties to be improved by conferring increased mechanical strength and durability, resistance to alkali-silica reactions, resistance to chloride diffusion, etc. [2-4]

Zeolites obtained via an industrial or laboratory route are used more frequently than natural zeolites due to their properties, especially their high purity and uniform particle size. The amounts produced also make these materials more suitable for industrial applications. However, the synthesis of zeolites from silica and alumina is a rather expensive process, and the search for affordable alternative raw materials is an interesting line of research. In this regard, our research group has recently reviewed the synthetic routes via which industrial by-products rich in Si and/or Al can be used to obtain zeolites [5]. For example, the possibility of obtaining zeolites from coal fly ash, biomass ash, Si and Al sources from industrial wastes and natural clays has been reported.

Various authors have reported the synthesis of zeolites using Al and Si sources from industrial wastes. Hiraki et al. [6], for example, described the synthesis of zeolite X using aqueous solutions of sodium silicate and $\text{Al}(\text{OH})_3$ from silicon sludge and aluminum black dross. The authors reported specific surface areas up to $589 \text{ m}^2/\text{g}$. Similarly, the synthesis of zeolites ANA, NaP1 and SOD in a single-step hydrothermal process has been studied by Sánchez-Hernández et al. [7]. These authors indicated that the formation of a type of zeolite is determined mainly by the temperature and alkali concentration of the hydrothermal process and specific surface areas of $14 \text{ m}^2/\text{g}$ are reported. The synthesis of zeolites with magnetic properties and specific surface areas of $231 \text{ m}^2/\text{g}$ using red mud as an alternative aluminum source has been reported by Belviso et al. [8] and Ma et al. [9]. The

selective synthesis of zeolites A and X from crushed stone powder and aluminum ash has been summarized by Kuroki et al. [10]. Finally, Kang et al. [11] reported the synthesis of zeolites using two types of waste: aluminum dross, as Al resource, and waste LCD glass powder, as Si resource. Zeolites with a specific surface area of 31 m²/g are obtained.

Various methods have been reported to obtain zeolites [1]. For example, hydrothermal treatments can be applied in one or two steps [12]. The single-step method uses all the alkaline-treated reagent as Al and/or Si source and has the advantage that no residual waste is generated, although the synthesized zeolite has particle irregularities and crystal differences. In contrast, the two-step method separates the alkaline aqueous solution from the residual waste. As the Al and/or Si source is pure, more regular and purer zeolites with higher quality and reproducibility are synthesized. Zeolite synthesis during the hydrothermal process is mainly affected by the temperature and pressure, although numerous other variables, such as the Si/Al molar ratio, alkalinity, aging process, crystallization temperature and time, nucleation temperature and time, amongst others, may also have an effect. The synthesis of zeolites in a hydrothermal process is, therefore, a multi-phase process involving liquids and solids.

The main objective of this work is to study the effect of the various parameters that can affect the hydrothermal synthesis of a zeolite from the aluminum extracted from an aluminum waste. A secondary objective is to determine whether it is possible to selectively synthesize a type of zeolite from this waste. Finally, we aim to determine whether the liquor obtained in the hydrothermal synthesis of zeolites can be used to extract aluminum from the waste, thus allowing the liquid stream to be reused in the zeolite-synthesis process.

2. Experimental procedure

2.1. *Materials*

The aluminum saline slag waste (AISSW) employed as aluminum source was obtained from *Iberica de Aleaciones Ligeras S.L. (IDALSA)*, a Spanish company that recycles Al by-products to produce ingots of various shapes and chemical compositions [13]. AISSW, which is a hazardous waste generated in *IDALSA* processes, is a powdered solid formed of particles smaller than 23 mm in diameter and rich in Al. The chemical composition of the waste has been reported in a recent study [14]. Other materials used were Na_2SiO_3 (37-46%), NaOH (Panreac) for aluminum extraction, and HNO_3 (65%, Panreac) for pH adjustment.

2.2. *Zeolite synthesis*

Zeolites are synthesized from AISSW as aluminum source using a two-step hydrothermal method involving alkaline extraction of aluminum, with separation of the residual waste [14], and hydrothermal treatment at low temperatures and long reaction times. The Si/Al molar ratio, pH and nucleation and crystallization times and temperatures used to obtain zeolites were studied (see Table 1).

Step 1: alkaline extraction of aluminum and residual waste separation

The AISSW was milled for 3 h in a bench-top grinding ball mill with alumina balls (diameter: 10 mm) to activate it by removing the surface oxides that protect the AISSW and limit its reactivity, thereby also increasing the total surface area. The alkaline extraction of aluminum was performed in a glass Erlenmeyer with a volume of 1 dm³, on a hot plate, with a double cooling condenser [8]. A single extraction with 0.75 cm³ of 2 mol/dm³ NaOH was performed using 37.5 g of AISSW, under reflux and stirring, for 1 h. The AISSW/NaOH ratio was 1:20. The alkaline-treated AISSW was filtered to separate the alkaline aqueous aluminum source from the residual waste in order to obtain a purer source of aluminum that allows the synthesis of purer and more regular zeolites with higher quality and reproducibility.

Step 2: hydrothermal treatment at low temperatures and long reaction times

Zeolite synthesis was performed in a 0.5 dm³ Teflon-lined hydrothermal autoclave reactor from Tefic Biotech. Na₂SiO₃ was placed in the Teflon liner and the AISSW-based aluminum source was added. The quantities depended on the Si/Al ratio defined for each sample. The solution obtained was stirred rapidly by hand at room temperature (RT) to mix the sources until formation of a white, homogeneously distributed and watery gel. The Teflon liner was placed in the stainless-steel kettle body and the autoclave closed and placed in the oven. The temperature and time for the nucleation stage, and for the crystallization stage, were set and applied. As soon as zeolite synthesis had finished, the reactor was extracted from the oven, cooled with cold water and opened. The Teflon liner was removed from the stainless-steel kettle and the material obtained was filtered to separate the zeolite and the zeolite synthesis mother liquor (ZSML). Filtration was performed using the same system described for Al source purification. The sample was washed with 50 cm³ of deionized water and, after filtration, was dried at 120 °C for 4 h. The ZSML was also used to extract aluminum from the waste and the aluminum extracted compared with that obtained when using a NaOH solution (Step 1). The extraction conditions were the same as those reported in Step 1.

The synthetic parameters studied to obtain zeolites were Si/Al molar ratio, pH, nucleation temperature, nucleation time, crystallization temperature and crystallization time. This study was performed in 10 series of synthesis involving 48 samples each. In each series of synthesis, some of the six synthetic parameters were given the same values as in the previous series and applied equally to all samples in that series. These are referred to as *fixed parameters*. The values of other synthetic parameters were changed from the values used in the previous series but were also applied equally to all samples in that series. These are referred to as *changed parameters* and their values were modified to compare the differences between a sample and their counterparts in previous and subsequent series. A *control parameter* is the only one whose value differs in each sample of the series in

order to study its effect on the synthetic conditions for that series. The synthetic conditions for all the series and samples prepared are summarized in Table 1, which lists fixed, changed and control parameters.

A scheme of the process used to synthesize zeolites in this study is summarized in Figure 1.

2.3. Characterization techniques

The Al and Si concentrations in the alkaline aqueous solutions were determined by inductively coupled plasma optic emission spectroscopy (ICP-OES) using a Varian ICP-OES Vista MPX with radial vision.

The AISSW and residual waste generated in the alkaline extractions were characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF) and N₂ (Praxair, 99.999%) adsorption/desorption measurements at -196 °C. The composition, structure and crystallinity of the AISSW, residual waste and synthesized zeolites were determined by XRD using a Siemens D-5000 diffractometer equipped with a CuK_α radiation source, operating conditions of 40 kV and 40 mA and 2θ from 5–80° with a continuous run. SEM analysis of the samples was made using a JEOL microscope, model JSM-6400. Images of the samples were taken at various scales to characterize size and shape of the particles. The chemical composition of the waste was determined using a sequential mass spectrometer with wave dispersion X-ray fluorescence PANalytical under vacuum. Before characterization, samples were calcined at 1050 °C for 1 h and agglutinated with Elvacite. The loss of ignition (LOI) of the samples was estimated by heating an aliquot of each sample at 1050 °C for 1 h in a muffle oven. N₂ adsorption/desorption measurements were performed at -196 °C using a Micromeritics ASAP 2020 Plus adsorption analyzer. All samples were calcined before adsorption experiments. The Brunauer-Emmett-Teller (BET) specific surface area was calculated in the relative pressure range of 0.05 to 0.20 and the pore volume at a relative pressure of 0.99. The main results are summarized in Table 1.

3. Results and discussion

3.1 Zeolite synthesis

The XRD patterns for the synthesized zeolites were compared with the reference powder patterns published by the SC-IZA for the low- and medium-silica zeolites that could be obtained under the conditions studied, namely NaX, NaP1, LTA, GIS, ANA and SOD [15]. The results revealed that all the zeolites synthesized were NaX, LTA and SOD, either as individual phases or as mixtures. No other zeolites or materials were found.

Samples from series 1 (see Table 1) were synthesized at a Si/Al molar ratio of 1.6, pH 14, with a nucleation time of 3 h at 70 °C and crystallization times of 24, 12, 8, 6 and 4 h at 100 °C. The XRD results revealed that, under these conditions, longer crystallization times led to a purer zeolite: sample (1-1) (24 h) is a mixture of NaX and LTA, samples (1-2), (1-3) and (1-4) are LTA as an individual phase, and sample (1-5) is SOD as an individual phase. A BET specific surface area of 236 m²/g was found for sample (1-4).

The synthetic parameter changed in series 2 was the nucleation temperature, which was increased from 70 to 100 °C. As such, the entire synthesis (24, 12, 8, 6 or 4 h) was performed at 100 °C. The XRD results revealed that, under these conditions, shorter times lead to purer zeolites: SOD was observed after 24, 12 and 8 h and LTA after 6 and 4 h, all of them as individual phases. A BET specific surface area of 264 m²/g was found for sample (2-9).

The samples in series 3 were obtained by reducing the crystallization temperature from 100 to 70 °C, with the other parameters equal to the previous ones. The results indicate that, at a lower crystallization temperature, longer crystallization times are better for obtaining zeolites. Thus, a mixture of NaX and LTA was obtained after 24 h, LTA as a single phase after 12 h and SOD after 4 h. No clear XRD peaks were observed in the samples isolated after 8 and 6 h. A BET specific surface area of 263 m²/g was found for sample (3-12). A comparison of the XRD and N₂

adsorption-desorption isotherms obtained for samples (1-1), (1-4), (2-9), (3-11) and (3-12) can be found in Figures 2 and 3. Type II adsorption isotherms in the BDDT classification are obtained.

The synthetic parameters in series 4 were the same as for series 1 except for the pH, which was lowered to 12. When the Al source was added to the Na_2SiO_3 and stirred manually, the same white gel as in the previous series was formed, but when HNO_3 was added the gel became thicker. The synthesized zeolite was also a gel and filtration to separate it from the mother liquor (ZSML) was more complicated and took too long. Moreover, although pH 11-12 is reported to be the best pH for zeolite X, the XRD patterns for these samples show the worse results, with SOD being obtained at both the maximum and minimum synthesis times. As such, the optimal pH is not 12 for these Si and Al sources. A BET specific surface area of $13 \text{ m}^2/\text{g}$ was found for sample (4-16).

The nucleation temperature was decreased to $50 \text{ }^\circ\text{C}$ in the fifth series, the nucleation time was increased to 24 and 12 h, and the crystallization time lowered to 3 and 4 h. A Si/Al molar ratio of 1.6, pH 12 and crystallization temperature of $100 \text{ }^\circ\text{C}$ were used for the two samples. Single LTA phases were observed in both cases, therefore longer times and lower temperatures for the nucleation stage improve the quality of the synthesized zeolite, although no NaX is obtained despite working at pH 12. The reason for this could be the use of too-short crystallization times. A BET specific surface area of $11 \text{ m}^2/\text{g}$ was found for sample (5-22).

As zeolite X was not found as a single phase in the series performed at pH 12, the effect of the Si/Al molar ratio (values of 2.2, 3.2 and 4.0) was studied in series 6. The reaction temperatures and times were the same as in series 2. For the three Si/Al ratios studied, the best samples were obtained with the longest crystallization time: NaX as a single phase with Si/Al = 3.2 (sample (6-23)), LTA as a single phase with 4.0 (sample (6-33)) and SOD with 2.0 (sample (6-28)). In summary, Si/Al = 3.2 is the best ratio to prepare the NaX zeolite using longer crystallization times. Sample (6-23) was homologous with samples (1-1) and (3-11), in which a mixture of NaX and LTA zeolites is observed. The three samples were synthesized with a total time

of 27 h (3 h of nucleation and 24 h of crystallization), therefore a synthesis time of 27 h is optimal for obtaining NaX. Samples (1-1) and (3-11) were prepared at pH 14 and sample 6-23 at pH 12, therefore a lower pH could explain why NaX was obtained as a single phase instead of a mixture of NaX and LTA. The crystallization temperature in sample (6-23) was 100 °C (70 °C for sample (3-11)). As such, a higher crystallization temperature seems to favor the synthesis of NaX over LTA. To confirm these conclusions, subsequent series were designed taking into account the synthesis time and crystallization temperatures as variables. A BET specific surface area of 62 m²/g was found for sample (6-24).

In series 7, nucleation was studied at a longer time and lower temperature (4 h and RT). Crystallization at a lower time and higher temperature (8 h and 120 °C) was also performed to compare these parameters. Additionally, a Si/Al ratio of 3.2 and pH of 12 was used. In the case of series 8, samples were synthesized under the same conditions but with a longer nucleation time (12 h and RT). In these series, the presence of SOD was observed in all cases. In order to evaluate the effect of the modified parameters, new series of samples were synthesized. As indicated above, difficulties were encountered when filtering the synthesized zeolite, which could confirm that lowering the pH is not appropriate for these Al and Si sources. A BET specific surface area of 11 m²/g was found for sample (7-38) under these synthetic conditions.

In series 9, the pH was kept constant at a value of 14 and nucleation was carried out at 50 °C for longer times (6 and 12 h). Crystallization was also carried out at 120 °C and for longer times (12 and 6 h). As in the previous series, SOD was again obtained, but in this case separation by filtration was carried out without difficulties, thereby confirming that a pH of 14 is the most suitable for synthesizing zeolites with Na₂SiO₃ and AlSSW. To confirm this conclusion and define the optimum pH, a solution of Na₂SiO₃ and aluminum extracted from the waste was mixed with a Si/Al ratio of 3.2 and HNO₃ until a pH of 12 was reached. Samples of the precipitate were taken before the addition of HNO₃, at pH 14, and at pH 12, then separated from their alkaline aqueous solutions by filtration. The Al content in the solution with pH

12 was found to be 25% lower than in the solution with pH 14. This may indicate that the aluminum present in solution is not available for zeolite synthesis at pH 12. If the Si/Al ratio changes, zeolite formation decreases as there is insufficient aluminum available. A BET specific surface area of 5 m²/g was found for sample 9-42.

Samples from series 10 were prepared at pH 14, Si/Al = 3.2, a nucleation time of 6 or 0 h at room temperature, and crystallization at 100 °C for 24, 18 or 12 h. The XRD patterns of samples (10-45) and (10-46) correspond to zeolite X (NaX) as individual phases, but the intensity of the main peak of XRD, 2θ at 6.10°, after crystallization for 24 h is lower than after 18 h. This result could be explained by considering that Si and/or Al are completely depleted before 24 h, thus meaning that NaX synthesis ends. Even if the crystallization time is extended, no further synthesis is possible and some of the NaX prepared dissolves as the medium is very alkaline. The sample obtained after crystallization for 12 h corresponds to SOD, thus suggesting that this time is insufficient time to obtain NaX. The XRD patterns for samples (10-47) and (10-48), with no nucleation stage, also failed to show any type of zeolite. A BET specific surface area of 454 m²/g was found for sample (10-44). The XRD and N₂ adsorption-desorption isotherms obtained for sample (10-44) are shown in Figure 4. A type I adsorption isotherm in the BDDT classification is obtained.

Representative SEM images of the synthesized zeolites are summarized in Figure 5. The samples show several morphologies, a result that confirms the analysis by XRD that indicated that the samples were not very pure. Only the particles from sample (10-44) show lower size, that can be characteristic of zeolite type NaX.

3.2 Extraction of aluminum using the alkaline mother liquor

A zeolite synthesis mother liquor (ZSML) with high NaOH concentration is obtained after Step 2. As this solution has a high concentration of alkali, it can be used as an extraction medium instead of the commercial NaOH solution. The

conditions used for aluminum alkaline extraction with NaOH were reported in a previous study [14] and were taken as reference here. Thus, 37.5 g of original waste was activated in a ball mill with 10 mm alumina balls for 3 h, then a single extraction with 0.75 dm³ of 2 mol/dm³ aqueous NaOH solution was performed for 1 h, under reflux and with stirring. Four consecutive extractions were completed and the aluminum extracted compared. Other experimental conditions have also been studied and are summarized in Table 2. The nomenclature used is *ZSMLxyz*, where *x* is the milling time, *y* the extraction time and *z* the number of consecutive extractions. This extraction procedure is a four-stage, crosscurrent aluminum leaching with NaOH and ZSML.

The Al and Si extracted into the alkaline aqueous solution were quantitatively determined by ICP-OES. The reference aqueous solution for this study was the optimized alkaline extraction with NaOH, obtained by activating the aluminum saline slag in a ball mill for 3 h and then performing a single extraction with 0.75 dm³ of commercial NaOH aqueous solution 2 mol/dm³ for 1 h, under reflux and with stirring [15]. NaOH-optimized contains 7.72 g/dm³ (15.4%) of Al and 0.32 g/dm³ (0.6%) of Si, therefore the Si/Al ratio is 0.04. As the synthesis of zeolites requires Si/Al ratios higher than 1, AISSW is a valuable source of Al but an extra source of Si is required to adjust the Si/Al ratio for each type of zeolite. NaOH-optimized was successfully used as an Al source for the synthesis of zeolite-X using commercial Na₂SiO₃ as the extra source of Si and generating a mother liquor rich in NaOH (ZSML) [16]. The study of Al extraction with ZSML started with the optimal conditions for commercial NaOH and activation by milling, subsequently optimizing the extraction time and number of consecutive extractions. The Al content after 1, 2 or 4 h of ZSML extraction was 6.84, 6.68 and 6.56 g/dm³, respectively, therefore the higher value of Al is obtained after 1 h. The optimum extraction time is the same as that determined for commercial NaOH extraction. As regards single and multiple consecutive extractions, it can be seen that the Al content in the second consecutive extraction is 25% that of the first one, decreasing to 10% in the third and 7% in the fourth consecutive extractions (see Table 2). This reduction is observed both when the aluminum saline slag is treated directly and when activated previously by milling for

3 h. As the extraction of Al decreases significantly in the second consecutive extraction and falls to essentially zero in the third and fourth extractions, a single extraction with ZSML appears to be the best procedure. These results are similar to those obtained in the study with commercial NaOH, although the decrease is slightly smaller. In relation to aluminum saline slag activation by milling, the Al extracted when the waste is milled for 3 h is 7.49 g/dm³, which is 10% higher than for the same sample treated directly, without milling. These results confirm that milling activates the waste due to elimination of the surface oxides that protect the waste and limit its reactivity, and also because the total surface area of smaller particles is higher than for larger particles. These results also support those obtained with commercial NaOH extraction [14]. As such, in light of these results, the best parameters for extraction with ZSML are: activating the aluminum saline slag in a ball mill with 10 mm alumina balls for 3 h and then performing a single extraction using 37.5 g of waste and 0.75 dm³ of ZSML for 1 h, at reflux temperature and with stirring. This optimal alkaline extraction with ZSML produces 7.49 g/dm³ (15%) of Al and 0.29 g/dm³ (0.6%) of Si, which are similar to the values for optimal alkaline extraction with commercial NaOH (7.72 g/dm³ (15.4%) of Al and 0.32 g/dm³ (0.6%) of Si). Consequently, as optimal alkaline extraction with ZSML results in the same chemical composition as that obtained with commercial NaOH, it is a valuable source of Al for zeolite synthesis, although an extra source of Si is required.

The main elements in the original waste were determined by XRF. The results showed that the content of the main constituents (i.e. Al and Si) is Al₂O₃ 54.41 wt.% and SiO₂ 5.69 wt.%, thus resulting in an SiO₂/Al₂O₃ ratio in the original waste of 0.10 (see Table 3). The quantities of Al₂O₃ and SiO₂ in the residual wastes generated in the Al alkaline extraction with ZSML are lower than in the original, which means that Al and Si are dissolved from the aluminum saline slag, thus confirming the results obtained during chemical characterization of the alkaline aqueous solutions obtained (see below). The values of Al₂O₃ upon optimal extraction with ZSML are similar to those obtained in the optimal treatment with NaOH, namely 40.98 wt.% and 40.39 wt.%, respectively. The quantity of SiO₂ is also the same (4.91 wt.% and 4.89 wt.%, respectively). These results reveal that the residual waste obtained after an

optimized alkaline extraction with ZSML has the same chemical composition as that obtained with NaOH. However, the amount of Na in the residual waste is high, and increases progressively in consecutive alkaline extractions with NaOH, thus reinforcing the idea that a single extraction is better than multiple consecutive extractions. However, the quantity of Na in the optimized purified waste is very low and similar to that found in the original waste. This finding demonstrates that washing the waste with deionized water dissolves the NaOH and purifies the sample, thus resulting in a non-hazardous waste.

As can be seen from Figure 5, the XRD patterns for AISSW show four crystalline phases, namely corundum (Al_2O_3), with peaks at 25° , 35° , 38° , 43° , 52° , 57° , 66° , 68° , 77° and 89° , hexagonal aluminum nitride (AlN), with peaks at 33° , 36° , 38° and 50° , metallic aluminum (Al), with peaks at 38° , 44° and 65° , and spinel (MgAl_2O_4), with peaks at 19° , 32° , 37° , 45° , 56° , 60° , 65° and 68° . No other compounds or elements were detected either because they are present as amorphous phases or because they are present as crystalline phases but in very low amounts. XRD tests were performed on both the original and calcined waste. The XRD patterns show the same profile for both samples but are better defined for the calcined waste, thus revealing that calcination could be considered to be a purification method for the original waste. The XRD patterns of the residual wastes generated after extraction with NaOH and with ZSML present the same peaks as the original waste.

The chemical composition of the aluminum saline slag before Al extraction (AISSW) and after it (residual waste) was calculated from the XRF and XRD results in order to determine the amount of metallic Al, AlN and Al_2O_3 present. The values, expressed in wt.%, are summarized in Table 4 and show that all the deliverable aluminum, metallic Al and AlN is extracted with ZSML. The optimal Al extraction with ZXML is slightly better than with NaOH. The results also show that Al from corundum and spinel is not dissolved with ZSML because their values in the residual wastes are the same as in the original one. The value for corundum increases because some of the Al is oxidized during extraction and/or purification. The quantity of non-

crystalline components and the LOI is higher in the original wastes than in the original because Al is extracted and volatile components are removed.

The N₂ adsorption-desorption values at -196 °C determined for the original waste and the residual wastes generated in the optimal extractions with NaOH and with ZSML, before and after washing with deionized water, are summarized in Table 5. The data reveal that raw and washed aluminum saline slag (AISSW) have the highest BET specific surface area and the smallest size and pore volumes, thus meaning that water does not modify the textural properties of the initial waste. However, the specific surface area and pore volume change when treated with bases, with values decreasing to 65% that for the original waste in the residual waste generated by ZSML extraction and increasing to 70% in the washed residual waste. The BET specific surface area of the residual waste generated in the optimal extraction with NaOH decreases to 40% of the original, subsequently increasing to 50% after washing. Although both treatments are alkaline, the decrease in the BET specific surface area in the residual wastes is lower after optimal extraction with ZSML than with NaOH, thus suggesting that ZSML alkaline treatment is less aggressive for their textural properties. For both types of residual waste, the BET specific surface area is higher for the washed samples than for the corresponding raw waste, thus confirming that Na is removed. The total pore volume increases slightly, and average pore sizes increase with treatment, from 6.1 to 10 and 20.2 nm, respectively.

4. Conclusions

In summary, the XRD results indicate that a Si/Al molar ratio of 3.2, a pH of 14, a nucleation time of 6 h at room temperature, and a crystallization time of 18 h at 100 °C are optimal for obtaining NaX as an individual phase using Na₂SiO₃ and AISSW as silicon and aluminum sources.

With regard to the synthesis of zeolite LTA, no differences between nucleation and crystallization parameters were observed. The reason for this could be that both

stages occur simultaneously throughout the synthesis. The XRD results show that there are two possible synthetic conditions for obtaining NaX as a single phase: a Si/Al molar ratio of 1.6, a pH of 14, and nucleation and crystallization stages of 6 h at 100 °C; or a Si/Al molar ratio of 1.6, a pH of 14, and nucleation and crystallization stages of 12 h at 70 °C.

The mother liquid generated in the zeolite synthesis (ZSML) can be used to extract the Al from AISSW instead of commercial aqueous NaOH solutions. The optimal conditions involve activating the original waste in a ball mill with 10 mm alumina balls for 3 h, then performing a single extraction with ZSML for 1 h, under reflux and with stirring. Under these conditions, and using 37.5 g of AISSW and 0.75 dm³ of ZSML, a solution of 7.49 g_{Al}/dm³ is obtained.

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References

1. S.M. Auerbach, K.A. Carrado, P.K. Dutta (Eds.), Handbook of Zeolite, Science and Technology, Marcel Dekker, Inc. 2003.
2. M. Najimi, J. Sobhani, B. Ahmadi, M. Shekarchi. An experimental study on durability properties of concrete containing zeolite as a highly reactive natural pozzolan. *Constr. Build. Mater.* 35 (2012) 1023-1033.
3. B. Ahmadi, M. Shekarchi. Use of natural zeolite as a supplementary cementitious material. *Cem. Concr. Compos.* 32 (2010) 134-141.
4. S.Y.N. Chan, X. Ji. Comparative study of the initial surface absorption and chloride diffusion of high performance zeolite, silica fume and PFA concretes. *Cem. Concr. Comp.* 21 (1999) 293-300.
5. M. Yoldi, E.G. Fuentes-Ordoñez, S.A. Korili, A. Gil. Zeolite synthesis from industrial wastes. *Micropor. Mesopor. Mater.* 287 (2019) 183-191.
6. T. Hiraki, A. Nosaka, N. Okinaka, T. Akiyama, Synthesis of zeolite-X from waste metals, *ISIJ International* 49 (2009) 1644-1648.
7. R. Sánchez-Hernández, A. López-Delgado, I. Padilla, R. Galindo, S. López-Andrés, One-step synthesis of NaP1, SOD and ANA from a hazardous aluminum solid waste, *Micropor. Mesopor. Mater.* 226 (2016) 267-277.
8. C. Belviso, A. Kharchenko, E. Agostinelli, F. Cavalcante, D. peddis, G. Varvaro, N. Yaacoub, S. Mintova, Red mud as aluminium source for the synthesis of magnetic zeolite, *Micropor. Mesopor. Mater.* 270 (2018) 24-29.
9. L. Ma, L. Han, S. Chen, J. Hu, L. Chang, W. Bao, J. Wang, Rapid synthesis of magnetic zeolite materials from fly ash and iron-containing wastes using supercritical water for elemental mercury removal from flue gas, *Fuel Proces. Technol.* 189 (2019) 39-48.
10. S. Kuroki, T. Hashishin, T. Morikawa, K. Yamashita, M. Matsuda, Selective synthesis of zeolites A and X from two industrial wastes: Crushed stone powder and aluminum ash, *J. Environ. Manage.* 231 (2019) 749-756.
11. Y. Kang, B. Swain, B. Im, J.-H. Yoon, K.H. Park, Ch.G. Lee, D.G. Kim. Synthesis of zeolite using aluminum dross and waste LCD glass powder: a waste to waste integration valorization process. *Metals* 9, (2019), 1240.

12. C.S. Cundy, P.A. Cox. The hydrothermal synthesis of zeolites: history and development from the earliest days to the present time. *Chem. Rev.* 103 (2003) 663-702.
13. A. Gil, Management of the salt cake from secondary aluminum fusion processes, *Ind. Eng. Chem. Res.* 44 (2005) 8852-8857.
14. M. Yoldi, E.G. Fuentes-Ordoñez, S.A. Korili, A. Gil. Efficient recovery of aluminum from saline slag wastes, *Minerals Eng.* 140 (2019) 105884.
15. <http://www.iza-structure.org/index.htm>.
16. A. Meshram, K.K. Sing. Recovery of valuable products from hazardous aluminum dross: a review. *Resour. Conserv. Recy.* 130, (2018), 95-108.

Captions

Table 1. Nomenclature, parameters, textural properties and information of the main phases observed by XRD.

Table 2. ICP-OES results for Al-extracted aqueous solutions.

Table 3. XRF analysis for the wastes. Values expressed in wt.% of oxides, except F and Cl, which are reported in wt.% of elements.

Table 4. Chemical composition of the aluminum saline slags before (original waste, AISSW), and after Al extraction (residual waste, RW).

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Figure 4. XRD pattern (A) and nitrogen adsorption-desorption isotherms (B) for sample 10-44. XRD pattern of NaX included.

Figure 5. SEM images of various magnifications of selected zeolites obtained from AISSW.

Figure 6. XRD patterns for the samples indicated.

Table 1. Nomenclature, parameters, textural properties and information of the main phases observed by XRD.

Series-Sample	Si/Al	pH	Nucleation		Crystallization		S_{BET} (m ² /g)	Vp (cm ³ /g)	dp (nm)	Zeolite (from XRD)
			(h)	(°C)	(h)	(°C)				
1 - 1	1.6	14	3	70	24	100	21	0.037	6.5	NaX + LTA
2 - 6	1.6	14	3	100	24	100	3	0.014	22.1	SOD
3 - 11	1.6	14	3	70	24	70	11	0.011	4.2	NaX + LTA
4 - 16	1.6	12	3	70	24	100	13	0.061	18.1	SOD
1 - 5	1.6	14	3	70	4	100	1	0.004	14.2	SOD
2 - 10	1.6	14	3	100	4	100	3	0.011	15.2	LTA
3 - 15	1.6	14	3	70	4	70	11	0.033	12.3	SOD
4 - 20	1.6	12	3	70	4	100	3	0.024	32.0	SOD
5 - 21	1.6	12	24	50	6	100	5	0.029	21.2	LTA
5 - 22	1.6	12	12	50	4	100	11	0.035	5.5	LTA all peaks
6 - 23	3.2	14	3	70	24	100	63	0.223	14.1	NaX
6 - 28	2.0	14	3	70	24	100	9	0.036	16.1	SOD
6 - 33	4.0	14	3	70	24	100	10	0.018	7.3	
6 - 25	3.2	14	3	70	8	100	6	0.031	19.3	No clear peaks
6 - 35	4.0	14	3	70	8	100	9	0.002	9.2	
6 - 24	3.2	14	3	70	12	100	62	0.243	12.2	NaX
1 - 3	1.6	14	3	70	8	100	4	0.032	30.2	LTA
1 - 2	1.6	14	3	70	12	100	11			LTA
3 - 12	1.6	14	3	70	12	70	263	0.587	8.9	LTA

1 - 4	1.6	14	3	70	6	100	236	0.495	8.4	LTA
2 - 9	1.6	14	3	100	6	100	264	0.604	9.2	LTA
6 - 26	3.2	14	3	70	6	100	11	0.039	14.7	
10 - 47	3.2	12	0	RT	18	100	11	0.065	23.4	No clear peaks
10 - 44	3.2	12	6	RT	18	100	454	0.274	2.4	NaX
10 - 45	3.2	14	6	RT	12	100	34	0.156	18.2	SOD
9 - 43	3.2	12	6	RT	12	100	3	0.014	21.2	SOD
9 - 42	3.2	12	12	RT	6	100	5	0.033	25.4	SOD
7 - 38	3.2	12	4	RT	8	120	11	0.055	19.4	SOD
8 - 40	3.2	12	12	RT	6	120	4	0.011	10.8	SOD
8 - 39	3.2	12	12	RT	4	120	4	0.022	20.5	SOD

Table 2. ICP-OES results for Al-extracted aqueous solutions.

Sample	Al (g/dm³)	Si (g/dm³)	Al (%)	Si (%)
OptimizedNaOH	7.72	0.32	15.4	0.6
ZSML021	6.68	0.35	13.4	0.7
ZSML011	6.84	0.30	13.7	0.6
ZSML041	6.56	0.38	13.1	0.8
ZSML011	6.92	0.33	13.8	0.7
ZSML012	1.93	0.22	3.9	0.4
ZSML013	0.69	0.20	1.4	0.4
ZSML014	0.43	0.21	0.9	0.4
ZSML311	7.49	0.29	15.0	0.6
ZSML312	2.00	0.31	4.0	0.6
ZSML313	0.83	0.25	1.7	0.5
ZSML314	0.35	0.23	0.7	0.5
OptimizedZSML	7.49	0.29	15.0	0.6

Table 3. XRF analysis for the wastes. Values expressed in wt.% of oxides, except F and Cl that are reported in wt.% of elements.

Sample	SiO₂	Al₂O₃	Fe₂O₃	MnO	MgO	CaO	Na₂O
Original waste	5.69	54.41	1.18	0.21	6.20	2.07	0.89
Optimized purified NaOH	4.89	40.39	1.17	0.20	6.05	2.00	1.38
Optimized purified ZSML	4.91	40.98	1.21	0.19	6.79	2.05	1.43

Sample	K₂O	TiO₂	P₂O₅	F	Cl	LOI
Original waste	0.56	0.56	0.07	0.64	0.58	25.23
Optimized purified	0.17	0.56	0.10	0.45	0.39	21.21
Optimized purified ZSML	0.21	0.56	0.08	0.44	0.44	22.23

Table 4. Chemical composition of the aluminum saline slags before (original waste, AISSW), and after Al extraction (residual waste, RW).

Compound	Chemical formula	AISSW (wt.%)	RW NaOH (wt.%)	RW ZSML (wt.%)
Deliverable aluminum	Al + AlN	19.2	0.0	0.0
Corundum	Al ₂ O ₃	21.7	25.1	24.5
Spinel	MgAl ₂ O ₄	21.9	21.4	24.1
Calcium carbonate	CaCO ₃	3.7	3.6	3.9
Silica	SiO ₂	5.7	4.9	4.9
Magnetite	Fe ₂ O ₃	1.2	1.2	1.2
Sylvite	KCl	0.9	0.3	0.3
Titania	TiO ₂	0.6	0.6	0.5
Total crystalline structures		74.9	56.9	59.4
Non crystalline + LOI		25.1	43.1	40.6

Table 5. Textural properties of the wastes.

Sample	BET surface area (m²/g)	V_{pT} (cm³/g)	d_{pBJH} (nm)
AISSW	129	0.197	6.1
NaOH-opti	48	0.170	17.8
NaOH-optipure	66	0.249	20.3
ZSML-opti	83	0.267	12.8
ZSML-optipure	90	0.223	10.0

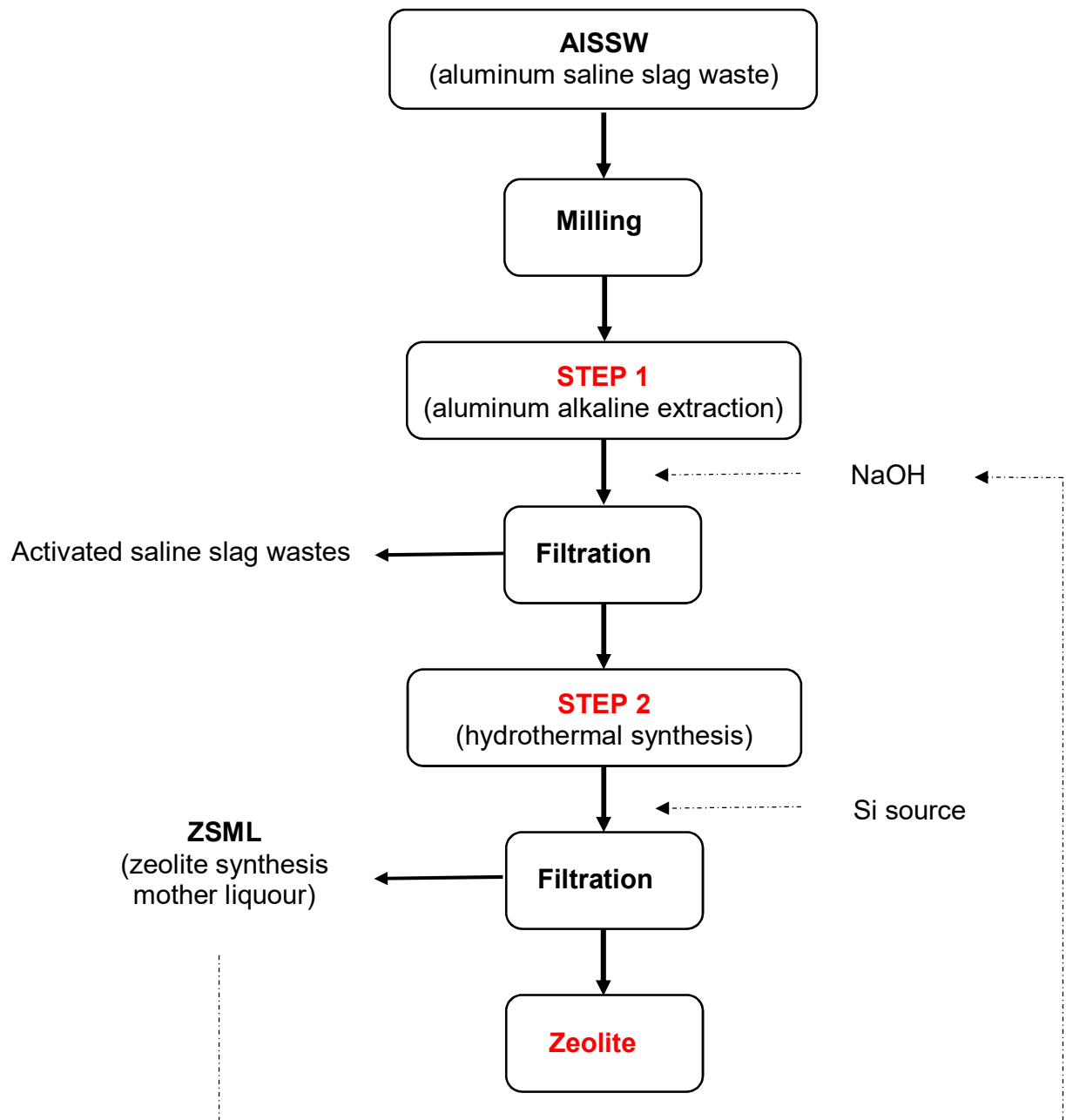


Figure 1. Procedure for synthesizing zeolite from an aluminum saline slag waste (AISSW).

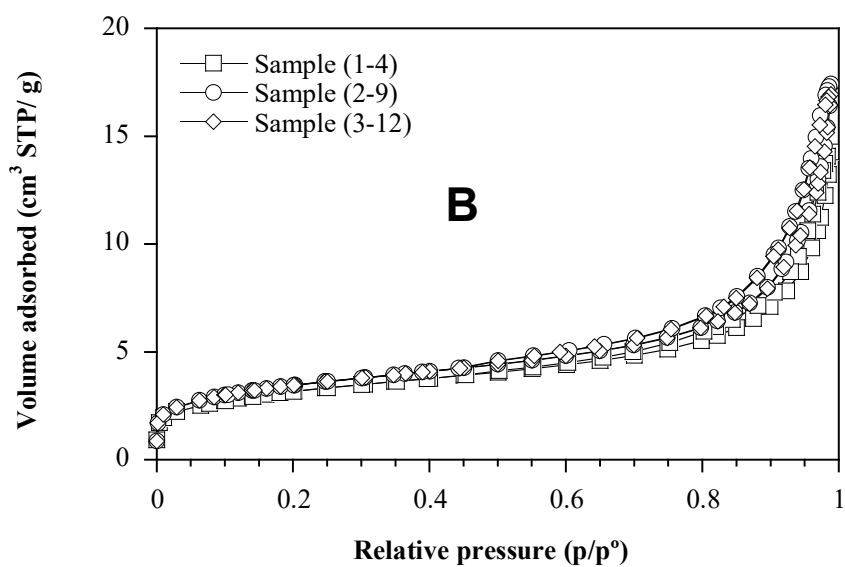
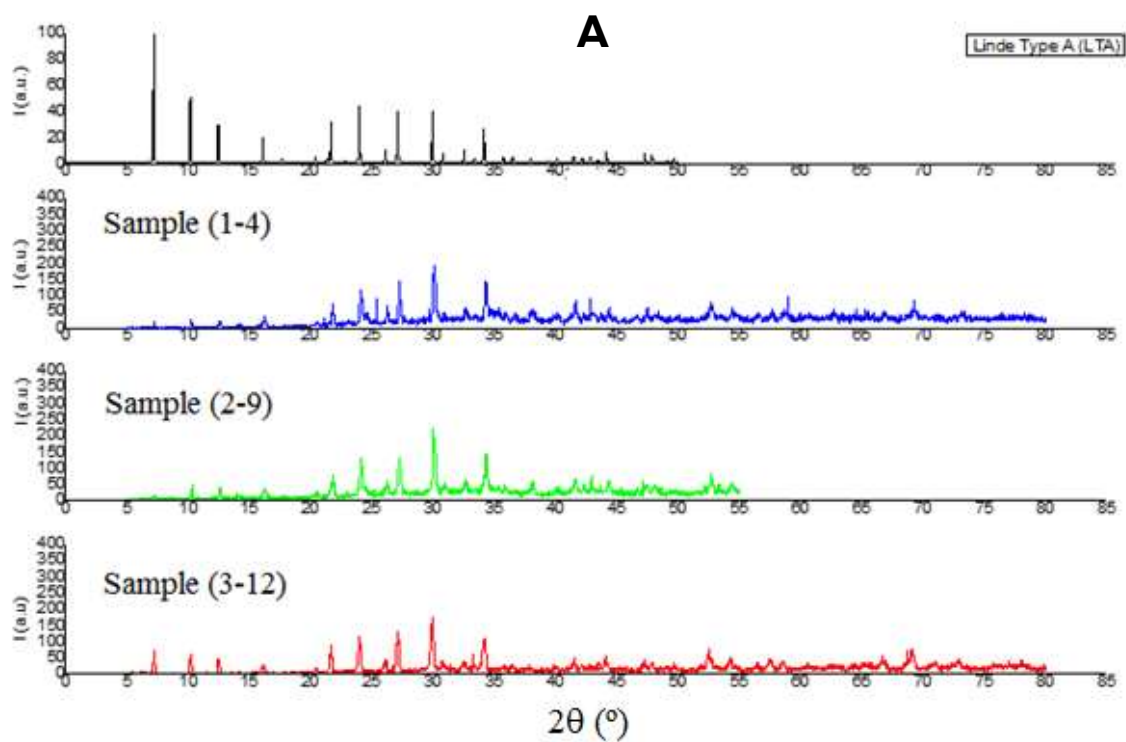


Figure 2. XRD patterns (A) and nitrogen adsorption-desorption isotherms (B) for samples (1-4), (2-9) and (3-12). XRD pattern of LTA included.

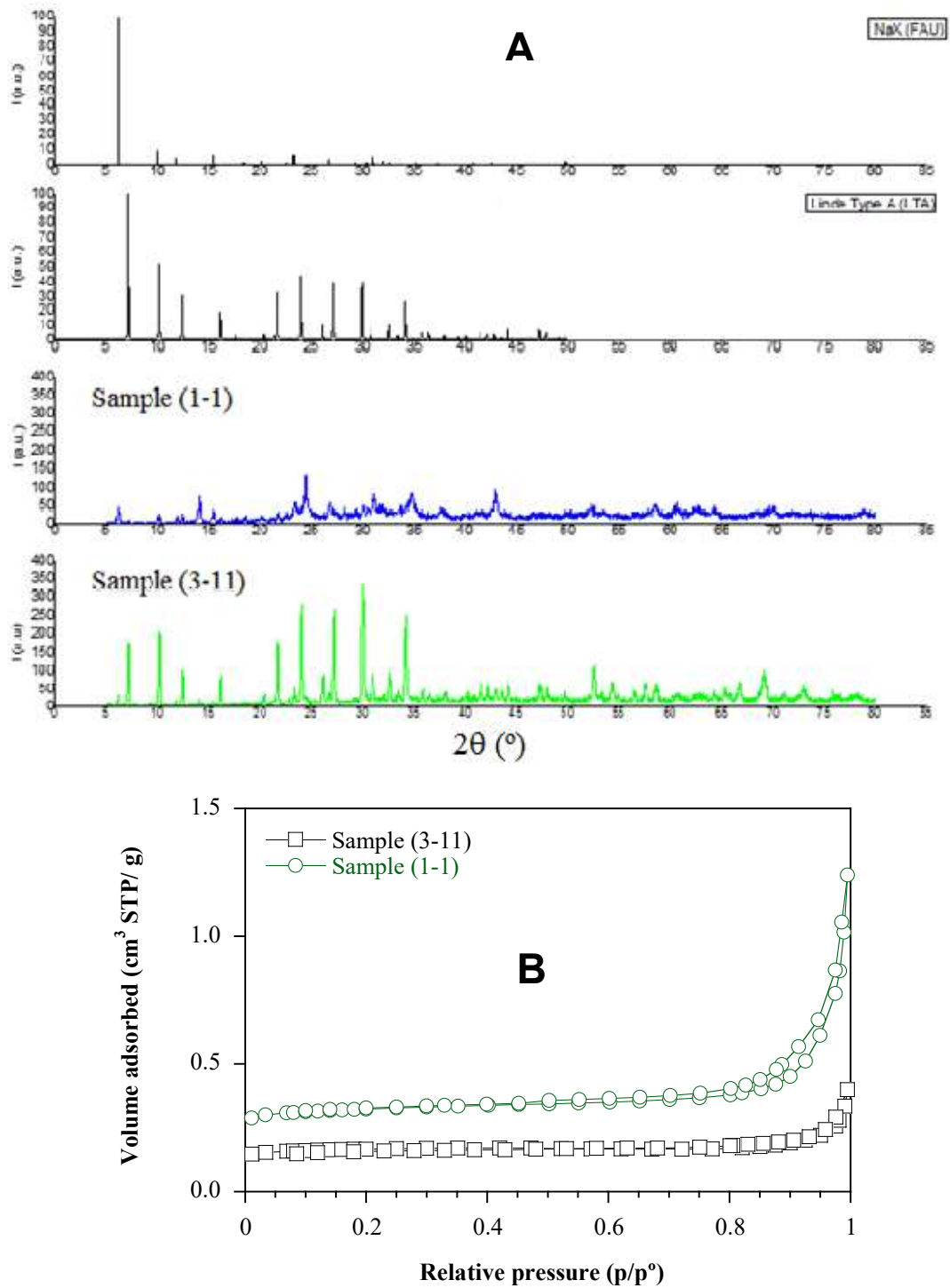


Figure 3. XRD patterns (A) and nitrogen adsorption-desorption isotherms (B) for samples (1-1) and (3-11). XRD patterns of NaX and LTA included.

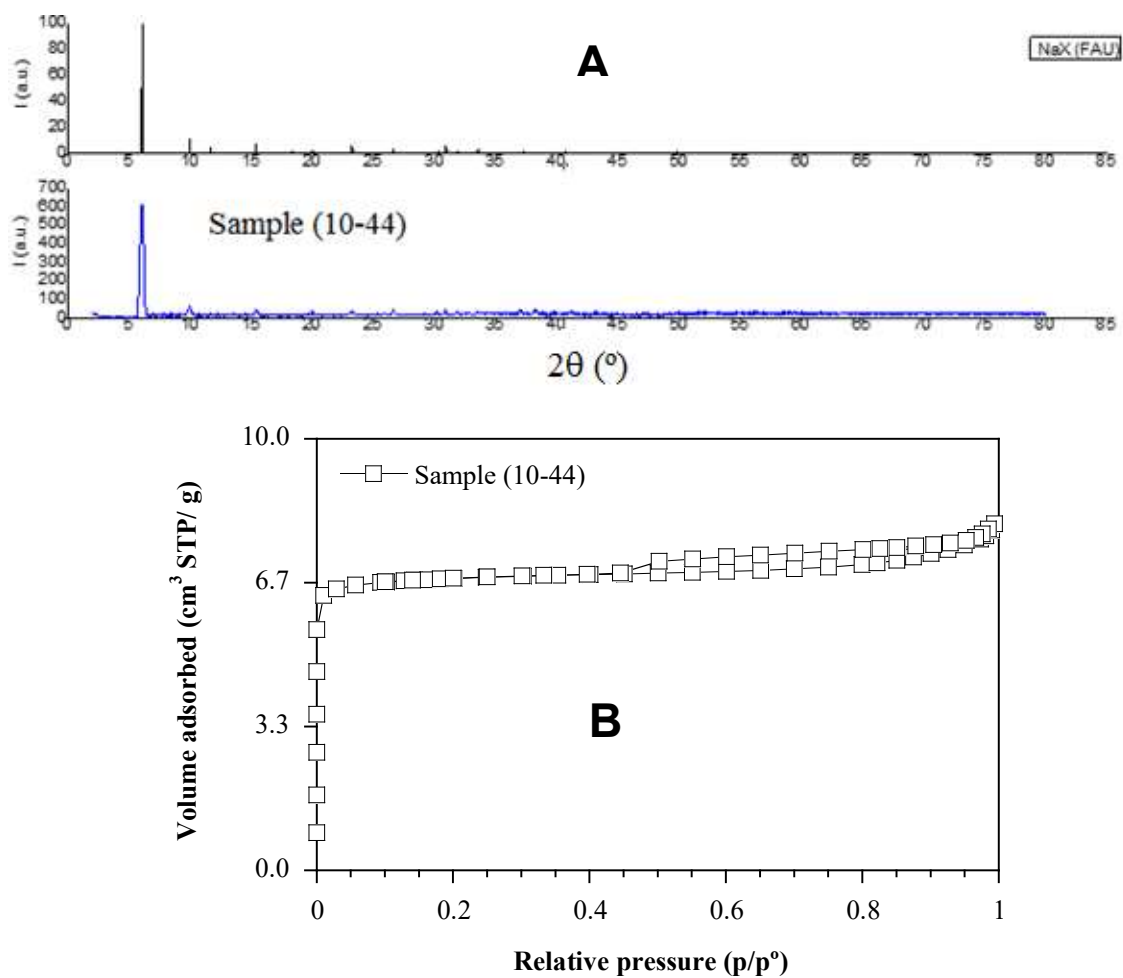


Figure 4. XRD pattern (A) and nitrogen adsorption-desorption isotherms (B) for sample (10-44). XRD pattern of NaX included.

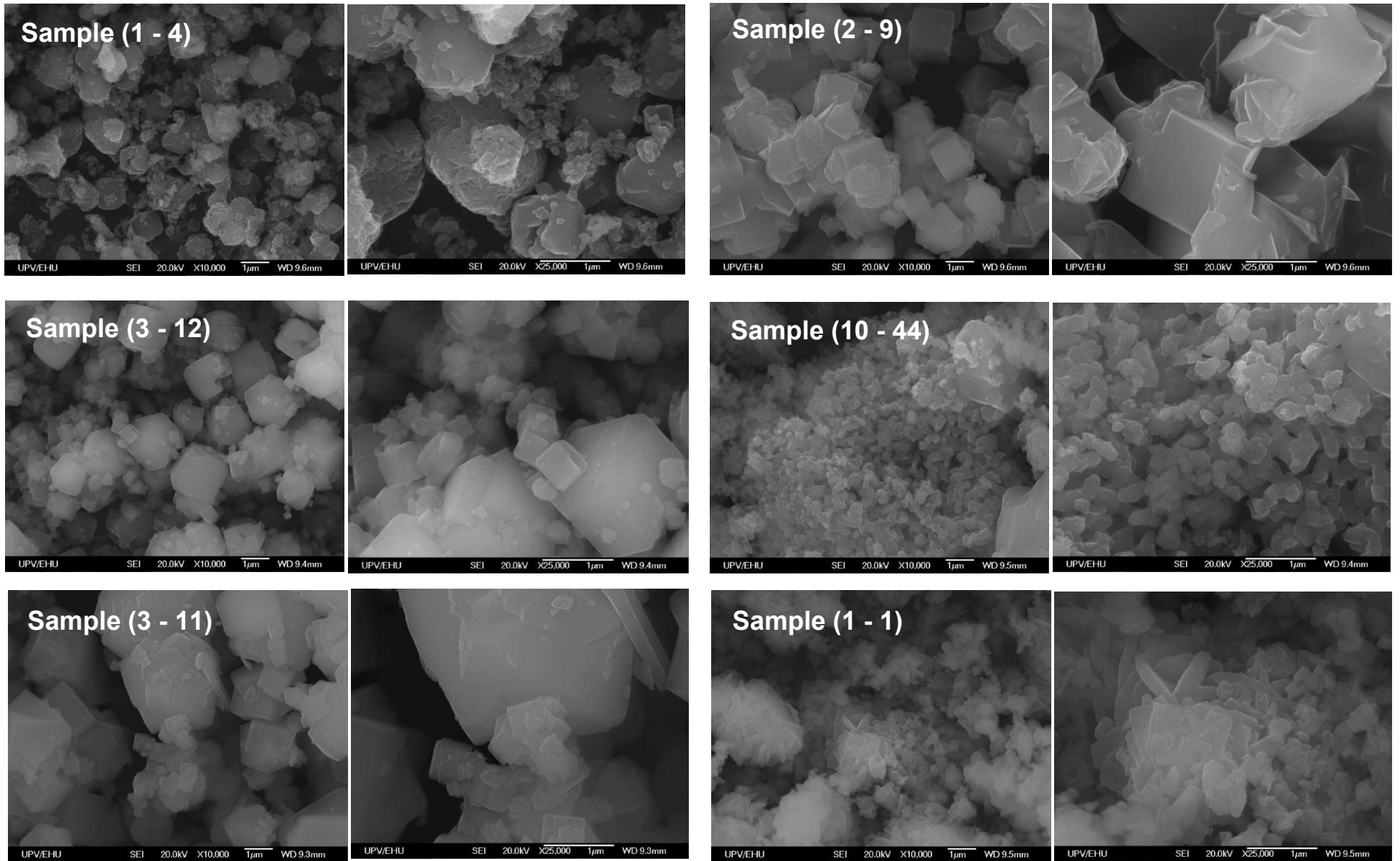


Figure 5. SEM images of various magnifications of selected zeolites obtained from AISSW.

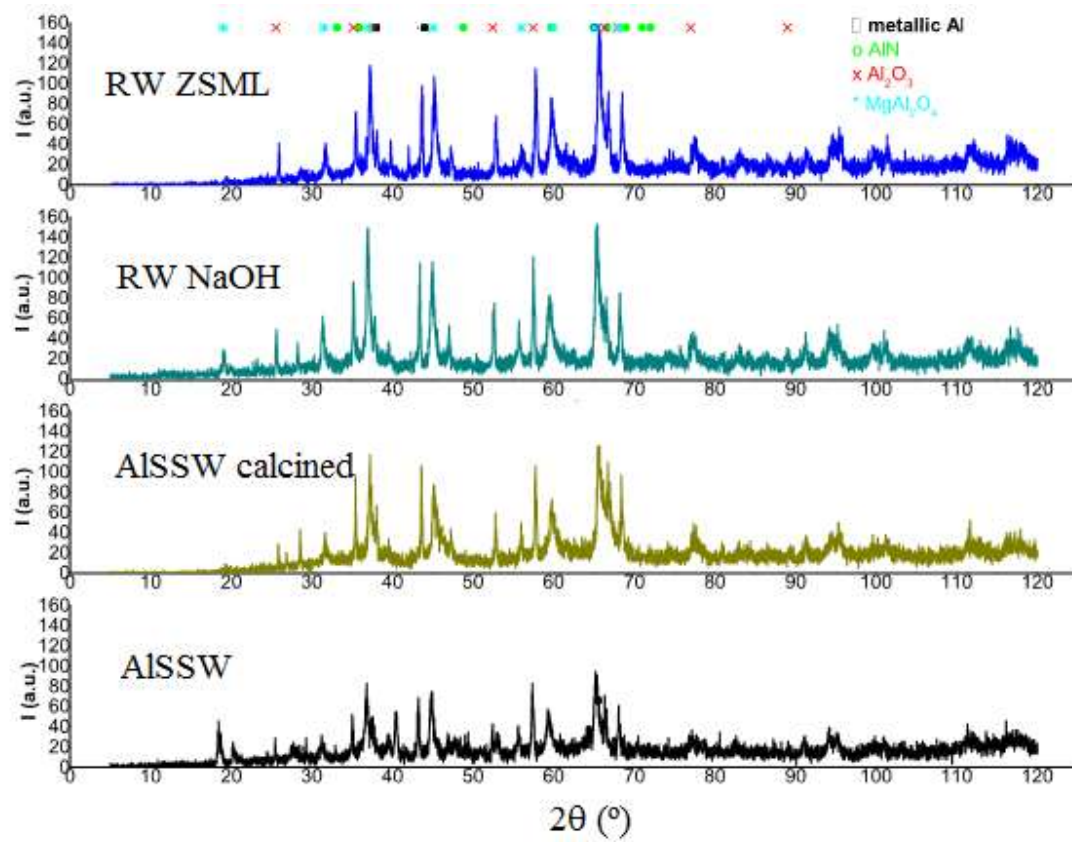


Figure 6. XRD patterns for the samples indicated.