

1 Conference Proceedings Paper

2 Preparation of pollucite and analcime zeolites as a 3 method to valorize aluminum saline slags

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12 **Abstract:** In this work, a valorization procedure is developed for the wastes generated during
13 aluminum recycling, namely, for saline slag. The procedure is divided into two steps: 1) recovery of
14 aluminum from various slag fractions, and b) the use of recovered aluminum in the synthesis of two
15 zeolites, namely, analcime (NaAlSi₂O₆·H₂O) and pollucite (CsAlSi₂O₆·nH₂O). Saline slag was
16 ground, sieved (1 mm), washed and separated into two fractions of different sizes, larger or lower
17 than 0.4 mm. The fraction < 0.4 mm was treated under reflux conditions with NaOH or CsOH
18 solutions of different concentrations. The extraction liquor contained aluminum and alkali metal
19 cations and allowed to obtain the zeolitic materials by hydrothermal synthesis at 200 °C for 24 hours
20 after adding the necessary amount of Si. These solids were fully characterized. The results of the
21 first step showed that a high percentage of Al (~44 wt.%) in the fraction < 0.4 mm, can be recovered.
22 The results of the second step indicated that crystalline analcime and pollucite zeolites can be
23 hydrothermally synthesized from extraction liquors and a source of Si, the zeolites being the only
24 phases detected by powder X-ray diffraction.

25 **Keywords:** Saline slag; aluminum recovery; zeolitic materials, analcime, pollucite.
26

27 1. Introduction

28 Aluminum properties, such as corrosion resistance, low melting point (660 °C) or low density
29 (2.70 g/cm³) [1] make it an ideal material for many applications. This element can be recycled and
30 reused without losing its properties. The recycling process requires less energy than primary
31 aluminum production (Bayer and Hall–Héroult processes [2–4]) but other wastes are generated, the
32 most important is the so-called *Salt Cake* or *Saline Slag*. It is produced when flux salts (mainly NaCl
33 and KCl) are used for melting aluminum. Salt cake is considered a hazardous waste by in the
34 European Union regulations [5]. Raw saline slag contains various aluminum species (metallic Al,
35 Al(OH)₃, different phases of Al₂O₃, etc.) forming aggregates of different sizes and can be managed in
36 different ways [2, 6–10].

37 Analcime (ANA) and Pollucite (POL) are zeolites belonging to the analcime family and their
38 structures are similar [13]. The diameter of channels in pollucite is 2.80 Å [14] while the diameter of
39 Cs⁺ is 3.34 Å [14, 15] and Cs⁺ is immobilized inside the pollucite structure, pollucite being a very
40 interesting material for storing ¹³⁷Cs in a safe way [11–13]. Analcime could be used as an ion
41 exchanger.

42 The objective of this work is to use the salt cake in the synthesis of applicable zeolites. Aluminum
43 from the non-metallic fraction of salt cake should be first recovered under reflux conditions. The
44 resulting liquor will be used to synthesize zeolitic materials under hydrothermal conditions. Metallic
45 aluminum could be separated beforehand and submitted to the recycling process. For this reason,
46 metallic Al will not be used in this work.

47 2. Materials and Methods

48 Saline slag was supplied by IDALSA, Spain. It was ground in a ball mill, using an alumina jar and
49 alumina balls, and sieved with a 1 mm light screen. The fraction smaller than 1 mm was washed with
50 water several times until chloride test was negative, and then dried in an oven at 70 °C at open air
51 overnight. The chloride free salt cake was sieved with a 0.4 mm light screen. The fraction with a size
52 between 1 and 0.4 mm was named *intermediate fraction* and the fraction less than 0.4 mm was named
53 *small fraction*. The recovery of aluminum was evaluated by treating portions of 7.5 g of the *small*
54 *fraction* with 25 mL of aqueous solutions of NaOH or CsOH, with concentrations 1, 2, 3 or 4 M, under
55 reflux conditions, for 2 h, while being magnetically stirred at a speed of 500 rpm. The slurries were
56 separated by filtration, using a Büchner funnel and a kitasato flask, and the liquid made up to a final
57 volume of 50 mL. The extraction liquors were named as follows: Name of the reagent (NaOH or
58 CsOH) – concentration of the reagent (M) – time of extraction (h). For instance, NaOH–3M–2h, when
59 the extraction was carried out with 3M NaOH for 2 h.

60 Both zeolites were synthesized adapting the method from Garney [16], but using the extraction
61 liquor as the source of aluminum. The amount of extracted Al was determined beforehand. The
62 source of Si was SiO₂, its stoichiometric amount was dissolved in the smallest possible volume of a
63 basic solution of the corresponding alkaline hydroxide, at a pH close to 13; this excess of alkali
64 warrants the solubility of Si species in the reaction medium. Then, both solutions were mixed and
65 placed in a stainless-steel reactor lined with Teflon and heated at 200 °C for 24 h. No templates were
66 used. Finally, the solid was recovered by filtration, washed with distilled water until the pH of the
67 filtrate was lower than 10, de-agglomerated by adding 10 mL of 10 % ethanol in water and immersed
68 in an ultrasonic bath for 1 h, and then dried at 100 °C in an oven at open air overnight.

69 The reagents used in this work were CsOH·H₂O (99.5 %, Sigma-Aldrich), SiO₂ (high purity
70 grade, 60 – 100 mesh, Sigma-Aldrich) and NaOH (technical grade, Panreac). All reagents were used
71 as received, without any further purification.

72 The power X-ray diffraction (PXRD) patterns of the solids were recorded in a Siemens D5000
73 instrument using Cu-K α radiation ($\lambda = 1.54050 \text{ \AA}$), at a scanning rate of 2°(2 θ)/min. ICDD database
74 was used to identify the crystalline phases [17]. The X-ray microfluorescence spectroscopy (XRF)
75 analyses were carried out using a Bruker M4 model micro-fluorescence spectrometer model (Nucleus
76 Research Platform, University of Salamanca, Spain). The scanning electron microscopy (SEM)
77 analyses were carried out in a Zeiss EVO HD 25 Scanning Electron Microscope, while the
78 Transmission Electron Microscopy (TEM) analyses were performed using a Tecnai Spirit Twin in 120
79 kV Transmission Electron Microscope, both at the Nucleus Research Platform, University of
80 Salamanca, Spain. The FTIR spectra were recorded in a Perkin-Elmer Spectrum Two instrument with
81 a nominal resolution of 4 cm⁻¹ from 4000 to 400 cm⁻¹, using KBr (Merck, grade IR spectroscopy)
82 pressed pellets and averaging 20 scans to improve the signal-to-noise ratio. Element chemical
83 analyses for different elements were carried out by ICP–OES in a Yobin Ivon Ultima II apparatus
84 (Nucleus Research Platform, University of Salamanca, Spain). Thermal analyses were performed on
85 a SDT Q600 apparatus (TA instruments) under an oxygen (Air Liquide, 99.999%) flow of 50 mL/min
86 and a temperature heating rate of 2°C/min from room temperature to 900 °C.

87 3. Results and Discussion

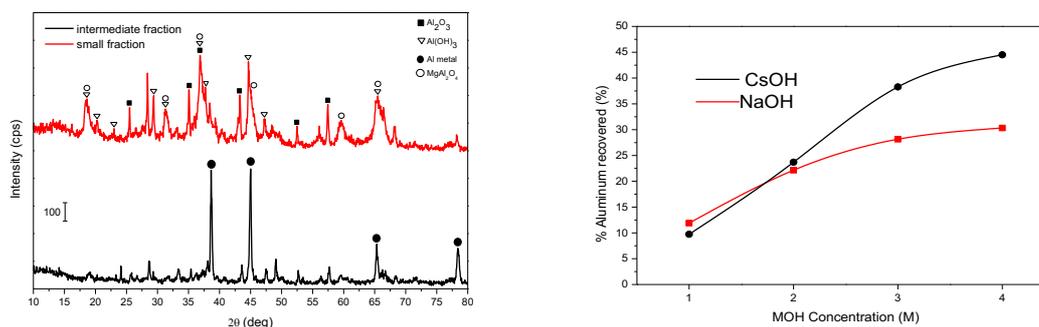
88 Raw salt cake, intermediate and small fractions show a complex chemical composition (Table 1).
89 In addition, other elements such as V, Cr, Mn, Ni or Pb are present in the range of ppm. The total Al
90 content (expressed as oxide) is high, although this is not conclusive for its possible recovery. After
91 washing treatment, sodium was not detected and the amounts of chlorine and potassium drastically

92 decreased. Aluminum, expressed as Al_2O_3 , represented now 70 or 77 % (intermediate or small
93 fraction, respectively) of the sample mass and may be present in many different phases [3, 4].

94 **Table 1.** Chemical compositions of the raw salt cake and the fractions with particle size smaller than
95 1 mm (expressed as oxides, except for chlorine). Elements with oxide content ≤ 0.2 % are not given.

Component	Raw salt cake	Intermediate fraction	Small fraction
Al_2O_3	21.30	70.00	76.80
Na_2O	18.90	Not detected	Not detected
K_2O	18.90	1.10	0.45
MgO	1.30	4.50	10.30
SiO_2	2.20	15.00	5.30
CaO	0.72	4.10	2.12
Fe_2O_3	0.70	1.40	2.00
CuO	0.34	1.10	0.78
SO_3	0.24	0.29	0.50
Cl	33.90	0.90	0.21

96 PXRD (Figure 1, left) showed that in the case of the intermediate fraction, the most intense peaks
97 corresponded to metallic aluminum, while in the small fraction the most intense peaks corresponded
98 to corundum, gibbsite, bohemite, bayerite and spinel. Thus, the small fraction was chosen for the
99 preparation of zeolitic materials because the experimental conditions applied allowed aluminum
100 dissolution as $[\text{Al}(\text{OH})_4]^-$ anions. Metallic Al from intermediate fraction could be re-incorporated into
101 the aluminum recycling process.



102 **Figure 1.** Powder X-ray diffraction patterns of Intermediate and Small fractions (left) and percentage
103 of recovered aluminum using different alkaline hydroxide concentrations (right).

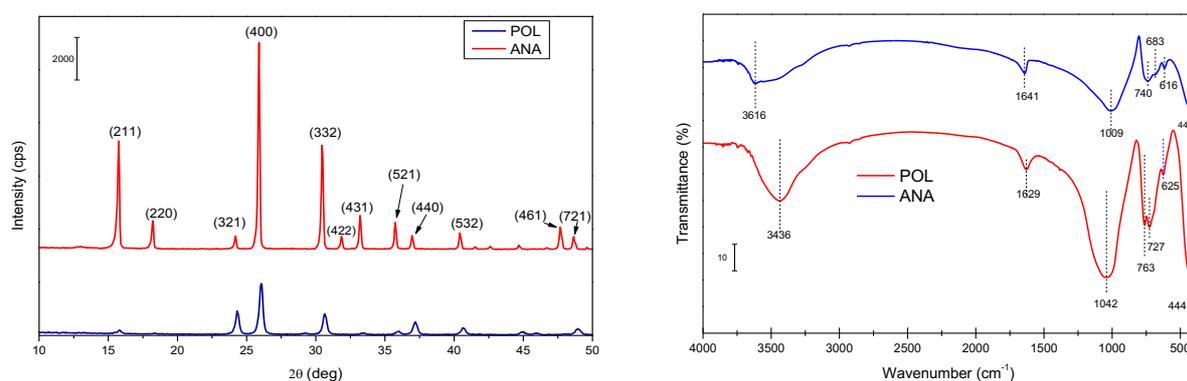
104 Figure 1 (right) gives information about the percentage of recovered aluminum when using
105 different NaOH and CsOH concentrations. A portion of 7.5 g of small fraction was treated with 25 mL
106 of 1,2,3 or 4 M MOH concentrations. The reflux time and the small fraction/dissolution volume ratio
107 were kept constant (reflux time 2 hours and small fraction/dissolution volume was 0.3). Under these
108 experimental conditions, an increase in the MOH concentration produced an increase in the
109 percentage of aluminum recovered. For MOH concentrations of 1 M and 2 M there were not
110 significant differences in the percentage of aluminum recovered, close to 10 % and 24 % respectively,
111 but for larger MOH concentrations there were differences in the of aluminum recovered. The
112 extraction liquors NaOH-1M-2h and CsOH-1M-2h were chosen for the synthesis of analcime and
113 pollucite, respectively. The final volume of both liquors was 50 mL (see their composition in Table 2).

114 **Table 2.** Chemical composition (mg/L) of the extraction liquors used in the preparation of zeolitic
115 materials.

Sample	Al	Si	Na	K	Cs
CsOH-1M-2h	5934	114	545	355	64081
NaOH-1M-2h	7159	129	10230	448	-

116 The PXRD patterns of both synthesized solids (Figure 2, left) show that ANA (ICDD 41–1478)
 117 and POL (ICDD 25–194) were prepared from the extraction liquors. Jing et al. [13] concluded that the
 118 Cs/Al ratio in the starting mixture had no significant effect on the crystallinity. This fact allows to
 119 explain that the Cs/Al ratio in the extraction liquor is not a limiting parameter for the crystallinity of
 120 the final solids. Jing et al. [13] also found that crystalline pollucite was not obtained with a Si/Al molar
 121 ratio lower than 1.5 at temperatures lower than 200 °C. Thus, Si/Al ratio of 2 and a curing temperature
 122 of 200 °C were selected for the syntheses. The Na/Al ratio has no significant effect influence on the
 123 crystallinity of the zeolitic material formed.

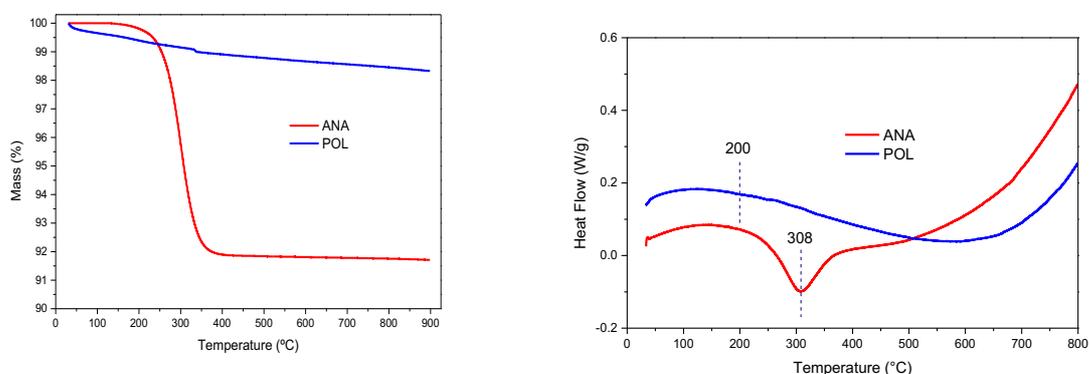
124 The PXRD patters of analcime and pollucite zeolites are very similar to each other. Both belong
 125 to the analcime family and have very similar structures; in fact, pollucite–analcime solid solutions
 126 with different Cs/Na ratios exist in Nature [13]. The ionic diameter of Cs⁺ (3.34 Å) [14, 15] is larger
 127 than that of Na⁺ (2.04 Å) [15]; and Cs⁺ occupies in POL sites which are occupied by H₂O molecules in
 128 ANA.



129 **Figure 2.** Powder X-ray diffraction patterns (left) and FTIR spectra (right) of ANA and POL.

130 The FTIR spectra of both zeolites (Fig. 2, right) show few differences. Bands at 1009 and 1042 cm⁻¹
 131 are in both cases assigned to the antisymmetric T–O stretching vibrations (T = Si or Al), while bands
 132 at 763 and 727 cm⁻¹ for POL and 740 cm⁻¹ for ANA are due to the symmetric T–O stretching vibrations.
 133 The bands at 625 cm⁻¹ and 616 cm⁻¹ corresponded to the bending vibration of O–T–O units. Bands due
 134 to stretching and bending vibrations of water are also recorded.

135 The main difference between the thermal curves of both zeolites (Figure 3) is their water content.
 136 In the case of POL, the water content is around 1.5 % while for ANA it is 8 %. This could be explained
 137 by the difference in ionic sizes between Cs⁺ and Na⁺, which implies that Cs⁺ occupies positions that
 138 in ANA are occupied by water. The DSC curves show dehydration of POL happens around 200 °C
 139 [13] and for ANA around 308 °C. This fact shows that water in POL is bonded more weakly than in
 140 ANA, being removed at a lower temperature.

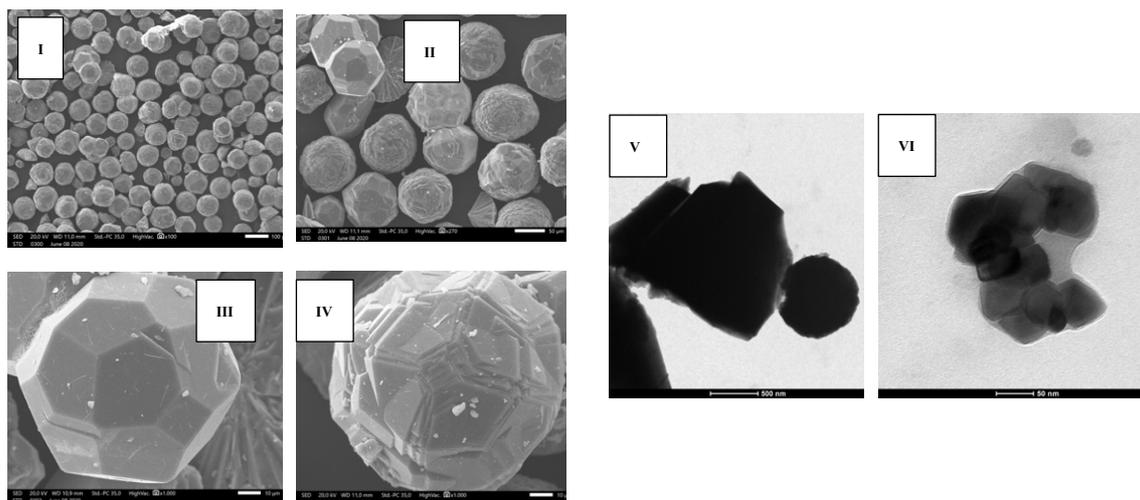


141 **Figure 3.** TG (left) and DSC (right) curves of ANA and POL zeolites.

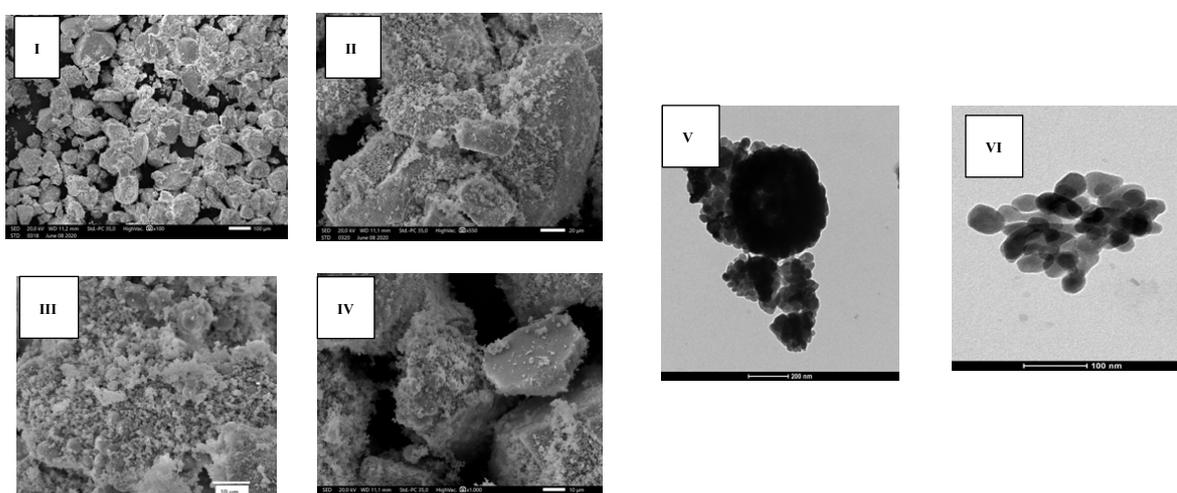
142 SEM micrographs of ANA (Figure 4 left) show the presence of homogenous and independent
 143 roughly spherical particles of diameter lower than 100 μm, while its TEM micrographs (Figure 4 right)

144 show two types of particles, one of them spherical and the other with an irregular morphology; in
 145 both cases, the particles do not seem to be hollow. SEM micrographs of POL (Figure 5 left)
 146 irregular particles with size lower than 100 μm , and spherical particle with different sizes (Figure 5-
 147 III). Its TEM micrographs show agglomerates of rounded particles with different diameters around
 148 30–50 nm.

149 Table 3 shows the mass percentages of Na, Cs, Si and Al in the final solids. In both cases, the
 150 Na/Al or Cs/Al molar ratios were roughly close to the expected value (1.0) for analcime or pollucite
 151 zeolites. Particularly, in the case of pollucite, there is a small amount of sodium (~1%), but the
 152 (Cs+Na)/Al molar ratio is close to 1. However, the Si/Al ratio was almost twice the value expected for
 153 these zeolites (2.0).
 154



155 **Figure 4.** SEM micrographs (left) and TEM micrographs (right) of ANA.
 156



157 **Figure 5.** SEM micrographs (left) and TEM micrographs (right) of POL.
 158

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

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

161 4. Conclusions

162 Analcime and pollucite zeolites can be synthesized from aluminum saline slag. First, it is
163 necessary to recover aluminum from the slag under reflux conditions with different alkaline
164 hydroxides. Extraction performance is improved when increasing the hydroxide concentration, being
165 the best extraction at high concentration of CsOH, under reflux for 2 h and a constant (small
166 fraction/dissolution volume) ratio. The liquor from the extraction is used as a source for Al in the
167 preparation of the zeolitic materials. Both zeolites are synthesized by the hydrothermal method at
168 200 °C for 24 h. Crystallinity and water content is higher for analcime than for pollucite. In both cases,
169 morphological analyses show that spherical particles are formed. The Si/Al ratio is high in both cases,
170 so substitution of Si⁴⁺ by Al³⁺ is small. Therefore, to use analcime as ion exchanger or pollucite for
171 cesium storage, this molar ratio should be smaller, to increase the performance of these materials in
172 these applications.

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174 Formal analysis, A.J., A. Misol, A. Morato, R.T. and S.A.K.; Investigation, A.J., A. Misol, A. Morato, R.T. and
175 S.A.K.; Resources, M.A.V., V.R., R.T., S.A.K. and A.G.; Writing—original draft preparation, A.J., A. Misol and A.
176 Morato; Writing—review and editing, M.A.V., V.R., R.T., S.A.K. and A.G.; Project administration, M.A.V. and
177 A.G.; Funding acquisition, M.A.V., V.R., R.T., S.A.K. and A.G. All authors have read and agreed to the published
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