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

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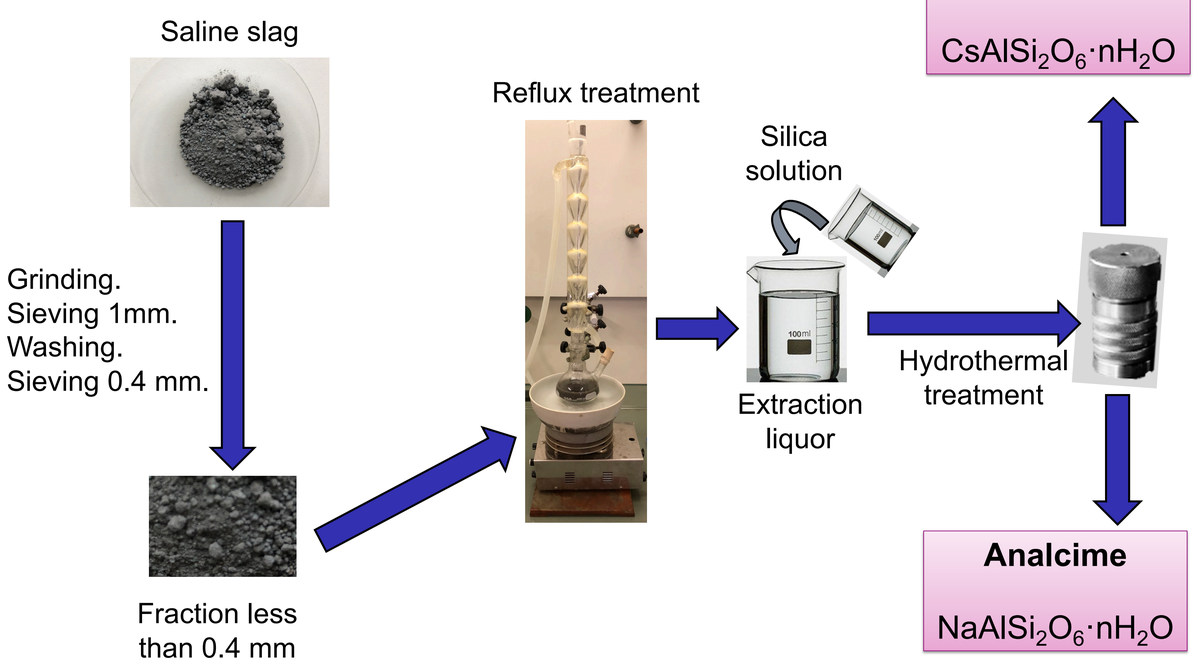
Introduction

Aluminum properties, such as corrosion resistance, low melting point (660 °C) or low density (2.70 g/cm^3) make it an ideal material for many applications. This element can be recycled and reused without losing its properties. Recycling process requires less energy than primary aluminum production (combination of the Bayer and Hall–Héroult processes but other wastes are also generated, the most important is the so-called *Salt Cake* or *Saline Slag*. It is produced when the flux salts (mainly NaCl and KCl) are used for melting aluminum. Salt cake is considered a hazardous waste in the European Union.

Analcime and Pollucite belong to zeolites from the analcime family and their structure are similar. The diameter of channels in pollucite is 2.80 Å while the diameter of Cs is 3.34 Å and Cs^+ is immobilized inside the pollucite structure. For this reason, pollucite is one of the most interesting materials for storing ^{137}Cs for a long period of time in a safe way. Analcime could be used as ion exchanger.

The objective of this work is to use the salt cake in the synthesis of applicable zeolites. Aluminum from the non-metallic fraction of salt cake should be recovered under reflux conditions. The resulting liquor will be used to synthesized zeolitic materials under hydrothermal conditions.

Experimental



Results

Chemical compositions of the raw salt cake and the fractions with particle size smaller tan 1 mm

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
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	18.90	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

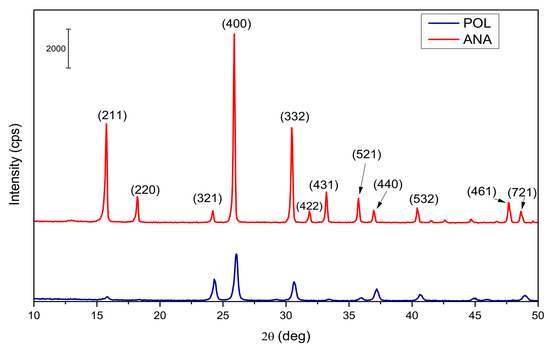
Element					
Sample	Al (mg/L)	Si (mg/L)	Na (mg/L)	K (mg/L)	Cs (mg/L)
CsOH-1M-2h	5934	114	545	355	64081
NaOH-1M-2h	7159	129	10230	448	-

Chemical compisitions of extractions liquors used in preparation of zeolitic materials

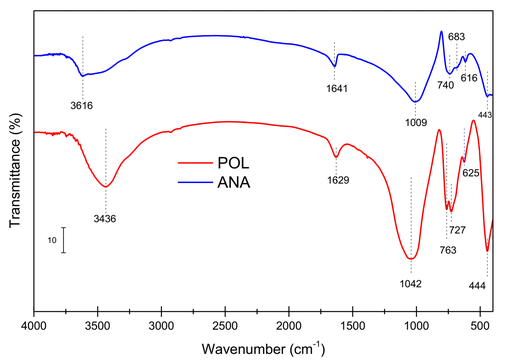
X-ray patterns of Intermediate and small fractions

Percentage of recovered aluminum for different alkaline hydroxide concentrations

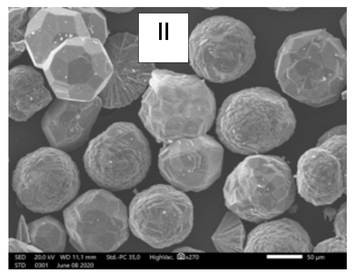
X-ray patterns of both solid prepared



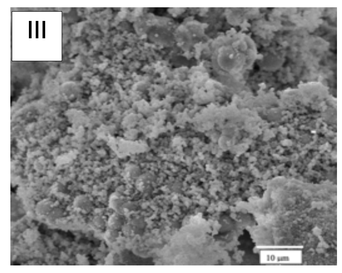
FT – IR spectra of ANA and POL



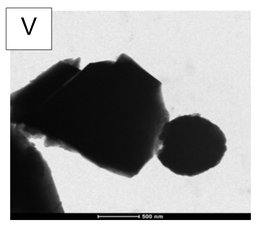
SEM micrograph of ANA



SEM micrograph of POL



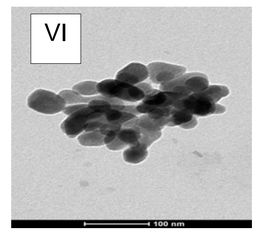
TEM micrograph of ANA



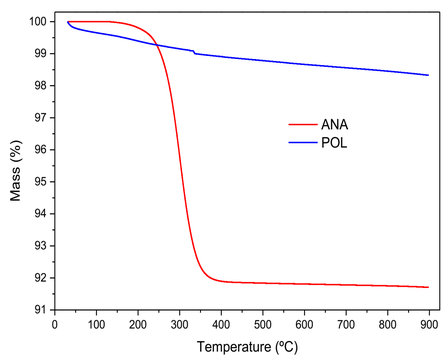
Chemical composition of the final solids (wt%)

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

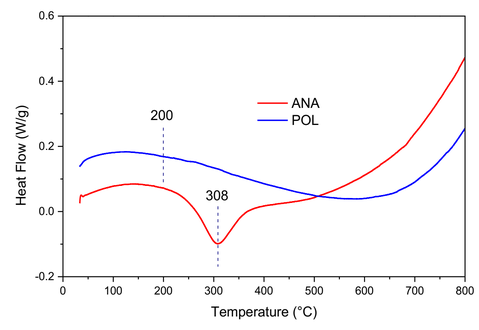
SEM micrograph of POL



TG curves of ANA and POL



DSC curves of ANA and POL



Conclusions

- **Analcime and pollucite zeolities can be synthesized from aluminum saline slag. First, it is necessary to recover aluminum from the slag under reflux conditions with different alkaline hydroxide.**
- **Extraction performance is improved when increasing the alkaline hydroxide concentration.**
- **The best extraction is obtained at high concentration of CsOH, keeping time reflux in 2 h and ratio small fraction/dissolution volume constant.**
- **The liquor from the extraction is used as a source of Al in the preparation of zeolites.**
- **Hydrothermal Synthesis is carried out at 200ºC for 24 hours.**
- **Crystallinity and water content is higher for analcime than pollucite.**
- **Si/Al ratio is high in both cases, so substitution of Si^{4+} by Al^{3+} is small. Therefore, to use analcime as ion exchanger or pollucite for cesium storage, this molar ratio should be smaller, to increase the performance of these materials in these applications.**

Acknowledgement

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MINISTERIO DE ECONOMÍA Y COMPETITIVIDAD

F.E.D.E.R.