

CONDITIONING OF ZEOLITE STONE FROM ZALAU. PHYSICAL-CHEMICAL STUDIES

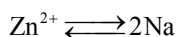
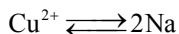
S. Neagoe*, O. Pântea*, Eva Trâmbițașu*, Daniela Popovici*, D. Bomboș**,
Fănica Bacalum***, Dorina Matei*, C. Neagoe****, T. Jugănaru* and M. Hotinceanu*

abstract: Paper presents investigation of the zeolite stone from Marsid – Salaj county, as well as its conditioning in view to retain ammonium ion from waste waters. S 0.04 mm and S 0.09 mm types of zeolite have been chemically analysed, and then analysed by X-ray diffraction method. Two methods have been used for acid activation: ammonium nitrate and ammonium chloride in acid medium, and 1N solution of hydrochloric acid. In order to establish the exchange capacity of the zeolite the overall acidity has been determined.

1. Introduction

Indigenous clinoptilolyte-rich zeolite stone which has a good selectivity for ammonium ion, has concerned others researchers too [1,2]. Chemically activated and inserted into the ion-exchange chromatographic columns it has been used to study its capacity to retain ammonium ion [3].

Senyavin et all [4] studied the possibility of copper recovery from sea waters, and R. Pode [5] studied the following ion exchange equilibriums:



on indigenous clinoptilolytic zeolite.

The zeolite content in SiO₂, Al₂O₃, CaO, MgO, Fe₂O₃, K₂O, and Na₂O has been determined by both classical and modern methods [6,7].

The paper presents the results and chemical and physico-chemical analysis of the zeolite stone, as well as the conditioning (activation) of the zeolite in the acid form.

* "Petrol-Gaze" University of Ploiesti, 39 Bucuresti Blvd., 2000, Romania

** "Politehnica" University of Bucharest, Romania

*** ICECHIM Bucharest, Romania

**** "I.G. Murgulescu" Institute of Physical Chemistry, Bucharest, Romania

2. Experimental part

At first, the two samples of zeolite have been analysed to determine their chemical compositions.

Desaggregation of the samples was made by treating them with a mixture solution of sodium carbonate and potassium carbonate, and then by hydrochloric acid solution, when SiO_2 precipitates. The gravimetric method was used to determine the SiO_2 content of the samples.

The Al, Ca, and Mg content has been determined by complexometry; also Fe and Ti content has been determined by photolorimetry, and K and Na content by inductive coupled plasma atomic emission spectroscopy (ICP-AES), using a Varian-type spectrophotometer.

Granulated zeolite has been characterised by X-ray diffraction, using a DRON 2-type diffractometer.

Thermal analysis of the two samples of zeolite has been performed on a derivatograph model TGA V5.1A DuPont 2000, and the determination of the specific surface has been done by Bett method.

The conditioning of the absorbent has been performed on a discontinuous assemble consisting of an autoclave with a detachable lid, and provided with a thermometer, a mixing device with variable spinning velocity, and a heating device.

All the reagents used in analysis were p.a. grade.

3. Results and Discussion

Table 1 presents the chemical composition of zeolite samples S 0.04 mm and S 0.09 mm, used to retain the ammonia for waste waters.

Table 1. The chemical composition of the two samples of zeolite

Marsid Zeolite	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	$\text{SiO}_2/\text{Al}_2\text{O}_3$	P.C
Granularity 0.04 mm	66.32	12.42	0.09	3.39	0.43	2.91	0.42	0.05	5.80	12.50
	67.30	12.05	0.12	3.88	0.53	3.75	0.35	0.05	5.60	
Granularity 0.09 mm	67.52	13.30	0.75	3.66	0.72	3.93	0.98	0.08	5.10	11.95
	67.90	12.55	0.52	2.89	0.95	3.25	1.20	0.07	5.40	

The data show a very similar composition of the two samples can be observed.

The X-ray analysis is based on the *Bragg-Brentano coupled $\Theta - 2*\Theta$* diffraction method on plane pulverulent samples, and the equipment used was a DRON 2.0 diffractometer having a characteristic radiation of $\text{CuK}_\alpha 1\&2$. In order to eliminate the CuK_β component of the radiation, a graphite monocromator has been placed into the diffracted beam.

The experimental data have been digitally acquired, using the *step by step scanning* method, within the angular range of $2*\theta$: 3 ÷ 70 degree. Qualitative phase analysis has been performed according to the Hanawalt standard method (A.S.T.M.).

Table 2 presents the composition of the 0.04 mm granulated sample, determined by X-ray diffraction.

Table 2. Composition of the 0.04 granulated zeolite, established by X-ray diffraction

No.	Phase	estimative vol.%
1	(Na,K) ₄ Ca(Si ₃₀ Al ₆)O ₇₂ *24H ₂ O - Clinoptilolite	~ 65
2	Na(Si ₃ Al)O ₈ - Albite	10 ÷ 15
3	(K,H ₃ O)Al ₂ Si ₃ AlO ₁₀ (OH) ₂ - Hydromuscovite	10 ÷ 15
4	SiO ₂ - α-Quartz	~ 5
5	CaCO ₃ - Calcite	< 5
6	Mg ₆ Fe ₂ CO ₃ (OH) ₁₆ *4H ₂ O - Pyroaurite	possible < 5
7	SiO ₂ -based material	

The resulted diffractogram for the S 0.04 mm zeolite sample is presented in Table 3.

Table 3. The recorded diffractogram

Peak 2*θ (degree)	d (Å)	Int. (%)	Phase
8.85	9.992	16	Hydromuscovite
9.85	8.979	49	Clinoptilolite
11.20	7.900	23	Clinoptilolite
			Pyroaurite
13.05	6.784	9	Clinoptilolite
			Clinoptilolite
14.90	5.945	10	Clinoptilolite
			Albite
15.85	5.591	1	Clinoptilolite
			Albite
16.95	5.231	9	Clinoptilolite
17.35	5.111	19	Clinoptilolite
			Hydromuscovite
19.10	4.646	14	Clinoptilolite
			Hydromuscovite
			Albite
20.45	4.343	6	Clinoptilolite

Peak 2θ (degree)	d (Å)	Int. (%)	Phase
20.95	4.240	4	α -Quartz
21.85	4.068	8	Albite
22.50	3.951	100	Clinoptilolite Hydromuscovite
22.80	3.900	26	Clinoptilolite Hydromuscovite Pyroaurite Albite
23.15	3.842	8	Clinoptilolite Calcite
24.00	3.708	8	Clinoptilolite Hydromuscovite
25.10	3.548	10	Clinoptilolite
26.10	3.414	24	Clinoptilolite Hydromuscovite
26.30	3.389	4	Clinoptilolite Hydromuscovite Albite
26.70	3.339	20	α -Quartz Clinoptilolite Hydromuscovite Albite
26.90	3.314	11	α -Quartz Clinoptilolite Clinoptilolite Hydromuscovite
27.70	3.220	2	Hydromuscovite Albite
28.15	3.170	47	Clinoptilolite Clinoptilolite Hydromuscovite Albite
28.60	3.121	15	Clinoptilolite Albite
29.10	3.069	13	Clinoptilolite
29.45	3.033	16	Albite Calcite
30.05	2.974	43	Clinoptilolite Hydromuscovite Albite

Peak 2θ (degree)	d (Å)	Int. (%)	Phase
30.10	2.969	52	Clinoptilolite Hydromuscovite Albite
32.00	2.797	21	Clinoptilolite Hydromuscovite
32.85	2.726	18	Clinoptilolite Hydromuscovite
33.40	2.683	1	Clinoptilolite Pyroaurite
35.15	2.553	7	Hydromuscovite Pyroaurite
35.55	2.525	8	Clinoptilolite Hydromuscovite Hydromuscovite Albite
36.10	2.488	7	Clinoptilolite Albite Calcite
36.80	2.442	8	α -Quartz Clinoptilolite Hydromuscovite Albite
37.05	2.426	16	Clinoptilolite
38.15	2.359	2	Clinoptilolite Albite
43.30	2.089	2	Clinoptilolite Albite Calcite
44.10	2.053	2	Clinoptilolite
44.95	2.017	4	Clinoptilolite Hydromuscovite
46.30	1.961	4	Clinoptilolite
46.90	1.937	3	Albite Calcite
50.10	1.821	3	α -Quartz Albite
51.60	1.771	3	Albite
52.10	1.755	3	Hydromuscovite
54.05	1.697	4	Hydromuscovite
55.55	1.654	0.5	α -Quartz

Peak 2* θ (degree)	d (Å)	Int. (%)	Phase
59.05	1.564	0.7	Pyroaurite
60.00	1.542	0.7	α -Quartz Hydromuscovite
60.15	1.538	0.6	α -Quartz
65.00	1.435	1	Calcite
67.90	1.380	0.5	α -Quartz
69.55	1.352	0.9	Pyroaurite Calcite

The diffractograms of six samples of activated zeolite (in acid form), before and after ammonia treatment, have been recorded. The comparison between them and standard ASTM-PDF diffractograms has been performed.

Thus, the 0.09 mm zeolite sample contains three crystalline phases: 1) clinoptilolyte with monoclinic structure ($a=17.63$ Å; $b=17.95$ Å; $c=7.399$ Å; $\beta=117^{\circ}3'$), according to ASTM-PDF 25-1149; 2) criophylite with monoclinic structure ($a=5.25$ Å; $b=9.18$ Å; $c=10.02$ Å; $\beta=100^{\circ}10'$), according to ASTM-PDF 14-565; 3) SiO₂ – quartz with hexagonal structure ($a = 4.913$ Å; $c = 5.405$ Å), according to ASTM-PDF 33-1161. Concentration of each phase in mixture is: clinoptilolyte 60%, criophylite 35%, and quartz 5%.

The zeolite sample S 0.09 mm, converted into acid form by nitric acid / ammonium nitrate method, contains the same crystalline phases as the initial one, but the peak at 5.64° suffers a displacement to approx. 7.00° (2θ), which corresponds to the substitution of larger metallic ions with smaller protons, H⁺.

The zeolite sample S 0.09 mm, activated by hydrochloric acid, contains the same crystalline phases as the initial one, the diffractogram indicating a reduction of the crystal size, especially for clinoptilolyte.

The zeolite sample S 0.04 mm, contains the same crystalline phases as the sample S 0.09 mm, the phase concentrations being: clinoptilolyte 75%, criophylite 20%, and quartz 5%.

The thermogravimetric analysis of the two samples of zeolite has been done by classical method, with the same heating rate of 20°C/min for inactivated zeolite as well as for the activated one. The thermograms show a continuous decrease in weight between 50°C and 500°C, the weight loss being 13.5%. This is more like an indication of the presence of interstitial water molecules and OH⁻ ions in the crystalline structure rather than the "crystallisation water".

Specific surface and pore distribution of the two samples of zeolite stone, S 0.04 mm and S 0.09 mm, has been determined by the Bett method, and Table 4 presents the results.

The ion exchange capacity of the zeolite samples is:

- sample S 0.04 mm: 0.75 mequiv./g;
- sample S 0.09 mm: 0.65 mequiv./g.

Table 4. Specific surface and pore distribution of the samples S 0.04 mm and S 0.09 mm

Sample S 0.04 mm		Sample S 0.09 mm	
Specific surface, m ² /g	40.954	Specific surface, m ² /g	43.411
Pore volume, m ³ /g	0.0546	Pore volume, m ³ /g	0.0612
Average pore radius	26.68	Average pore radius	28.18
Pore distribution, % vol.			
0 – 10	4.35	0 – 10	6.46
10 – 15	30.47	10 – 15	28.73
15 – 20	15.89	15 – 20	14.29
20 – 25	10.49	20 – 25	9.46
25 – 50	35.26	25 – 50	23.65
50 – 100	2.12	50 – 100	10.42
100 – 150	0.87	100 – 150	4.27
150 – 200	0.27	150 – 200	1.33
200 – 300	0.28	200 – 300	1.39

Conditioning of the Adsorbent

In order to obtain the adsorbent in the active form, a set of 40 experiments have been made, by varying conditioning temperature and time, for both samples of zeolite. Two different techniques have been applied, namely:

- a) treatment with HNO₃ / NH₄NO₃;
- b) conditioning with 1N solution of HCl, at ambient temperature, directly in the adsorption column, followed by conversion to sodium form, upon treatment with 1N solution of NaCl.

Activation by the HNO₃ / NH₄NO₃ technique has been performed at 600 spins/min rate of the mixing device, for 6 hours, followed by filtration and washing with distilled water until pH reaches 5.5-6.0 level, and drying in oven at 105°C. Then the material is blended for 2 hours, and extruded for 1 hour, after that being roasted at 550°C for 3 hours. The resulted form is then used to build up the columns for the determination of the ion exchange capacity.

After activation, the ion exchange capacity, in mequiv./g, has been determined. Table 5 presents the results of correlation between the ion exchange capacity and activation conditions, according to the HNO₃ / NH₄NO₃ technique. One can observe that the ion exchange capacity is weak for both samples, the average being 0.80 mmol NH₄⁺/ g of adsorbent, conditioned at 20°C, and 0.15 NH₄⁺/ g of adsorbent, conditioned at 100°C, as compared to the inactivated zeolite, which shows an insignificant capacity of ion exchange.

Analysis of the results shows that the optimal range of conditioning temperature is 60–70°C, and the conditioning time is 2.5 hours, followed by filtration, washing, blending, extruding, and roasting steps.

Table 5. Correlation between ion exchange capacity and activation conditions

Exp. no.	Granulation, (mm)	Temperature ($^{\circ}$ C)	Mixing time (h)	Exchange capacity, (mequiv./ g)
1.	0.09	20	6	0.78
2.	0.09	20	12	0.80
3.	0.04	20	12	0.86
4.	0.04	100	2	0.15
5.	0.04	60 - 65	2.5	1.75
6.	0.09	60 - 65	2.5	1.62
7.	0.09	70	2.5	1.67

In such conditions the ion exchange capacity has been improved, reaching an average value of 1.70 mmol NH_4^+ / g of conditioned adsorbent, for both samples of zeolite.

Conclusions

The physico-chemical studies on the two samples of zeolite from Zalau have evidenced the high level of clinoptilolyte content: 60% for S 0.09 mm, and 7% for S 0.04 mm, respectively.

Activation conditions and optimal condition has been established, the activation with nitric acid and ammonium nitrate being recommended, because the crystal size of clinoptilolyte is reduced in the case of 1N HCl activation, and a higher concentration of HCl solution destroys the crystals.

Activation with nitric acid and ammonium nitrate does not affect the crystalline structure of the zeolite; the ion exchange capacity increases, attaining an average value of 1.70 mmol NH_4^+ / g of conditioned adsorbent, for both samples of zeolite.

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