

INVESTIGATION OF THE PROCESSES OF CHEMICAL (ACID) LABILIZING OF CLINOPTILOLITE

Volodymyr Troszkiy, Zoriana Hnativ, Vasyl Duleba, Tetiana Kriuchenko

*Lviv Polytechnic National University, Institute of Chemistry and Chemical Technology,
12, S. Bandery Str., 79013, Lviv, Ukraine
e-mail: zoriana.y.hnativ@lpnu.ua*

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Abstract. The results of research of the chemical activation process of clinoptilolite from Sokirnytskyi field are shown. As a result of the research, the effectiveness of the influence on zeolite hydrochloric and sulfuric acids are compared. It should be noted that the advantage is on the side of hydrochloric acid. It was established that the increase in the concentration of sulfuric acid and the time of zeolite processing leads only to the increase in the content of the amorphous phase. As a result of the experiment, optimal conditions for zeolite activation: reagent – hydrochloric acid, concentration of acid – 7 %, the processing time – 2 hours, phase ratio T:R – 1:2 were selected.

Key words: zeolite, acid activation, clinoptilolite, adsorbent.

Formulation of the problem. Requirements to the methods of sewage treatment are determined by the volumes of their formation at enterprises and the amount of harmful components that they contain. These methods should be firstly and foremost simple in technological and equipment design and provide a high degree of wastewater treatment. At the same time, the raw material, used in the process of removal of harmful components must be effective, accessible and have a low price.

Worsening of water quality is the result of undercutting of substandard natural waters at violation of the usage intake. The main contaminants are petroleum products, phenols, heavy metals (copper, zinc, lead, cadmium, nickel, mercury), sulfates, chlorides and nitrogen compounds.

One of the factors that contribute to the accumulation of iron in the human body is drinking water with high content of this element. Prolonged use of water with iron content of more than 0.3 mg/l leads to liver diseases, increases the risk of heart attack, negatively influences the central nervous system and the

reproductive function of the organism. The enhanced content of iron adds water brown colouring, an unpleasant taste and odour, causes overgrowth of water supply networks, and is the reason of shortages in the textile, food, paper and cosmetics industries.

In order to use zeolites in technological purposes, their physical and chemical modification is necessary. Physical modification (grinding, classification) provides conditions for product application in industrial technologies – uniformity of chemical and particulate composition. The purpose of chemical modification is to change the adsorption properties of zeolite to achieve maximum absorption capacity relative to a specific type of pollution, for treatment of which zeolite will be used.

At the same time the use of cheaper adsorbents - natural zeolites is not possible without additional researches on the mechanism, kinetics and apparatus design of the process.

Analysis of sources of literature. Natural zeolites is a relatively new class of minerals used in the manufacturing processes of cleaning and purification of industrial wastewaters and surface waters. The developed specific surface, good adhesion, adsorption and ion exchange properties of zeolites enable to withdraw them effectively from the liquid, which is purified; suspended, colloidal and dissolved pollutants of organic and inorganic origin, among them – ammonium ions, heavy metals and radionuclides. [1].

An important property of natural clays is the possibility of their activating using chemicals such as acids (hydrochloric, sulfuric, acetic, etc.), salt, alkali and heat treatment with different combinations and duration of action.

Activation of clay is the increase of sorption capacity of clay that is the ability to adsorb and retain heavy metal ions [2].

Activation of clays is based on the change of their electro-kinetic potential (replacement of a diffuse layer

of clay particles Ca^{2+} , Mg^{2+} , Fe^{3+} , Al^{3+}). Electro-kinetic potential of clays increases because of such replacement [3].

Analysis of scientific publications on technologies of natural sorbents showed that in recent years more perspective direction for modification of natural sorbents is activating by chemical reagents. Thus, for example, it was found that the result of chemical influence of acids directly on the structure of zeolites is artificial expansion of adsorption capacity and to some extent of the volume of effective pores as a result of processes of dealumination [4].

As it is known, Na-form of zeolites is inactive in the processes that take place in the acid-base mechanism. Therefore, in such processes decationization zeolites, containing hydrogen ions or certain amount of polyvalent cations, are used [5].

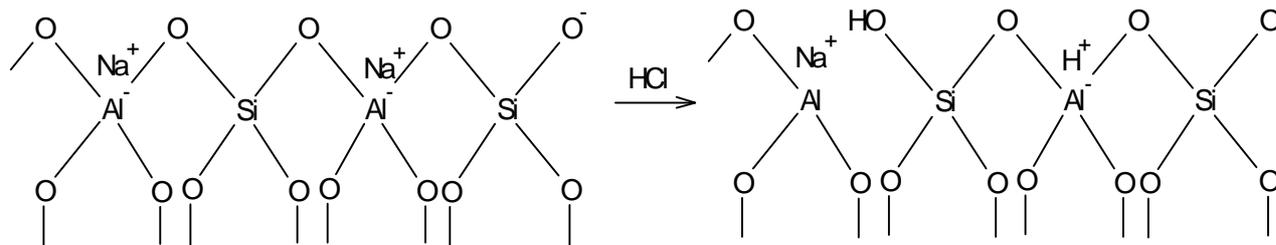
In [6] the treatment of zeolite with hydrochloric acid was carried, which led to the appearance of mesopores, volume of which increases in the process of dealumination. At the same time, it was established that acids of different concentration act selectively in certain areas of the crystal structure of zeolite: strong acids wash out the skeletal tetrahedra of aluminum, while the acids of low concentration interact with bars of zeolite mainly in mechanism of ion exchange. This gives grounds to select as a modifying agent the acids of high concentration that ensure the effective dealumination at comparatively small decationization [7].

With the increase of concentration of acids, zeolite adsorption capacity increases and has a certain extremum, that allows choosing the optimal mode of dealumination (44.6 %) [8–9].

To activate natural zeolite with hydrochloric acid, many other variants were offered, including not only processing with different acid concentrations, but steam treatment, compressed air, etc. [10].

In order to increase mechanical durability, acidoresistance and dynamic capacity on water natural zeolite dealuminate to 88–95 mas. % [11].

Analysis of the literature review showed that there is a number of effective methods of chemical and physical surface modification of natural mineral sorbents in order to regulate their adsorption and cation exchange ability.



Taking into account the above described mechanisms, the acidic activation of natural mineral sorbents in the mode of boiling was conducted.

However, many of these methods often result in inconsistent and incomparable results. Therefore, in this study not only existing methods of modification and activation of natural sorbents were experimentally tested, but also new technological techniques that can significantly improve the adsorption characteristics of natural sorbents were offered.

The purpose of the work. The aim of the work is to study the processes of chemical activation of clinoptilolite of Sokirnytskyi field and development of technology of purification of natural waters from iron ions with the use of sorption cleaning in apparatus with a mixer and in a layer.

Experimental part. The nature of aluminosilicate sorbents determines their widespread use in the processes taking place according to acid-base mechanism. Therefore, the use in these processes of natural sorbents containing in an exchange complex only alkaline or alkaline earth cations, requires converting them to a hydrogen form by chemical modification. Hydrogen form of zeolites, as known, can be obtained by acid treatment of sorbents.

Processing of natural sorbents by mineral acids is one of the most widespread methods of producing high-quality activated adsorbents used in different branches of industry.

The nature of surface acid centers of zeolites is still a subject of discussions and research. According to existing notions, at decationization of zeolites, which begins with getting the hydrogen form of zeolite, there is a break of Si-O-Al connections in the adjacent tetrahedrons, resulting in formation of OH groups connected to an atom of silicon, and three coordinated aluminum atoms, and also Brenstedivskyi center.

After further heat treatment of a hydrogen form, decationization of the surface with the formation of new active centers occurs. In this case, along with three coordinated aluminum atoms $\text{Al}_{3/2}$, representing Lyuisovkyi center, electron-seeking $\text{Si}^+\text{O}_{3/2}$ and stabilizing center $\text{AlO}_{4/2}$. Are also formed

Basic information about the processes occurring in natural sorbents during acid treatment gives the chemical analysis, mainly relation $\text{SiO}_2/\text{Al}_2\text{O}_3$, type and

quantity ration of exchange cations, water content. For example, in the Table. 1 shown the change of this indicator for natural sorbent aluminosilicate (zeolite).

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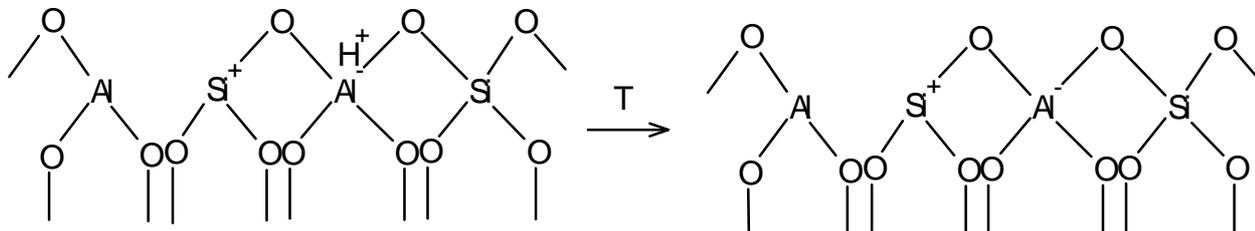


Table. 1 shows that the acid treatment is characterized by transition of metal cations to solution. With increase of acid concentration, the content of Na_2O decreased almost five times, and CaO (for natural zeolite) more than doubled after

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treatment by 10 % HCl. The content of silica increases to 81 %, and the most significant increase was detected after treatment by 7 % HCl. At the same concentration a sharp increase in the interrelation $\text{SiO}_2/\text{Al}_2\text{O}_3$ (9.45 to 16.6) is observed.

Table 1

The chemical composition of output and the acid-activated zeolite in boiling mode

| Conditions of activation | Moisture at 105° | | | | | | | | Molar correlation $\text{SiO}_2/\text{Al}_2\text{O}_3$ | Contact module $\text{Al}_2\text{O}_3/\text{SiO}_2 \cdot 10^3$ | The exchange volume mg-ekv. |
|-----------------------------------|------------------|----------------|-------------------------|-------------------------|--------------|--------------|-----------------------|----------------------|--|--|-----------------------------|
| | | SiO_2 | Al_2O_3 | Fe_2O_3 | CaO | MgO | Na_2O | K_2O | | | |
| Zeolite output | 3.08 | 70.41 | 12.64 | 1.07 | 2.16 | 0.73 | 1.32 | 3.04 | 9.45 | 105 | 66.35 |
| HCl 5 % | 3.76 | 72.57 | 10.88 | 1.55 | 2.08 | 0.79 | 0.55 | 3.18 | 11.32 | 88 | 39.20 |
| HCl 7 %, 1 h. | 6.15 | 78.52 | 8.18 | 1.50 | 1.41 | 1.01 | 0.35 | 2.37 | 16.29 | 61 | 36.18 |
| - " - 2 h. | 4.10 | 80.74 | 8.25 | 0.28 | 0.99 | 0.15 | 0.26 | 1.46 | 16.61 | 60 | 26.14 |
| - " - 3 h. | 4.32 | 80.71 | 8.37 | 0.17 | 0.85 | 0.28 | 0.26 | 1.49 | 16.36 | 61 | 29.20 |
| - " - 2 h. without washing | 4.40 | 78.33 | 9.47 | 0.43 | 1.13 | 0.89 | 0.31 | 1.71 | 14.04 | 71 | 28.13 |
| HCl 10 % 1h. | 2.95 | 79.60 | 9.29 | 0.44 | 0.77 | 0.45 | 0.28 | 1.43 | 14.54 | 69 | 30.16 |
| - " - 2 h. | 2.52 | 81.63 | 8.78 | 0.22 | 0.90 | 0.20 | 0.28 | 1.38 | 15.78 | 64 | 29.11 |
| - " - 3 h. | 2.06 | 82.25 | 7.41 | 0.03 | 0.80 | 0.25 | 0.27 | 1.36 | 18.97 | 53 | 33.87 |
| HCl 7 % T:P=1:1 | | 69.81 | 11.25 | 1.13 | 1.61 | 0.87 | 0.41 | 2.56 | 10.53 | 95 | 32.35 |
| T:P=1:2 | 4.10 | 80.74 | 8.25 | 0.28 | 0.99 | 0.15 | 0.26 | 1.46 | 16.61 | 60 | |
| T:P=1:3 | | 70.28 | 10.79 | 0.94 | 1.34 | 0.81 | 0.43 | 2.53 | 11.50 | 87 | 25.16 |
| T:P=1:6 | | 70.40 | 11.00 | 0.71 | 1.25 | 0.82 | 0.42 | 2.65 | 10.86 | 92 | 20.18 |
| HCl 7 % after a single processing | | 71.66 | 10.73 | 0.85 | 1.98 | 0.68 | 0.36 | 2.36 | 11.33 | 88 | 32.35 |
| after 2-fold processing | | 69.01 | 12.01 | 1.13 | 2.66 | 0.98 | 0.47 | 2.56 | 9.75 | 102 | 28.14 |
| after 3-fold processing | | 68.38 | 12.47 | 1.26 | 2.63 | 0.97 | 0.36 | 2.44 | 9.31 | 107 | 22.15 |
| H_2SO_4 5 % | | 72.70 | 10.76 | 1.22 | 2.82 | 0.87 | 0.38 | 2.74 | 11.47 | 87 | 40.18 |
| 10 % | | 72.96 | 10.66 | 1.01 | 2.73 | 0.76 | 0.38 | 2.56 | 11.61 | 86 | 40.13 |
| 13 % | | 73.14 | 10.05 | 1.06 | 2.57 | 0.66 | 0.35 | 2.30 | 12.35 | 81 | 36.17 |
| 17 % | | 73.92 | 9.39 | 0.82 | 2.48 | 0.60 | 0.53 | 2.20 | 13.36 | 75 | 36.3 |
| 20 % | | 73.28 | 10.05 | 0.82 | 2.67 | 0.65 | 0.42 | 2.50 | 12.25 | 82 | 32.35 |

With increase of molar interrelation $\text{SiO}_2/\text{Al}_2\text{O}_3$, ion exchange capacity of acid-activated zeolite in comparison with output zeolite decreases, which is associated with decrease of the total number of cation exchange centers and replacement of the portion of cations of exchange complex by hydrogen ions. With increase of acid concentration, oxide content of mono- and divalent metals continues to decrease. The loss during ignition does not depend on the concentration of the activator. Increase of acid exposure time from 1 to 3 hours leads to minor changes in the chemical composition.

It was found that the area of selection of acid concentration depends mainly on the interrelation $\text{SiO}_2/\text{Al}_2\text{O}_3$ and it meets the rigid structure of the zeolite. These changes in the structure of zeolite are confirmed by X-ray products by acid treatment (Table 2).

It was revealed that zeolite consists of clinoptilolite mixed with quartz, mica and feldspar. During acid treatment of zeolite by solutions of hydrochloric acids, partial destruction of the crystal structure of clinoptilolite was observed, that promotes the decrease of intensity of diffraction peaks on radiographs of acid activated zeolite. The intensities of the four most powerful reflex: 020 ($d \sim 9\text{A}$); 200 ($d \sim 7.9\text{A}$); 400,300 + 421 ($d \sim 3,98\text{A}$) and 151,350 ($d \sim 2,9\text{A}$) were compared.

Table 2 shows the value of integrated intensities of clinoptilolite reflections, intensity of peaks of initial sample taken as 100%. Table 2 shows that the concentration of crystalline phase decreases with increase of acid concentration (increase of J_{020} value associated with the orientation of particles in the unit.). At the same time, there is increase on the background of radiographs of acid-activated samples, which indicates the emergence of X-ray amorphous phase. The difference between the samples treated with 7% HCl and 10% HCl is not very significant. The value of residual crystalline phase of zeolite is 66% (Table 2).

Table 2

**The dependence of the integrated intensity
(% RH) of reflexes of natural zeolite
vs acid activation**

| Integral intensity of reflections | Daily treatment | | |
|-----------------------------------|-----------------|---------|----------|
| | sample output | 7 % HCl | 10 % HCl |
| J_{020} | 100 | 85 | 75 |
| $J_{400/300+421}$ | 100 | 61 | 61 |
| $J_{151.350/020}$ | 100 | 53 | 45 |
| Average value | 100 | 66 | 60 |

As already mentioned, during selection of optimal modes of acid activation of zeolite, its acid stability is important. Acid stability of zeolite was determined by the method based on treating of zeolite with solution of hydrochloric acid with concentration from 2 to 15% during four hours at 90 °C, and a ratio of 1:15. Monitoring was carried out by RKFA and chemical analysis.

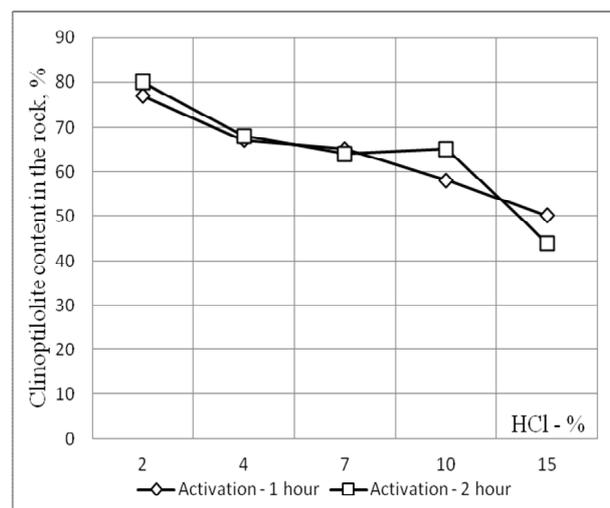
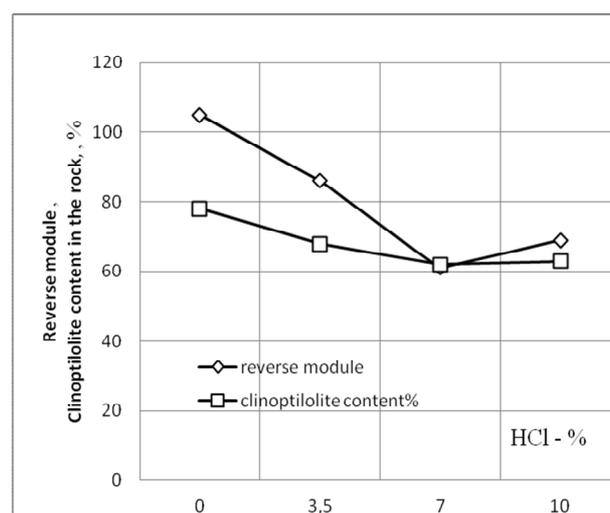


Fig. 1. The acidity of the zeolite according to RKFA

Figure 1 shows the effect of concentration of hydrochloric acid and activation time for the maintenance of a zeolite clinoptilolite according to RKFA. For ease of comparison of chemical and X-ray analysis, a reverse module, i.e. the value of $\text{Al}_2\text{O}_3/\text{SiO}_2$ was designed (Table 2).

Fig. 2. Effect of acid concentration on changing of clinoptilolite content and value of feedback module $\text{Al}_2\text{O}_3/\text{SiO}_2$

Feedback module was compared with the change of clinoptilolite content in the acid treated zeolite. Thus there is a good correlation between these values (Fig. 2).

The change is planned in the middle of the curve, ie when the acid concentration is less than 7 % processes proceed more rapidly, and when the concentration increases processes slow down.

Thus, X-ray phase analysis showed that acid treatment not only provides a hydrogen form, but also affects the structure of the zeolite, causing the dealumination of crystal lattice. Moreover, influence of acid on zeolite structure depends on its concentration and processing time.

For comparison, Table 1 shows the chemical composition of the zeolite activated by hydrochloric acid, but not washed with water. The results do not provide the high indexes achieved in the washed zeolite, so they are no longer analyzed.

Table 1 also presents data of studying the opportunities of multiple use of hydrochloric acid for activation. The results of these tests show that the multiple use of hydrochloric acid is possible with proper feeding by fresh acid solution to the needed concentration for complete decationization Ca^{2+} , K^+ , Na^+ from the zeolite. The use of hydrochloric acid at a ratio of T:P less than 1: 2 is impractical because there is incomplete development of zeolite surface and incomplete decationization.

For comparison, natural aluminosilicate sorbent (zeolite) was activated by sulfuric acid concentrations of 5 %, 10 %, 13 %, 17 % and 20 % for 2 hours (Table 1). Processing of natural zeolite by sulfuric acid was less effective: the silica content increased slightly, and the identified oxides Al_2O_3 , Fe_2O_3 , CaO , MgO i K_2O remained unchanged, only the acid content of Na_2O in the activated zeolite decreased up to 2.5 times. It should be noted, that the intensity of amorphization structure during the influence of sulfuric acid on zeolite is much lower than with by using of hydrochloric acid.

Increase in concentration of sulfuric acid and zeolite processing time only leads to increase in content of amorphous phase. Thus, during the comparison of efficient influence on zeolite by hydrochloric and sulfuric acids, it should be noted that the advantage is on the side of hydrochloric acid. As a result of the experiment, the optimal conditions for activation of zeolite were selected. They are: the reagent-hydrochloric acid, concentration of acid – 7 %, the processing time – 2 hours, phase ratio T: R -1: 2.

Conclusions

From the experiments, it was found that increase in sulfuric acid concentration and processing time of zeolite only leads to increase in content of amorphous phase. Thus, during the comparison of efficient influence on zeolite by hydrochloric and sulfuric acids, one should note, that the advantage is on the side of hydrochloric acid. The optimal conditions for activation of zeolite were selected. They are: the reagent-hydrochloric acid, concentration of acid – 7 %, the processing time – 2 hours, phase ratio T: R -1: 2.

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