

EXPERIMENTAL STUDY OF HYDROTHERMAL TRANSFORMATIONS OF CLINOPTILOLITE IN NaOH WATER SOLUTIONS

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Introduction

Zeolites are distributed world-wide and are found naturally in different forms. Zeolite-containing tuffs have volcano-precipitation origin. Variety of zeolite types is determined by geological conditions of their formations, namely, temperature, pressure, chemical content of surrounding medium, etc.

This paper is devoted to the study of influence of different experimental conditions on formation and transformation of different modifications of zeolites.

Experimental

As a starting mineral we have used the averaged clinoptilolite rocks from Noyemberyan region of Armenia. The rock consists from 85 – 87 % of main mineral. The remaining part is presented by quartz (5 %), clay (5 %), feldspar and ore minerals (5 %). The samples were grinded to a powder with particle size of 20 - 70 microns and carefully washed. They were analyzed by methods of thermographs and XRD [1]. Hydrothermal treatment of clinoptilolite was performed in NaOH water solutions in special autoclave with stirring. The regimes of treatment are the following:

Temperature	100-300 ⁰ C
NaOH concentration	5-30% (w)
Duration	1-50 hours
Vapor pressure	1-85 bar

Results and Discussion

It has been found that in water solutions of sodium alkali at certain interval of temperatures, pressures and concentration clinoptilolite holds its stability and capacity for regeneration. However outsides of these intervals clinoptilolite transforms into another newly formed phases.

In the result of hydrothermal treatment of clinoptilolite it has been found the possibility of formation of new mineral phases. So, in the presence of aqueous NaOH solutions at various temperatures and by using of mineralizes (NaCl) the series of following minerals were synthesized: analcime → Na-garronite → Na-chabazite → Na-faujazit.

The corresponding treatment without mineralizer results in the following series: clinoptilolite → mordenite → gismondine → philipsite → garronite → analcime → sanidine → sodalite → cancrinite.

Some results of the chemical analysis of monomineral phases are presented in Table 1.

Table 1. Results of Chemical Analysis of Newly Formed Phases

New phases	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	K ₂ O	CaO	MgO	Other	SiO ₂ / Al ₂ O ₃
Na-garronite	49.6	15.35	3.41	8.44	3.92	2.74	1.42	14.83	5.49
Analcime	45.6	23.15	4.49	10.61	4.14	2.56	1.30	8.62	3.35
Hydrocancrinite	40.2	24.21	4.68	16.35	1.72	3.41	1.26	9.65	2.82
Hydrosodalite	41.1	26.80	2.79	13.20	1.31	2.32	0.34	12.01	2.63

The intervals of stability of new-formed phases in alkaline solutions are presented in Table 2.

Our experiments on transformation of clinoptilolite as a starting material allow simulating the geological natural formation processes of zeolites and other mineral phases.

Table 2. Stability Intervals for Various Zeolite Phases

Zeolite	Stability Interval			
	NaOH , %	Temperature, °C	Duration, h	Vapor Press., bar
Clinoptilolite	5-10	100	1-10	1
Gismondine	5	100	50	1
Philipsite	5 - 20	100 - 200	3 - 50	1 - 15
Na-garronite	5 - 10	100 - 250	1 - 50	1 - 40
Analcime	5 - 20	100 - 300	1 - 50	1 - 85
Sanidine	10 - 30	200 - 300	1 - 50	15 - 85
Hydrocancrinite	10 - 30	250 - 300	1 - 50	40 - 85
Hydrosodalite	20 - 30	2000 - 300	1 - 50	15 - 85

As follows from the Table 2, clinoptilolite keeps its stability in NaOH solutions at concentrations 5 – 10 % and temperature up to 100⁰ C during 10 hours. Then, with increase of treatment time, concentration and pressures, further transformations take place.

At similar conditions but in presence of mineralizers (NaCl) it was possible to synthesize the following phases (see Table 3):

Table 3. Phase Transformations in Presence of Mineralizer

Zeolite	Experimental Conditions				
	NaOH , %	t, °C	Duration, h	P _{H2O} , bar	Mineralizer (NaCl) amount, w. %
Clinoptilolite	5 - 10	100	1 - 10	1	5 - 10
Garronite	5 - 20	100 - 200	1 - 50	1 - 15	5 - 10
Analcime	5 - 10	100 - 200	1 - 50	1 – 85	5 - 10
Chabazite	20 - 30	100 - 300	1 - 50	1 – 85	10 - 15
Faujazit	5 - 20	200 - 300	1 - 50	1 - 85	5 - 10

Data in Table 3 show that mineralized promotes the formation of chabazite and faujazite at high temperatures and alkaline concentrations. This occurs due to dissolution of SiO_2 from the clinoptilolite framework resulting in decreasing of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio from 9 to 2 – 3.

Conclusions

The regions of clinoptilolite stability are established in NaOH water solutions. Over these intervals clinoptilolite easily transforms into another almost monomineral (95 – 97 %) zeolite phases. The rise of alkali concentration leads to formation of low silica minerals due to SiO_2 leaching. NaOH acts as catalyst, i.e. with increase of concentration the time of phase crystallization is reduced and amount of formed phase in reaction product is increased. At constant content of reaction system the order of new phase's formation is determined by process duration and temperature regimes.

The using of mineralized sharply changes the direction of clinoptilolite crystallization. The cubic (halite type) lattice is the main element for transferring of SiO_4 and AlO_4^- tetrahedrons into faujazite lattice.

The experimentally obtained principles of zeolite phase's transformation may be useful in simulating of natural geological processes.

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