

Physical Chemistry

Laumontite – Natural Zeolite Mineral of Georgia

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ABSTRACT: Integrated research of Georgian laumontite-containing tuffs and their modified (treated with water solutions of HCl and NH₄Cl) forms was carried out to create the scientific basis for their use. Zeolite phase content in rocks (50-90% in untreated samples) as well as the laumontite resistance to the treatment with ammonium chloride tuffs (up to 3N) and hydrochloric acid (up to 1N) were determined on the basis of X-ray diffraction pattern analysis. Thermogravimetric methods show the complete stability of crystalline microporous structure of laumontite up to ~ 450°C. Chemical composition of laumontite-containing rocks, water sorption capacity, ion exchange capacity relative to alkali and alkali earth metal cations ammonium cation and selectivity of the laumontite relative to single- and double-charged cations of metals were discovered. Quite high content of zeolite phase in rocks determines the prospect of their mining, and physical-chemical properties of laumontite-containing rocks give the basis of their applicability as adsorbents and ion exchangers in catalytic systems and as a raw material for the production of nano-materials. © 2016 Bull. Georg. Natl. Acad. Sci.

Key words: natural zeolite, laumontite, adsorption, I.R. specter, thermography, ion exchange, selectivity

Wide application of the “magic stones” [1] in industry and agriculture, environment protection and medicine requires inclusion of different natural zeolites (phillipsite, analcime, laumontite, mordenite) in corresponding technological regulations alongside with the well studied and many times tested clinoptilolite [2]. In particular, natural laumontite was successfully used in plant-growing [3, 4]. It is one of the widely spread zeolite minerals known on the territory of Georgia. In some cases its concentration in rocks reaches 85 – 90%, while thickness of laumontite layer exceeds 500 meters [5].

Laumontite (IUPAC crystal chemical formula Ca₄(H₂O)₁₆[Al₈Si₁₆O₄₈] LAU) [6] has the framework density of 17.8 T/1000Å³ Channels: [100] 10.4.0 x 5.3 10-ring viewed along [100] (Fig. 1).

Materials and Methods

Performed research pursued study and characterization [7,8] of initial and modified forms (treated by HCl and NH₄Cl solutions) of laumontite-containing tuffs in Georgia with the purpose of formulation of scientific grounds for their practical application.

Chemical composition of laumontite samples was

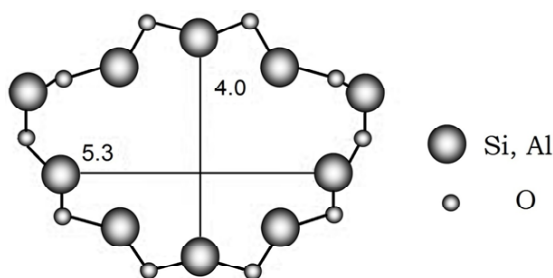


Fig. 1. 10-ring viewed along [100]

determined by elemental analyses carried out using a Spectromom 381L plasma spectrometer and a Perkin-Elmer 300 atomic absorption spectrometer. X-ray powder diffraction patterns were obtained from a DRON-2 diffractometer, employing the Cu-K α line and scanning at 1° per minute. IR spectra were recorded in the region of 1600-400 cm $^{-1}$ in a Karl Zeiss UR-20 spectrometer using the KBr pellet technique. Thermal analyses were performed on a Paulik-Paulik-Erdei OD-102 thermal analyzer at heating rate of 10°C/min up to 1000°C with reference to Al $_2$ O $_3$. Water adsorption capacity was studied under static conditions (p/p $_s$ =0.40, 20°C). The ion exchange capacity was determined in 0.5N solutions under static conditions at room temperature and with solid:liquid ratio of 1:6 and under dynamic conditions at rate of 5 ml / min using ionic chromatography (Tsvet-3006). Table 2 offers chemical composition of laumontite-containing rocks of Georgia in oxide form. As in the ideal LAU structure, calcium is exchange cation, while a sample taken in Chkherimela gorge (L-M) is charac-

terized by rather high concentration of sodium, and a sample taken in Gupta (L-G) contains significant amount of potassium. In some samples relatively high concentration of silicium (especially in L-B sample taken from Tbilisi Botanical Garden) is conditioned by abundance of silicium-containing admix-quartzs. Admixes also the condition presence of iron and manganese.

According to the results of X-ray diffraction phase analysis of modified forms laumontite (tested samples with approximately 70% zeolite phase) retain crystalline structure after their treatment by NH $_4$ Cl solutions up to 3N concentration, while after their treatment by hydrochloride acid 1N solution certain changes are observed in aluminum silicate lattice. Treatment by 3N solution results in destruction of micro-porous crystalline structure and its transfer into silicate one. This conclusion is certified by the results of IR spectroscopic analysis: in the samples treated by ammonium chloride solution the inter-tetrahedral anti-symmetrical valence oscillation bands (990, 1040, 1080, 1165cm $^{-1}$) are observed, which in contrary from other zeolites, is characteristic only for laumontite, while for samples treated even by diluted hydrochloride acid solutions the weakening of the above referred bands is observed. Besides, at acidic treatment of laumontite, intensity of bands characteristic for zeolitic microporous structure (410 and 440 cm $^{-1}$) decreases. Inter-tetrahedral deformation oscillation bands are shifted from 445 to 475cm $^{-1}$,

Table 1. Laumontite-containing tuffs of Georgia.

| # | Date of sample taking | Code | Laumontite concentration, % | Rock capacity, m | Sample color |
|---|-----------------------------------|--------|-----------------------------|----------------------|-----------------|
| 1 | Gupta(Java region) | L - G | 50 – 90 | 5– 10 | Yellowish –grey |
| 2 | River Chkherimela gorge (Molithi) | L - M | 50 – 70 | 50 500 – 600 | Greenish -grey |
| 3 | Khvedureti water (Trekhvi) | L - Kh | 50 – 70 | 10 | Yellowish –grey |
| 4 | Tbilisi Botanical Garden | L - B | 60 – 90 | 2.5 – 3 20 – 25 | Yellowish |
| 5 | Bagebi (Tbilisi suburb) | L - T | 60 – 75 | 3 – 4 20 – 25 | Yellowish –grey |
| 6 | Ateni Sioni gorge | L - A | 60 – 85 | 25 – 30 500 – 700 | Yellow-grayish |
| 7 | Ponichala | L - P | 70 - 75 | 2.5- 3 | Yellowish |

Table 2. Chemical composition of laumontite-containing rock of Georgian origin, %

| Samples | SiO ₂ | TiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | FeO | MnO | MgO | CaO | Na ₂ O | K ₂ O | P ₂ O ₅ | H ₂ O |
|---------|------------------|------------------|--------------------------------|--------------------------------|------|------|------|------|-------------------|------------------|-------------------------------|------------------|
| L - B | 67.25 | 0.30 | 13.03 | 1.98 | 0.44 | 0.03 | 0.90 | 4.90 | 2.40 | 0.99 | 0.20 | 7.50 |
| L - G | 63.30 | 0.45 | 14.80 | 2.55 | 0.64 | - | 1.90 | 4.60 | 1.80 | 2.30 | 0.08 | 7.90 |
| L - T | 62.75 | 0.31 | 14.45 | 2.30 | 0.50 | 0.04 | 1.30 | 5.70 | 3.70 | 0.40 | 0.30 | 8.30 |
| L - M | 55.60 | 0.40 | 17.85 | 4.30 | 1.80 | 0.08 | 2.70 | 5.30 | 5.10 | 0.15 | 0.10 | 6.80 |
| L - Kh | 52.40 | 0.65 | 17.20 | 4.90 | 3.30 | 0.20 | 3.50 | 7.70 | 3.20 | 0.30 | 0.10 | 6.40 |
| L - P | 62.75 | 0.31 | 14.45 | 2.32 | 0.51 | 0.04 | 1.32 | 5.67 | 3.73 | 0.42 | 0.32 | 1.90 |

which refers to the alteration of dimensions of “entry apertures” (windows).

Chemical composition of initial and modified samples of laumontite is given in Table 3, which shows that treatment in diluted solution of hydrochloride acid (0.1N) results in significant dealumination of laumontite, while further increase of concentration has almost no impact on ejection of the remaining aluminum.

Alongside with dealumination of crystalline structure gradual ejection of sodium cations possessing exchange capacity takes place; at its treatment by 3N hydrochloric acid solution at about 8.5 % of initial calcium quantity is expelled. It appears that calcium ion is localized in the positions where a bond with aluminosilicate lattice is strong and it is hardly exchanged with hydrogen ion. Besides, a process of internal crystalline ion exchange is not excluded, when calcium cations occupy positions of expelled cations. Table 4 offers results of thermal analysis of laumontite - containing rock.

The results of thermographic investigation of ini-

tial samples (Table 4) show that laumontite crystalline micro-porous structure is stable up to 450 °C and suffers complete destruction at a temperature above 800 °C. Total mass loss undergoes change in wide interval (8-12%) and is mainly conditioned by the removal of adsorbed and inner structural water. Dehydration process takes place in wide interval (500-600 °C) and dehydration occurs step-wise. Main mass loss is observed at relatively low temperature (up to 300 °C), which refers to development of the system of macropores and transitional pores and their wide spreading according to dimensions.

It also becomes apparent that treatment of laumontite in diluted solutions of hydrochloride acid (up to 0.25N) has no significant result to change the laumontite structure, but total mass loss decreases from 10.7% to 8.2% (Table 5). On a thermogram of a sample treated by hydrochloric acid 3N solution we observe low-temperature exo-peak at (310 °C), which proves partial destruction of laumontite zeolite structure, since in this region of temperature at DTG and TG curves, mass loss is not observed. According to

Table 3. Changes in chemical composition of laumontite-containing rock (L-B) at its treatment in various concentration of hydrochloride acid solution

| Components | Initial sample | 0.1 N | 1 N | 3 N |
|-----------------------|----------------|-------|------|------|
| Si | 31.4 | 33.75 | 35.2 | 36.1 |
| Al + Fe ³⁺ | 8.3 | 5.81 | 4.7 | 4.4 |
| Ca | 3.5 | 3.4 | 3.2 | 3.2 |
| Na | 1.8 | 1.4 | 0.6 | 0.05 |
| K | 0.80 | 0.65 | 0.45 | 0.15 |
| Mg | 0.5 | 0.2 | 0.04 | 0.04 |
| Ti | 0.2 | 0.07 | 0.06 | 0.01 |
| P | 0.08 | 0.03 | 0.02 | 0.00 |
| Mn | 0.02 | 0.01 | 0.01 | 0.00 |
| H ₂ O | 7.52 | 7.05 | 6.54 | 5.91 |

Table 4. Results of thermal analysis of laumontite-containing (L-A) rock samples

| Samples | Total mass TG, m / % | DTA | | Temperature interval of dehydration, °C | Maximal dehydration temperature, °C |
|---------|----------------------|---------------|-------------------|---|-------------------------------------|
| | | Reaction type | Temperature, °C | | |
| # 1 | 10.3 | endo | 120,250,450, 800 | 50 - 600 | 120,250, 450 |
| #2 | 12.0 | endo | 120,260, 460,820 | 50-600 | 120,260, 480 |
| #3 | 8.3 | endo | 110,240, 450, 850 | 50-600 | 120,240, 450 |

the obtained thermograms, treatment in various concentrations of ammonium chloride solutions (up to (0.25 - 3N) has no marked impact on DTA curve character. Sorption volume of micropores to water vapor in initial samples (Table 6) suffers change from 1.17 to 1.84 mmol/g;

Acidic treatment of laumontite initially increases (up to 1N) adsorption capacity due to cleaning the samples from crystalline and amorphous admixes and then, (1-3N) decreases its adsorption capacity, which is conditioned both by expulsion of unscreened cations

from microporous structure and by destruction of this structure. Similar effect is observed during preparation of hydrogen forms by the so-called “soft” method (by NH_4Cl water solution); increase of ammonium chloride concentration initially incites increase in water vapor adsorption, and then its decrease, which can be explained by changes of inner crystalline structure of the zeolite. Ion-exchange capacities of laumontite to various cations in dynamic and static conditions are given in Table 7.

Exchange of single-charged ions in laumontite

Table 5. Results of thermal analysis of laumontite-containing rock (L-B) samples treated in various concentration of hydrochloric acid solution

| Hydrochloric acid concentration. | TGA | | DTA | |
|----------------------------------|--------------------|-----------------|---------------|-------------------------------------|
| | Total mass loss, % | Temperature, °C | Reaction type | Temperature °C |
| 0 | 10.7 | 120,250,440,520 | endo | 120,250,440,520, (720, 880 a trace) |
| 0.025 N | 8.9 | 100,250,430 | endo | 100,250,430,570 |
| 0.05 N | 8.9 | 100,250, 430 | endo | 100,250,430,570 |
| 0.1 N | 8.7 | 100,250, 430 | endo | 100,250,430,570 |
| 0.25 N | 8.2 | 90,250, 430 | endo | 90,250,430, 570 |
| 1 N | 4.0 | 90 | endo | 90,430, 570 |
| 3 N | 3.9 | 90 | endo exo | 90,570, 310 |

Table 6. Sorption capacity of laumontite-containing tuffs of Georgia to water vapor

| Sample | a, mmol/g | V, cm ³ / g |
|--------|-----------|------------------------|
| L – G | 1.17 | 0.021 |
| L – M | 1.38 | 0.025 |
| L – Kh | 1.39 | 0.025 |
| L – B | 1.84 | 0.033 |

takes place by clearly expressed selectivity towards large non-hydrated cations (Cs^+ and Rb^+). Low selectivity to lithium cation might be conditioned by its high hydration capacity, because of which its adsorption in zeolite crystalline lattice is limited. On the base of the obtained results the selectivity order was determined $\text{Cs}^+ > \text{Rb}^+ > \text{NH}_4^+ > \text{Li}^+$ for single-charged cations and $\text{Ba}^{+2} > \text{Sr}^{+2} > \text{Ca}^{+2} > \text{Mg}^{+2}$ for double-charged cations. At the exchange of double-charged cations we observe relatively high selectivity of laumontite to large Ba^+ and Sr^+ cations, which is explained by structural specificity of laumontite: dimension of entrance channels, localization and distribution of cations in a lattice. It was established that further increase of solution concentration up to 1N results in increase of laumontite selectivity to double-charged cations, while further increase of concentration results in decrease of zeolite selectivity to all cations; It appears that the above referred peculiarities of micro porous crystalline structure of laumontite exerts influence on the exchange process of relatively small size cations. The obtained results show that in case of metal cations chosen by us, the process of es-

tablishing ion-exchange equilibrium going on on zeolite surface and in its crystalline structure pores is less connected with dimensions of cations and is conditioned greatly by structural characteristics of the zeolite.

Impact of temperature (50-80°C) on laumontite ion-exchange capacity was studied with respect to single-charged cations. Increase of temperature results in increase of laumontite ion-exchange capacity towards all cations; in case of lithium cation, at 80°C we observe significant increase of capacity, which is probably conditioned by dehydration process of lithium ions, which facilitates their diffusion in zeolite lattice and increases zeolite sorption capacity. It was also established that treatment by solutions of single-charged metal chlorides (0.1 – 0.5N) results in increase of laumontite ion-exchange capacity, while selectivity order is not changed.

Conclusion

On the base of the performed researches we can make the following conclusions.

Zeolite phase concentration in laumontite-containing rocks of Georgia is rather high, which determines perspectives of their mining;

Laumontite-containing rocks are characterized by comparatively high thermal and acid resistance, acceptable sorption and ion-exchange capacities, which will condition the feasibility of their application as adsorbents and ion-exchangers, as well as in catalytic systems and raw materials in production of nano-materials.

Table 7. Ion-exchange capacity of laumontite-containing rock (L-B) to various cations.

| Ion-exchange capacity mg/equiv/g | | |
|----------------------------------|-------------------|--------------------|
| Cation | Static conditions | Dynamic conditions |
| Single-charged | | |
| Cs^+ | 3.1 | 2.8 |
| Rb^+ | 3.0 | 2.6 |
| NH^+ | 2.8 | 2.4 |
| Li^+ | 2.1 | 1.9 |
| Double-charged | | |
| Ba^{+2} | 3.8 | 2.9 |
| Sr^{+2} | 3.3 | 2.8 |
| Ca^{+2} | 3.0 | 2.5 |
| Mg^{+2} | 2.5 | 2.1 |

ფიზიკური ქიმია

საქართველოს ბუნებრივი ცეოლითური მინერალი -
ლომონტიტი

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ჩატარებულია საქართველოს ადგილმდებარეობის ლომონტიტშემცველი ტუფების საწყისი და მათი მოდიფიცირებული ფორმების (HCl და NH₄Cl-ის ხსნარით დამუშავებული) კომპლექსური კვლევა მათი პრაქტიკული გამოყენების მიზნით. რენტგენოფაზური ანალიზით დადგენილია, ცეოლითური ფაზის შემცველობა (საწყის ნიმუშში 50–90%) და ლომონტიტის მედეგობა ამონიუმის ქლორიდის (3 N-მდე) და მარილმჟავას (1 N-მდე) ხსნარებით დამუშავების მიმართ. თერმული ანალიზით ნაჩვენებია ლომონტიტის კრისტალური მიკროფოროვანი სტრუქტურის სრული სტაბილურობა ~450°C-მდე. დადგენილია ლომონტიტშემცველი ქანების ქიმიური შედგენილობა, სორბციული ტევადობა წყლის ორთქლის მიმართ, მიმოცვლითი ტევადობები ტუტე, ტუტემიწა და ამონიუმის კატიონების მიმართ, ასევე ლომონტიტის სელექტიურობა ერთ- და ორმუხტიან მეტალთა კატიონების მიმართ. საქართველოს ლომონტიტშემცველ ქანებში ცეოლითური ფაზის მაღალი შემცველობა განსაზღვრავს მათი მოპოვების პერსპექტივას, ხოლო ფიზიკურ-ქიმიური თვისებები განაპირობებენ მათი გამოყენების შესაძლებლობას ადსორბენტებისა და იონმიომცვლელების სახით, აგრეთვე კატალიზურ სისტემებსა და ნედლეულად ნანო-მასალების წარმოებაში.

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