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## Boron recovery from separate of Pauzhetskaya geothermal station based on modified zeolites of Yagodninsky deposit of Kamchatka

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# Boron recovery from separate of Pauzhetskaya geothermal station based on modified zeolites of Yagodninsky deposit of Kamchatka

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**Abstract.** Experimental data on boron sorption from separate of Pauzhetskaya geothermal station by sorbents obtaining by directional modification of zeolites surface of Kamchatka Yagodninsky deposit are presented. The modification was carried out with urotropine (ZEO-U<sub>B</sub>) or mannite (ZEO-M<sub>B</sub>). It was determined, that sorbent ZEO-M<sub>B</sub> has better properties in comparison with ZEO-U<sub>B</sub>. Sulfate-ions concentration does not affect on sorption capacity; chloride-ions concentration effects negligible. The sorbent is selective relative to boric acid due to reaction of mannite-boric acid formation. Sulfate- and chloride-ions greatly influence on H<sub>3</sub>BO<sub>3</sub> chemisorption with ZEO-U<sub>B</sub> due to reaction of amino radicals salification with amines of urotropine.

**Key words:** complex use, geothermal heat carries, boron, boric acid, extraction, sorption, zeolites, technogenic solutions.

## 1. Introduction

The world experience of boron recovery from hydrothermal solutions begins its history in Italy on Lardarello field in XVIII century, where nowadays the boron compounds are recovered from the solution using the partial condensation method for concentration. On the hydrothermal field in Turkey the tests to recover different forms of boron using sorbent selective to boron – resin of Amberlit IRA 743 – were successfully carried out.

Boron and its compounds are used in agriculture, metallurgy, oil and gas industry, building industry, cement industry, nuclear power engineering, healthcare service, in waste water purification, production of glass, glass-wool and etc.

Much attention of boron recovery from hydromineral materials using sorption and extraction technologies is given in literature. The methods of sorption by non-organic sorbents should be noted among sorption technologies. Sokolov M M at all [1] investigated the properties of non-organic sorbents for boron sorption on the bases of double hydroxides of metals with bedded structure like:  $Mg_{0.85}Al_{0.15}(OH)_2(NO_3)_{0.15-m} X_{m-n}H_2O$  and  $Mg_{0.85}Fe_{0.15}(OH)_2(NO_3)_{0.15-m} X_{m-n}H_2O$ , where  $X=OH^-$ ,  $\frac{1}{2}CO_3^{2-}$ . Double hydroxides of – magnesium-aluminum and magnesium-iron (III) – with hydrotalcite structure are effective sorbents for complex boron ions  $[B_4O_5(OH)_4]^{2-}$ . They can work stable in repeated cycles of sorption-desorption purifying solutions from boron ions up to the level which does not exceed maximum permissible concentration equaled to 0.5 mg/g for drinking water.

Govorova Zh M [2] presents the technological scheme of ground water conditioning on the models of filters of the first and second stages with ion-exchange resin Purolite S-108 and AmberliteIRA with ion-exchange groups selective to boron. The next processing provides standards on boron with its initial concentration from 1.8 mg/l. Selectivity of Purolite S-108 anionite to boron is provided by presence of polyatomic alcohols  $R-CH_2-N(CH_3)-CH_2-CHOH-CHOH-CHOH-CHOH-CH_2-OH$ , enabled to form ester bonds by boron-anions in its structure of lateral residuals.

The works on the use of such sorbents as Lewatit MK51, Diaion CRB 02, Dowex XUS 43594.00 [3], Resin Tech SIR 1100, Amberlite IRA-743, Doshion DCHR 75, Granion D 403 in many countries, including Russia [4] are famous. Boron concentration decreased from 5.1 mg/l up to 0.2 mg/l in wasted water during the processing on the sorbents.



Tanasheva M R et al. [5] showed the application prospects of industrial lignin waste activated by infra sound to recovery boron from natural water. Boron recovery from the solutions with boron concentration from 0.01 up to 0.8 g/l for a single sorption by activated lignin reaches almost 70% with phases ratio 1:10.

RGC FEB RAS studies boron recovery from model solutions and technogenic solutions by industrial ion-exchanges ASD-4-1p, AV-16 GS, AN-31, AV-17-8 and modified zeolites of Yagodninsky deposit of Kamchatka region (ZEO<sub>B1</sub>, ZEO<sub>B2</sub>). Analyzing the experimental results the authors determined that sorption of boric acid by anionites happens quickly and sorption capacity weakly depends on pH in an analyzed range pH = 6 – 9. The zeolites modified by hydroxylamine hydrochloric acid or urotropine can be used for sorption of boric acid from natural and technogenic solutions, as well as for reduction of boric acid concentration up to the values of maximum permissible concentration. Industrial ion-exchangers have less sorption capacity in comparison with modified zeolites with sorption capacity by 30% higher on average [6–9].

The extraction is the most important promising method of separation and concentration. The octanol extractants in kerosine oil with addition of Yarrezine-B or n-octyl alcohol can be prospectively used for boron ions recovery from natural and waste waters and as well as for drinking water preparation. The efficiency of boron recovery according to the proposed scheme is 77%, summary number of theoretical stages is 2, 3 in the columns [10]. The extraction and sorption technology prospective for boron recovery was tested in the Institute of Chemistry of FEB RAS. The boron extraction was made by n-octyl alcohol with subsequent re-extraction by sodium carbonate solution. Re-extract was returned to the stage of extraction after its deacidification by acid [11].

The bio-degradable, water soluble surface-active reagents [12] are used to increase security and efficiently of extraction. The application possibility of extraction systems with non-ionic surface-active reagents – synthanols for boron concentration from bischofite salt brines and wastes production of boric acid was presented.

## 2. Materials and methods

The data of experimental studies of boron sorption from technogenic solutions in a dynamic mode using sorbents obtaining by the modification of natural zeolites of Yagodninsky deposit of Kamchatka region are presented. The use of high-silica aluminosilicates such as zeolites as sorbents is based on their ion-exchange and molecular sieve properties. Zeolites belong to a middle class of sorbents, but high porosity allows carrying out directional modification of the surface. Selective sorbents can be obtained depending on the method of modification.

The modification of zeolites was carried out by 5% solution of urotropine – (ZEO-U<sub>B</sub>), or zeolites was modified by 10% solution of hexatomic alcohol of mannitol - ZEO-M<sub>B</sub>. Sample weight of zeolite with fraction size from 0.25 to 0.50 mm was poured by modifier solution and kept within 24 hours, then sorbent was washed and air dried. 10 g of modified sorbents were put into sorption columns of 12 mm in diameter and 300 mm of height. Sorption from model and natural solutions was carried out by the method of down flow with the speed 1 ml/min.

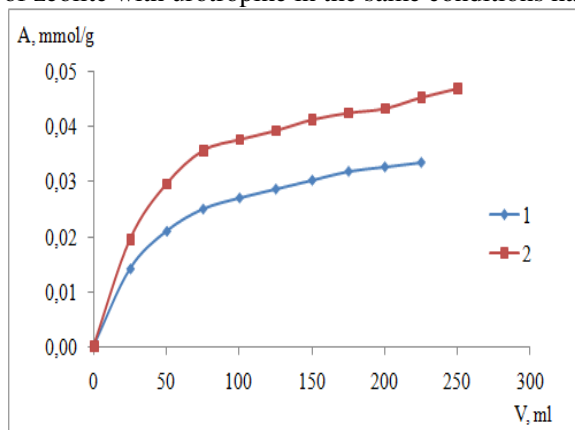
The model solutions were made of boric acid (chemically clean) by dissolution of precisely weighed quantity in a delivery flask. pH was assigned by adding NaOH (reagent grade) solution. Standardization of model solution was made by the method of photometric titration. The titration standard of NaOH on boric acid was preliminarily assigned in similar conditions on standard solution of boric acid (National standard-7337-96). Solutions acidity was controlled on ionomer «Expert-001» with universal electrode ESK-10601/7 with accuracy no worse than  $\pm 0.02$  units of pH.

Separate composition of Pauzhetskaya geothermal station used in work, mg/l: K<sup>+</sup> – 44.0; Na<sup>+</sup> – 670; Li<sup>+</sup> – 2.26; NH<sub>4</sub><sup>+</sup> – 1.0; Ca<sup>2+</sup> – 42.4; Mg<sup>2+</sup> – 1.87; Fe<sub>(total)</sub> < 0.3; Cl<sup>–</sup> – 1028; HCO<sub>3</sub><sup>–</sup> + CO<sub>3</sub><sup>2–</sup> – 29.3; SO<sub>4</sub><sup>2–</sup> – 76.8; H<sub>4</sub>SiO<sub>4</sub> – 183; H<sub>3</sub>BO<sub>3</sub> – 135; pH = 8.32. (Selection date: 12.06.2018. Engineer Ershov S.I.).

## 3. Results and discussion

Separate of Pauzhetskaya geothermal station, used in the work, had the following mole ratios: (SO<sub>4</sub><sup>2–</sup> / (H<sub>3</sub>BO<sub>3</sub>) = 0.733;  $\nu(\text{Cl}^-)/\nu(\text{H}_3\text{BO}_3) = 13.3$ . The graphs of sorption capacity increase while passing technogenic solution through the columns with sorbents were made according to experimental researches data. Boric acid, sulfate- and chloride ions concentration were controlled on the exit of columns. The sorbent ZEO-M<sub>B</sub>, obtaining by the modification of zeolite of Yagodninsky deposit of Kamchatka with mannite – ZEO-M<sub>B</sub>, has larger sorption capacity. The dynamic sorption capacity of

ZEO-M<sub>B</sub> on boric acid, achieved within the experiment conditions, was 0.047 mmol/g. Sulfate-ions concentration does not vary, mole ratio  $\nu(\text{SO}_4^{2-})/\nu(\text{H}_3\text{BO}_3)$  in eluate increases by 22.6% in comparison with initial water. Chloride-ions concentration decreases due to competing sorption. The dynamic sorption capacity on chloride-ions is 0.45 mmol/g, mole ratio  $(\text{Cl}^-)/(\text{H}_3\text{BO}_3)$  increases up to value 14.2. The specified facts confirm that the sorbent is selective in relation to  $\text{H}_3\text{BO}_3$  due to reaction of formation of mannite-boric acid during sorbent phase. Sorbent ZEO-U<sub>B</sub> obtained by the modification of zeolite with urotropine in the same conditions has capacity equaled 0.034 mmol/g on  $\text{H}_3\text{BO}_3$ .



**Fig.1.** Dynamics of increase of sorption capacity depending on volume of solution passed: 1 – ZEO-U<sub>B</sub>; 2 – ZEO-M<sub>B</sub>

The absorption of sulfate-ions occurs, their concentration in eluate reduces by 16.7% and mole ratio  $(\text{SO}_4^{2-})/(\text{H}_3\text{BO}_3)$  decreases by 4.8%. The absorption of chloride-ions by sorbent ZEO-U<sub>B</sub> also occurs; mole ratio  $(\text{Cl}^-)/(\text{H}_3\text{BO}_3)$  decreases up to 11.4. Probably, the process of salt formation of amino group of urotropine with chloride- and sulfate-ions, presenting in initial water is competitive.

### Conclusion

Sorbent ZEO-M<sub>B</sub>, obtaining by directional modification zeolites of Yagodninsky deposit of Kamchatka, is recommended to use for recovery of boric acid from technogenic solutions of geothermal plants. Concentration of chloride- and sulfate-ions up to 29.0 mmol/g and 1.6 mmol/g, respectively, doesn't influence on chemisorption.

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