PROCEEDINGS, Thirty-Fourth Workshop on Geothermal Reservoir Engineering
Stanford University, Stanford, California, February 9-11, 2009
SGP-TR-187

STUDY OF SORPTION EXTRACTION OF BORON FROM THE GEOTHERMAL HEAT CARRIERS

Belova T.P., Parshin B.E., Latkin A.S., Yakovishina O.A.,
Zernova L.D., Kornilova T.I., Ratchina T.I.

Research Geotechnological Centre, Far Eastern Branch of Russian Academy of Sciences
Severo-Vostochnoye shosse, 30, p/b 56
Petropavlovsk-Kamchatsky, 683002, Russia
e-mail: tpbel@yandex.ru

ABSTRACT

Processes of extraction of boric acid from the model and technogenic solutions by anionites ASD-4-1p, by AV-16GS, AN-31, AV-17-8 are investigated. It is ascertained that sorption capacity of the investigated sorbents makes up 3,7–4,1 mg/g depending on the form, poorly depends from pH in an investigated range. At sorption from natural and technogenic solutions the increase of sorption capacity up to 7,7–41,5 % is observed.

In the conditions of developing of the geothermal power engineering on Kamchatka there is an important question concerning the utilization of the spent heat-carrier for the aim of preservation of ecological conditions in the areas of the geothermal power plants.

The utilization can be carried out in two directions: injection of spent heat-carrier into wells and chemical-and-technological purification. In the first variant the valuable components such as boron, lithium, silica oxide, etc. are irrevocably lost. The second variant requires the additional technological equipment (Belova T.P, Latkin A.S., 2003). However, cost of the extracted components makes us to give preference to the chemical-and-technological method of cleaning of spent heat-carrier. Sorption technologies dominate among well-known methods of purification of natural waters and sewage.

Specificity of the industrial process of extraction of the chemical compounds from natural water is in necessity to process a huge amount of water, as a content of extracted components is usually not great. Therefore, for extraction of the valuable components the sorption methods (Belova T.P, Latkin A.S., 2006) are widely applied. For these methods the following characteristics are required: high selectivity, small power intensity, the minimum expense of reagents, possibility of multicyclic use of a sorbent. One of the elements which could be extracted from natural waters is boron. At the present time it is profitable to extract boron from technogenic solutions of the working geothermal power plants: Pauzhetsky and Mutnovsky.

World experience of extraction of boron in the form of boric acid from hydrothermal solutions began its history on a deposit Lardarello (Italy) in XVIII century, for a long before the energy of the geothermal heat-carriers began to be used for power generation.
On the hydrothermal deposit in Turkey for successful extraction of various forms of boron a sorbent– Amberlit IRA 743 is used. A group of employees have investigated the processes of sorption of boron and other components from the spent heat-carrier (Paholkov V.S, and all., 1979; "Technology of boric compounds," 1980) in 80-th years of XX century on the first Russian geothermal power plant (Pauzhetka, Kamchatka). However, the technology has not been introduced in manufacture for the objective reasons.

EXPERIMENTAL

The purpose of the present work is to analyze the possibility of application of the industrial anionites for extraction of boron from geothermal heat-carriers. Research of sorption characteristics of industrial anionites (GOST 20301-74) AV-17-8, AV-16GS, AN-31, ASD-4-1p was implemented by a standard method, in a static regime. The anionites AV-17-8 and ASD-4-1p are strong-basic multipurpose ionites, the anionite AV-16GS is medium- basic, the anionite AN-31 is weak-basic.

Initially ionites were prepared for research by a method described in (Arinushkina E.V., 1961). Appointed amount of anionite with granulation 0,25-0,5 mm was filled in with solution of Na_2CO_3 10 % for 24 hours to neutralize the acid surplus contained in a marketable product.

Then it was washed with distilled water till absence of alkaline reaction on phenolphthalein. Saturation of anionite by the gidroksid-ions was conducted in a dynamic regime by passing 10-15 columnar volumes of solution NaOH 2% through a column with anionite. Conversion of anionite in chloride form was conducted similarly, using solution NaCl.

Prepared anionites were discharged from a column and dried up on air. Then the appointed amount of dry anionite was filled in with model or technogenic solution H:S = 1:50, and aliquots were selected for definition of boron through certain time intervals.
Model solutions were prepared from boric acid by dissolution of the appointed amount of anionite in a measured bottle, pH was settled by addition of solution NaOH.

Standardization of a model solution was realized by a method of potentiometry based on the following: the investigated boron-contained solution is potentiometry titrated by alkali or acid (depending on initial value of its pH) till pH=7, then the mannitol as a catalyzer is added, as a result the value of pH mix is reduced. Then it is potentiometry titrated by solution of alkali to initial value of pH (before addition of a catalyzer). Titre NaOH for boron preliminary was formed in similar conditions using a standard solution of boric acid (7337-96, C=1,03 g/dm^3). Acidity of solutions was controlled by the ionometer "Ekspert-001" with universal electrode ESK-10601/7 with accuracy not worse than ± 0,03 units pH.

The composition of the technogenic solutions used for research is given in tab. 1. (1 – composition of fluid of the Mutnovsky GeoPP; 2 – composition of fluid of the Pauzhetsky geothermal field).

	1	**2**
pH	9,2	8,5
K^+	53	89
Na^+	273	815
NH_4^+	0,8	1,0
Ca^{2+}	3,8	46
Mg^{2+}	< 0,1	1,22
$Fe^{2+} + Fe^{3+}$	< 0,3	< 0,3
Cl^-	234	983
HCO_3^-	42	12,62
CO_3^{2-}	5,2	
SO_4^{2-}	210	112
H_4SiO_4	1180	96
H_3BO_3	183	125

Tab. 1: Composition of the technogenic solutions (mg/dm3)

The value of sorption capacity SC mg/g was calculated according with the results of analysis

$$SC = \frac{m_{sorb}}{m} \cdot \qquad (1)$$

$$m_{sorb} = V_o\,(C_o - C_t) - V_{al}\,(C_1 + C_2 + \ldots.. + C_{t-1} - (t-1)\,C_t) \qquad (2)$$

Where C_0 и $C_1 \ldots C_t$ -are initial and current concentration of adsorbate in a solution (mg/ dm^3), V_o – initial volume of a solution dm^3, V_{al} - volume of aliquot, m – mass of a sorbent (g), m_{sorb} – mass of a substance in a sorbent (mg), calculated taking into account a decrease of volume of a solution during selection of aliquot for the analysis.

The analysis of the results of the experimental researches has shown that the process of extraction of boric acid from solutions passes quickly enough, the equilibrium state occurred to the second hour of sorption. It is became clear that the sorption capacity poorly depends from pH in an investigated range pH = 6–9. Results of experimental researches are given on schedules (fig. 1-6). Kinetic dependences C(H_3BO_3) on time for a model solution at pH = 8 are given for an illustration of the results.

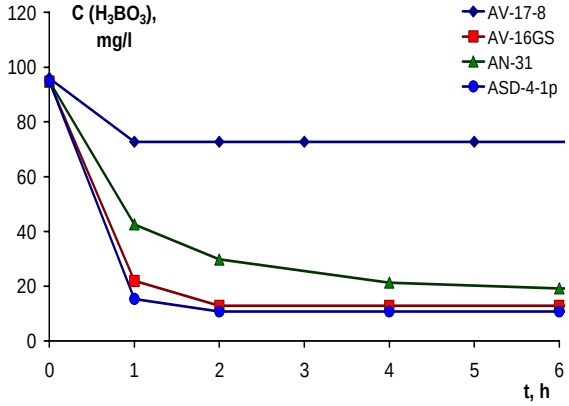

Figure 1: Sorption of boron from model solution pH=8 on an anionites in OH – form

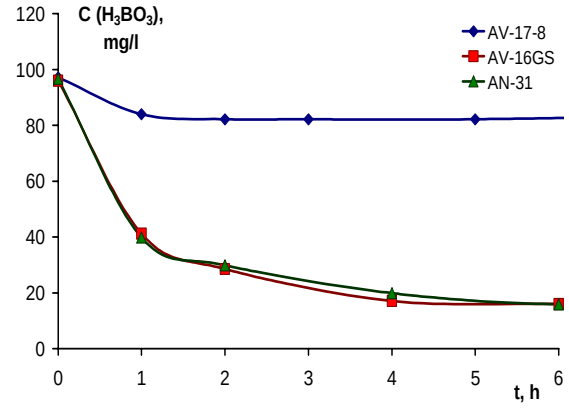

Figure 2: Sorption of boron from model solution pH=8 on anionites in Cl – form

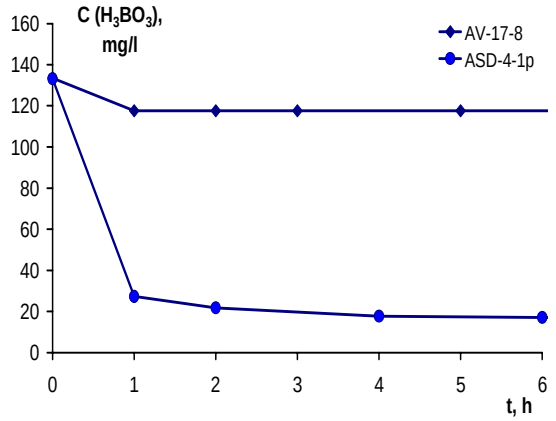

Figure 3: Sorption of boron from the heat-carrier of the Pauzhetsky geothermal field on anionites in OH - form

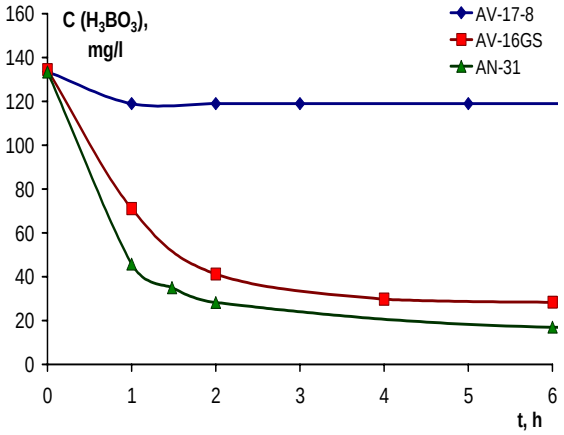

Figure 4: Sorption of boron from the heat-carrier of the Pauzhetsky geothermal field on anionites in Cl – form

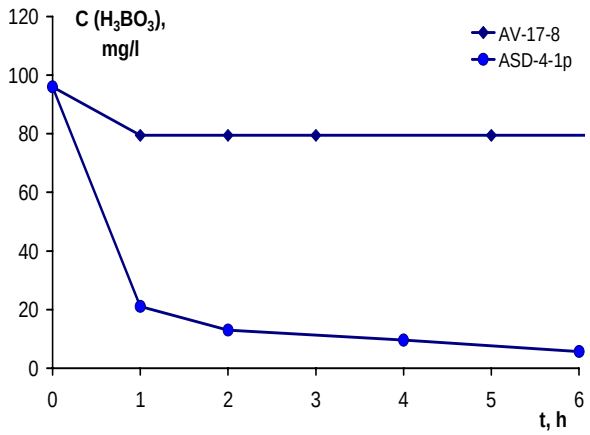

Figure 5: Sorption of boron from the heat-carrier of the Mutnovsky GeoPP on anionites in OH - form

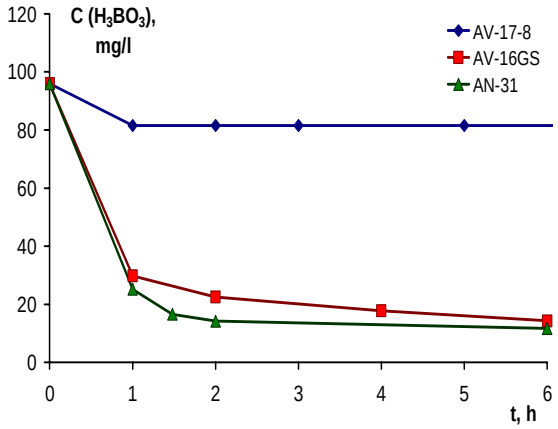

Figure 6: Sorption of boron from the heat-carrier of the Mutnovsky GeoPP on anionites in Cl – form

As it is shown on the figures, the anionite ASD-4-1p in OH-form, the SC=4,1 mg/g has the largest static exchange capacity regarding to a model solution, the least static exchange capacity has anionite – AV-17-8 in Cl-form SC=0,6 mg/g in OH-form SC =1,4 mg/g. Medium- basic anionite AV-16GS and weak-basic anionite AN-31 show approximately identical sorption capacity in hydroxyl and in chloride forms (tab. 2).

Form	OH^-	Cl^-
anionite	model solution	
ASD-4-1p	4,1	–
AV-16GS	3,7	3,5
AN-31	3,8	3,9
AV-17-8	1,4	0,6
	fluid of the Pauzhetsky geothermal field	
ASD-4-1p	5,8	–
AV-16GS	–	4,7
AN-31	–	5,4
AV-17-8	0,8	0,7
	fluid of the Mutnovsky GeoPP	
ASD-4-1p	4,5	–
AV-16GS	–	4,1
AN-31	–	4,2
AV-17-8	0,8	0,7

tab. 2: Static exchange capacity (SC, mg/g) of anionites

During research of sorption from the technogenic solutions of the Mutnovsky GeoPP the increase of sorption capacity for anionite ASD-4-1p in OH-form up to 9,75 % was observed. During sorption of the fluid of the Pauzhetsky geothermal field the increase of sorption capacity up to 41,5% was observed.

For anionite AV-16GS in the chloride form the sorption capacity increases up to 11,4 and 31,4%

accordingly. For anionite AN-31 in the chloride form the sorption capacity increases up to 7,7 and 38,5% accordingly.

It is necessary to notice that during research of sorption of the boric acid from technogenic solutions by strong-basic anionite AV-17-8 in the hydroxyl form the reduction of the sorption capacity on average 43 % was observed.
It is obvious that a compound of the technogenic solutions influences essentially on exchange capacity value.

CONCLUSIONS

For extraction of boric acid from the technogenic solutions the anionites ASD-4-1p, AV-16GS, AN-31 can be used. It is ascertained that sorption capacity of the investigated sorbents makes up 3,7–4,1 mg/g depending on the form, poorly depends from pH in the investigated range. At sorption from natural and technogenic solutions the increase of sorption capacity up to 7,7–41,5 % is observed.
The content of the sulphates-ions up to 3 mg-equ/l and chlorides-ions up to 30 mg-equ/l in solutions does not influence essentially on process of extraction of boric acid.

REFERENCES

Belova T.P, Latkin A.S. (2003), "The principles of complex use of resources of high-temperature geothermal fluid," *Vladivostok: Dalnauka,* **206**.

Belova T.P, Latkin A.S. (2006) "Application of sorption technologies for solving of the environmental problems," *Petropavlovsk-Kamchatsky. Publishing house KamchatGTU*.. **117**.

Paholkov V.S, Shuvalov R.A. (1979) "Pollution of water surface by boric acid during exploitation of the geothermal fields. Thesis of the reports of scientifically-practical conference concerning of nature protection and rational use of natural resources of Kamchatka," *Petropavlovsk-Kamchatsky* 91-93.

"Technology of boric compounds," (1980) *Transactions of UNICHIM*, **138**, 51.

Arinushkina E.V. (1961), "Manual for the chemical analysis of soils," M: *Publishing house of the Moscow State University*, **490** .