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BORIC ACID OF HIGH PURITY RECOVERED FROM GEOTHERMAL WATERS

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ABSTRACT

The paper presents an original method of recovering boric acid from geothermal waters. The tests shows interesting economical results. On the other hand this is a depollution method in the same time. In Romania there is no other exploited boron resource. The boric acid is present in some geothermal sources from Bihor-county Romania at good enough level to be recovered from this poor in borori source. The method was patented by us.

RECOVERY OF THE BORIC ACID FROM WATERS

mineral or geothermal water. In the volcanic areas even the rain waters or the snow contains metaboric acid; thus in the Kirin district Japan the boron concentration in the rain water reaches up to 0.1 mg/L, whereas the water in the main ***stream*** of the river Tone contains **0.345** mg/L boron..

The boric acid can be encountered also in a series of used industrial waters, which might be a potential for recovering it.

The purpose of the paper is to remove boric acid from mineral waters or geothermal waters. The lowest oncentration of boric acid considerate to be conomical for recovery is about 50 mg acid per litre f water.

n Romania we have following situations:

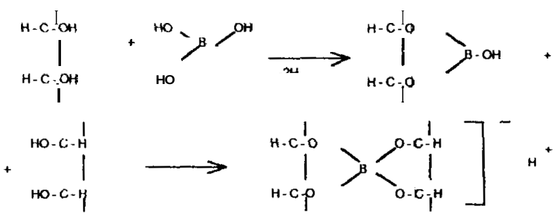
- mineral waters which have medium concentration around 800 **mg** acid per litre of water, with respect of 70 mg the low limit and 1300 mg the highest ;
- geothermal waters where the limits of concentration of the boric acid are among 50 to 200 mg/L.

Obtaining the Boric Acid from Geothermal Waters

A procedure of obtaining the boric acid from geothermal waters, has been accomplished in Romania in 1978 .The procedure uses a battery of columns filled with conventional ions' exchangers for retaining all the cations and anions, followed by the selective elution of the boric acid with warm water. In this case the disadvantage of the procedure is the price. The prime costs depend of the complete mineralization of the processed water. The high salt background of the water it will consume for regeneration more hydrochloric acid and ammonia.

We have used a certain adsorbent resin named Vionite **AS-111,** a resin on the divinyobenzen skeleton framework of which the glucaminical group is grafting. As a structure this resin is similar to the resin Amberlite XE-243, and it is a selective resin for retaining the boron

The Vionite AS-111 is a weak basic anionite, having in its structure an atom of tertiary aminical nitrogen, which can retain a certain quantity of anions in the solution. Retaining the boric acid is achieving by means of forming a complex combination between itself and the hydroxilical by structures in the glucaminical rest'



For extracting the boric acid in geothermal waters we have used the three different sources. These are the drill wells 4058-S; 4667-S and 4158-B. The most important features of the above-mentioned source are presented in **Table** 1. near-by:

Table 1. The physico-chemical characteristics of geothermal water sources

Source	**4058 S**		**4667 S**		**4158 B**	
Temperature °C	80				120	
Flow-rate l/s	20		8		20	
pH	7.20		7.80		7.15	
Conductivity. µS	7750		7400		22200	
TDS g/l	4.337		4.384		11.826	
Hardness germ.grd.	2.99		2.77		15.61	
Mineralization	5713.14		5554.95		12793.77	
Organic Subs. mg/L	46.99		140.20		27.07	
SiO_2 mg/L	47.50		60.00		106.00	
Phenol mg/L	5.25		18.50		a	
HBO_2 mg/L	75.09		120.00		299.05	
ANIONS	**mg/L**	**meq/L**	**mg/L**	**meq/L**	**mg/L**	**meq/L**
Cl^-	S36.84	23.500	638.28	17.998	6075.48	171.333
NO_2^-	a	-	a		4.41	0.096
NO_3^-	a	-	a		0.11	0.002
HCO_3^-	2951.91	48.392	3080.20	50.495	1627.84	26.686
SO_4^{2-}	a	-	51.03	1.067	139.49	2.906
PO_4^{3-}	a	-	a	-	0.30	0.009
Total anions		**72.992**		**69.556**		**201.02**
CATIONS	**mg/L**	**meq/L**			**mg/L**	**meq/L**
NH_4^+	7.40	0.411		0 389	8.33	0.463
Na^+	1650.00	71.739	1550.00	67.391	4484.36	194.972
K^+	24.50	0.626	30.00	0.676	[redacted]	
Ca^{2+}	14.43	0.720	12.72	0.635	75 15	31.750
Mg^{2+}	4.26	0.350	4.19	0.344	22.19	1.825
Fe^{2+}	1.20	0.040	1.53	0.055	0.63	0.022
Total cations		**73.886**		**69.581**		**201.03**

The flow of water in all cases of experiment was downflow.

The first series of experiments has been performed with the geothermal waters fiom a drilling source 4058 S. The geothermal water contains metaboric acid as 59,45 mg/L, this corresponding to 86,17 mg/L acid boric.

A glass column filled with 50 ml resin Vionite AS-111 has been used. The resin has been preconditioned by passing sulphuric acid solution 4%, and rinsing with deionized water, again passing 4% natrium hydroxide and rinsing with deionized water.

The tlow rate of the influent geothermal water was 500 ml/h. In these experiments the organic substances have not been eliminated out of the water. The results are presented in the table 2 and in figure 1.

Table 2. The repartition of boric acid on the column filled with Vionite AS-111 after source 4058 S.

Volume of water L	Conc. of HBO_2 mg/L	Conc. of H_3BO_3 mg/L	H_3BO_3 on column mg/L	Efficiency %
10	0.00	0.00	0.8617	100.00
12	2.28	3.29	0.1657	96.16
14	8.17	12.21	0.1479	85.83
16	16.72	24.14	0.12441	78.01
18	23.16	47.30	0.0777	45.11
20	34.08	49.20	0.0739	42.90
22	42.00	60.54	0.0511	29.63
24	53.50	77.24	0.0179	10.36
26	58.20	84.03	0.0043	9.93
28	60.00	86.63	0.0000	0.00
			1.5243	

The column retained 1.52g boric acid, that is due to an adsorption capacity of **30.486** mg/ml or **1.48** meq/L resin. The adsorption curve graph for this experiment is plotted in figure 1.

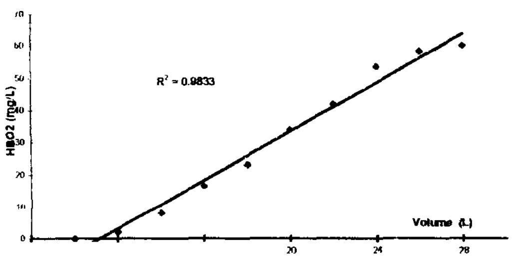


Figure 1. The adsorption on Vionite-AS 111 of boric acid from geothermal water source 4058-S.

The experiments for retaining the boric acid made on the same type of waters from the same region, without a preceding adsorption of organic substance have yielded contradictory results. In spite with resemblance of chemical composition of waters from source **4058** S to **4667 S,** the results were not reproducible. Thus wc have concluded that the experiments are disturbed because of the high concentration in organic substances, which **restrain** the adsorption of the boric acid on the resin. Without insisting further on the experiments of retaining the organic substances on a phenol selective resin CA-30 Romanian products we have established that the limit to which the presence of the organic substance does not disturb retaining of the bonc acid **as** being of 50 mg/L. Probably there where the water contains petrol fractions, these cover the resin with a pelt that will avoid the proper retaining of boric acid.

In this situation a column filled with **CA-30** a phenol selective resin adsorbent is inserted before the Vionite **AS-I** 11 column.

Our hypothesis was confirmed repeating the expenments on the water from the well 4667 S. Under the new conditions has yielded reproducible results. Following is such an example.

A glass column **350** mm high and 40 mm diameter , having a heating cover, has been filled in with **240 ml** Vionite **AS-** i11 **resin** After activation, being treated with 2,4 L sulfuric acid **4%,** after being washed with deionized water, and with **2,4** L sodium hydroxide **4%** has been poured over the column, at a temperature of 40-50°C, and it **has** been washed at free of the hydroxide.

Table 3. The distribution of the boric acid amongst the Vionite AS-I 11 resin and geothermal water from the well 4667 S

Volume of water L	Conc. of HBO_2 mg/L	Conc. of H_3BO_3 mg/L	H_3BO_3 on column mg/L	Efficiency %
8	0.00	0.00	1.1028	100.00
10	0.96	1.39	0.2729	99.49
12	1.22	1 76	0.2722	98.72
14	1.22	1.76	0.2722	98.72
16	2.39	3.45	0.2688	37.50
18	3.34	4.82	b.2661	96.50
20	5 67	8.19	0.2593	94.06
22	6.i9	8.94	0.2578	03.52
24	6.31	9.11	0.2575	93.39
26	10.74	15.51	0.2447	88.74
28	16.50	23.82	0.2280	82.72
30	17.33	25.05	0.2256	81.83
32	23 90	34 51	0 2067	74 97
34	26 04	37 60	0 2005	72 73
36	2980	4302	0 18896	68.79
38	31 10	4490	0 1859	67 43
40	32.20	46.49	0.1827	66.21
42	29.70	42.88	0.1S99	68.89
44	36.30	52.41	0.1708	61.98
46	38.75	ss.95	0.1638	59.41
48	41.71	60.22	0.1552	56.31
50	46.11	66.57	0.1425	51.70
52	58.42	84.35	0.1070	38.81
54	62.02	99.65	0.0760	27.71
56	74.60	107.71	0.0602	21.87
58	82.00	118.39	0.0389	14.11
60	90.09	130.07	0.0155	5.64
62	94.00	135.72	0.0043	1.55
64	95.24	137.50	0.0007	0.25
66	96.02	138.63	0.0000	0.00
68	95.50	137.88	0.0000	0.00
70	95.50	137.88	0.0000	0.00
			6.0172	

Over the column prepared this way the geothermal water from well 4667 S, has been poured, which was passed beforehand over the organic substances adsorbent **CA-30.** The initial concentration of bonc acid in influent was 94,48 mg HBO_2/L 137,85 mg

H_3BO_3/L . The experimental data are presented in table 3 and in figure 2

The retaining capacity of Vionite **AS-I**11 is 25,07 **mg/ml** or 1,21 meq/ml boric acid.
The adsorption diagrams are plotted **in** figure 2

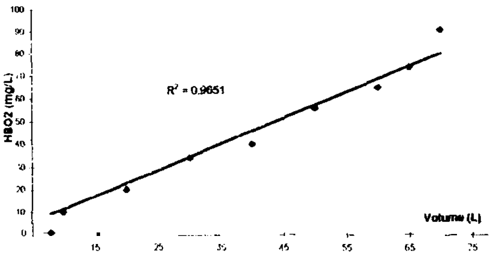


Figure 2 The adsorption on Vionite-AS I I I of boric acid from geothermal water source 4667-S.

The **series** of experiments carried out on geothermal waters from **well** 4158 B have been performed in similar conditions. The inttial concentration of metabonc acid was 299.75 **mg/L** that corresponds 432.78 **mg/L** boric acid. The experimental results are presented in table 4 and in figure 3.

***Table 4.** The distribution of the boric acid for the well 4158 B, thai has been passed over Vionite AS-111.*

Volume of water L	Conc. of HBO_2 mg/L	Conc. of H_3BO_3 mg/L	H_3BO_3 on column mg/L	Efficiency %
7	0.00	0.00	3.0295	100.00
8	1.22	1.76	0.4310	99.59
9	1.44	2.08	0.4307	99.52
10	2.39	3.45	0.4293	99.20
11	8.94	12.91	0.4199	97.02
12	10.86	15.68	0.4171	96.38
13	43.44	67.44	0.3693	85.52
14	107.40	155.06	0.2777	64.20
15	119.55	172.61	0.2602	60.15
16	137.79	198.94	0.2338	54.07
17	155.50	224.51	0.2083	48.17
18	188.70	286.88	0.1459	33.71
19	238.70	344.63	0.0881	21.00
20	238.70	344.63	0.0881	21.00
21	258.70	373.53	0.0593	13.69
22	268.50	387.67	0.0451	10.50
23	286.43	413.54	0.0192	4.53
24	298.88	431.52	0.0013	0.40
25	299.50	432.41	0.0004	0.08
			6.9542	

The retaining capacity of the column is 228.97 mg/ml or 1.41 meq/ **ml** bonc acid . The adsorption diagram is presented in figure 3. Studding the behavior of Vionite **AS-1**11 resin for retaining the boric acid from geothermal water, one *can* notice a very good adsorption capacity of 1.2- 1.4 meq/ml, compared to 1.35 meq/ml, which is the adsorption capacity if the Amberlite XE-243.

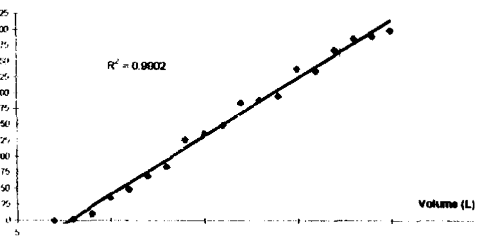


Fig. 3 The adsorption on Vionite-AS 111 of boric acid from geothermal waier source 4158-B.

Elution The Boric Acid** On The **Column

The removal of the boric acid on the column has been done with a solution of sulfuric acid 4%. One can notice that the elution curve **given** this circumstance, presents a peak. The boric acid migrates in to a sulfuric acid medium in a very narrow band. The distribution of boric acid during the elution is represented in tables 5; 6 and 7.

***Table 5.** The distribution of the boric acid during the elution for well 4667 S,*

No.	Vol. of eluent L	HBO_2 on resin mg/L	H_3BO_3 in efluent mg/L	H_3BO_3 recovered g
1	0.250	2052.31	2968.13	0.3254
2	0.500	7478.21	10793.1	2.6993
3	0.750	5622.12	8117.22	2.0293
4	1.000	1441.49	2081 22	0.5203
5	1.250	87.84	126.83	0.0317
6	1.500	0.00	0.00	0.0000
				6.0214

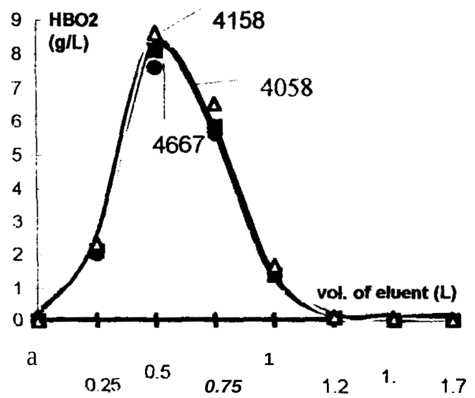
***Table 6.** The distribution of the boric acid during the elution for well 4058 S*

No .	Vol. of eluent L	HBO_2 on resin mg/L	H_3BO_3 in efluent mg/L	H_3BO_3 recovered g
1	0.250	2141.77	3092.29	0.7731
2	0.500	7804.25	11267.8	2.8169
3	0.750	5867.29	8471.20	2.1178
4	1.000	1405.42	2172.08	0.5430
5	1.250	92.15	133.05	0.0333
6	1.500	0.00	0.00	0.0000

*able. 7. **The distribution of the boric acid during the elution for well 4158 B***

No.	Vol. of eluent L	HBO_2 on resin mg/L	H_3BO_3 in effluent mg/L	H_3BO_3 recovered g
1	0.250	2351.73	3396.43	0.8488
2	0.500	8622.18	12448.70	3.1122
3	0.750	6477.15	9351.71	2.3379
4	1.000	1666.84	2405.14	0.6010
5	1.250	113.04	161.77	0.0404
6	1.500	51.00	76.63	0.0184
7	1.750	0.00	0.00	0.0000
				6.9587

oncluding the results of the retained and cleansed oric acid, it can be noticed that can this to be found ithin the limit if the experimental errors.
he elution graphs are plotted in figure 4.



ure 4. The elution curve of the **3 cases**

n view of reducing the sulfuric acid consumption uring the elution, we have used only 240 ml H_2SO_4, ı two **stages** of 120 ml each.

No.	H_3BO_3 on resin	H_3BO_3 eluted g
1	6.2473	5.9839
2	5.9889	5.9589
3	6.0149	6.0021
4	6.3964	6.4005
5	6.2954	6.2001
6	5.8375	5.1982

Consequently we have pasted over the resin 120 ml ulfuric acid **4%;** after an hour paused the second ›ortion of 120 **ml sulfuric** acid **we** have over pasted.

Waiting for one hour again we started to wash with deionized water until **free** of sulphuric acid.
Table 8. presents the boric acid elution.
The efficiency is 95%, which corresponds to our purpose.

Isolating The ***Boric Acid***

The boric acid solution, obtained by elution with sulfuric acid, turns out like a colorless and clear liquid. **Its** concentration **varies** among 5-6 **g/L**. The solution thus obtained is neutralized with calcium hydroxide at a pH = 5-6, after which it is filtered and concentrated at 50 ml. After cooling, the boric acid crystallizes, and then is filtered and dried. **A** quantity of **4.5** g to 5.2 g boric acid of 98-99% pure has been obtained.

Another variant by which the sulfuric acid is eliminated is treating it with limestone or dolomite. On this way diluting the solution with water is eliminated. The disadvantage ***of*** this method ıs the quite intense foaming, requiring much care during the experıment.

A final variant suggested, perhaps the most advantageous one, is interposing during the final stage, of a column filled with weak basic anionite that retains the sulfuric acid, and being a strongly acid medium, the boric acid will not be retained. In this case, as well, the staples will be diluted.

We have opied for the variant with lime stone or dolomite because their lower costs.

Conclusions

The efficiency of the procedure is 95-96%, which corresponds to our purpose.

Applying this procedure to **4158-S** the figures shows the possibility of recovering aprox.195 t per **year** of bonc acid of 96-99% **purity.**

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