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Experimental Study of Boron Recovery from Geothermal Water on Ion Exchange

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ABSTRACT

This paper presents studies regarding the process of boron recovery from geothermal waters using the method of ion exchange. The optimal conditions of this process were determined using fluids with a methaboric acid content in the range of 59 to 100 mg/l, and a good retention degree was achieved. Geothermal wells in northwestern Romania were selected after being found to have high borate contents during chemical analysis. First it was realized the retention of boric acid from waters on a resin Vionit AS-116 produced in Romania. It was noticed that waters that contain organic compounds like phenol reduce the retention process of boric acid. For these waters, a retention process of the phenols on a copolymeric resin CA-30 produced in Romania was applied, and a good resin performance was achieved;. After the phenol was removed, the retention of boric acid from water on Vionit AS-116 resin was performed under favorable conditions. The retained boric acid was then eluted from the resin with a diluted sulphuric acid solution. The ion exchange AS-106 was proven to have a high retention capacity. In the situation where the phenol content was high, a treatment was first applied to eliminate it from water, and then the procedure of boron recovery from water was continued under favorable conditions.

1. INTRODUCTION

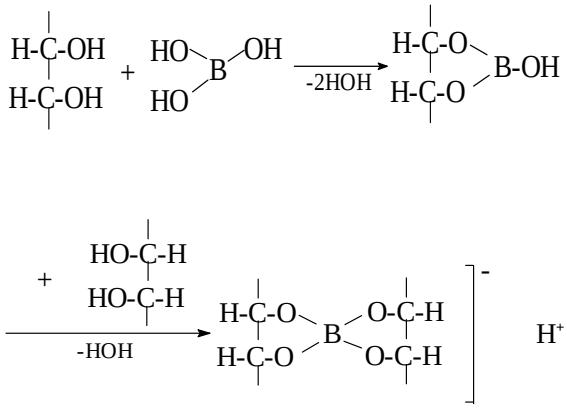
The majority of boron used in Romania is supplied from abroad. Therefore, all natural resources with boron content must be considered. The western side of Romania has plenty of geothermal resources, two of which were considered in this study. Comparative studies of boron recovery from geothermal waters were performed using low temperature geothermal waters with comparable boron contents but different phenol contents.

Good resin performance was achieved in the removal of the phenols from the geothermal waters, and the optimal conditions of boron recovery were determined.

In order to extract boric acid, water from the production wells 4058 Săcuieni and 4667 Salonta were used, both of which have arthesian flowrates of about 10 l/s.

2. EXPERIMENTAL PROCEDURES

The retention of boric acid from waters of the studied wells was tested (Crişan, et. al) using Vionit AS-116 ionic exchange resin produced in Romania. This selective resin has a glucaminic substituent on a divinilbenzenic structure. It is a slightly basic anion. The retention of boric acid is realized by forming a complex between the boric acid and the hydroxilic substituents from the glucaminic rest, as shown:



Geothermal water from well 4058 was passed through the column with 50 ml Vionit AS-116 at a starting flowrate of 500 ml/hour. Samples were collected, and the methaboric acid concentration was detected using a spectrophotometric method (Stănăşel, 2003).

Due to a difficult retention of metaboric acid in water with high contents of organic compounds (***, 1992), it was attempted to first retain the phenols on a copolymeric resin. In order to facilitate boric acid retention from waters from well 4667, the behavior of a copolymeric resin CA-30, which retains phenols from aqueous solutions, was studied (Gilău, 1997). The copolymers of this resin are characterized by the fact that they do not present ionic substituents. They are hydrophobic, and the adsorption properties result from the porous structure, large specific surfaces and aromatic character of the basic compound. This kind of resin fits to adsorption from aqueous solutions of organic compounds with rather small molecular masses. A positive aspect is that this resin has a good thermal resistance, making it possible to utilize it at temperatures up to 250ºC. Water from well 4667 containing 50 ml resin CA-30 was passed through the column. A repartition of phenols occurred between the aqueous solution and the copolymeric resin. The phenol from the CA-30 resin was then removed by passing methanol through the column at a flowrate of 500 ml/hour.

These experiments of boron recovery were repeated after the phenols were adsorped on a CA-30 resin. A column with 240 ml of Vionit AS-116 resin was used (Gilău). Geothermal water from well 4667 with 134 mg boric acid/l was passed through the resin.

3. RESULTS AND DISCUSSION

The results of boron and phenol analysis from these waters are shown in Table 1.

The resin retained a total of 1.52 g of boric acid. Based on data in Table 2, the capacity of adsorption of the resin was calculated to be 30.48 mg H_3BO_3/ml resin.

The experiments of boron recovery from geothermal water from well 4667 were fairly unsuccessful, even if the concentration of methaboric acid in water were comparable to that of well 4058. It was assumed that the plugging process of the resin was caused by retention of the organic compounds presented into the water. The experimental results of the retention of phenols from the water of well 4667 on CA-30 resin are summarized in Table 3.

Based on the data from Table 3, the adsorption capacity of CA-30 was calculated to be 6.62 mg phenol / ml resin. The phenol from the CA-30 resin was removed by passing methanol through the column. These results are presented in Table 4. The elution of the phenol from the column is illustrated in Figure 1. As can be seen in the Figure, a good efficiency was achieved when removing the phenol from the resin with methanol, with a maximum value corresponding to a volume of 125 ml methanol, after which the elution process experienced a suddenly decrease. Even if methanol continues to pass through the column, the extracted phenol from the resin is insignificant.

Table 1. Chemical content of boron and phenol (mg/l)

Well	HBO_2 [mg/l]	Phenol [mg/l]
4058	59.45	5.25
4667	95.10	115.00

The Vionit AS-116 resin kept the boric acid from water, as indicated in Table 2.

Table 2. Repartition of boric acid between water from well 4058 and the Vionit AS-116 resin

Volume of water [l]	HBO_2 in water [mg/l]	H_3BO_3 in water [mg/l]	H_3BO_3 kept on resin [g]
10	0.00	0.00	0.8614
12	2.28	3.19	0.1657
14	8.17	11.43	0.1479
16	16.72	23.40	0.1244
18	23.16	32.42	0.0779
20	34.08	47.71	0.0739
22	42.00	58.80	0.0511
24	53.50	74.90	0.0179
26	58.20	81.48	0.0043
28	60.00	84.00	0.0000
			1.5245

Table 3. Repartition of phenol between water and resin CA-30

Water volume [l]	Concentration of phenol in water [mg/l]	Concentration of retained phenol on resin CA-30 [mg/l]
2.10	0.00	241.50
2.20	1.24	11.38
2.30	3.40	11.06
2.40	7.20	10.78
2.50	14.70	10.03
2.60	18.40	9.66
2.70	32.20	8.28
2.80	40.00	7.50
2.85	52.00	3.15
2.90	56.00	2.95
2.95	56.50	2.92
3.00	68.50	2.32
3.05	73.00	2.15
3.10	76.00	1.95
3.15	84.00	1.55
3.25	95.00	2.00
3.40	101.00	2.10
3.55	115.00	0.00
4.00	115.00	0.00
		331.00

Table 4. Phenol repartition during elution with methanol

Volume of methanol [ml]	Phenol [mg/1]	Extracted phenol [mg]
25	222.40	5.56
50	1641.60	41.04
75	2975.20	74.38
100	3852.40	96.31
125	4353.60	108.84
150	100.40	2.51
175	41.60	1.04
200	26.80	0.67
225	14.40	0.36
250	9.60	0.24
275	0.00	0.00
		330.95

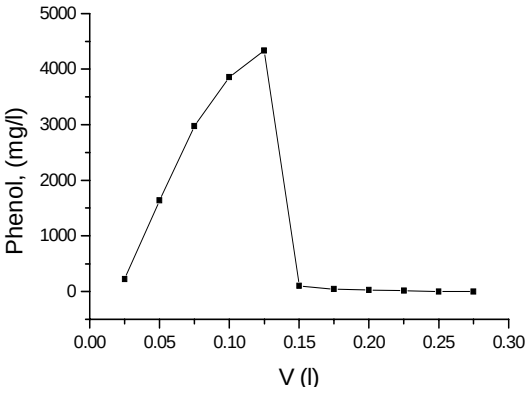


Figure 1. Elution of phenol with methanol.

Table 5. Repartition of boric acid between water from well 4667 and the Vionit AS-116 resin

Volume of water [l]	HBO_2 in water [mg/l]	H_3BO_3 in water [mg/l]	H_3BO_3 kept on the resin [g]
8	0.00	0.00	1.1028
10	0.96	1.34	0.2729
12	1.22	1.70	0.2722
14	1.22	1.70	0.2722
16	2.39	3.34	0.2688
18	3.34	4.67	0.2661
20	5.67	7.93	0.2593
22	6.19	8.66	0.2578
24	6.31	8.83	0.2575
26	10.74	15.03	0.2447
28	16.50	23.10	0 2280
30	17.35	24.29	0.2256
32	23.90	33.46	0.2067
34	26.04	36.45	0.2005
36	29.80	41.72	0.1890
38	31.10	43.54	0.1859
40	32.20	45.08	0.1827
42	29.70	41.58	0.1899
44	36.30	50.82	0.1708
46	38.75	54.25	0.1638
48	41.71	58.39	0.1552
50	46.11	64.55	0.1425
52	58.42	81.78	0.1070
54	62.02	86.82	0.0760
56	74.60	104.44	0.0602
58	82.00	114.80	0.0389
60	90.09	126.12	0.0155
62	94.00	131.60	0.0043
64	95.24	133.33	0.0007
66	94.68	133.42	0.0000
68	95.50	133.70	0.0000
70	95.50	133.70	0.0000
			6.0172

Table 6. Extracted boric acid

Volume of H_2SO_4 4% [l]	Extracted H_3BO_3 (from well 4058) [g]	Extracted H_3BO_3 (from well 4667) [g]
0.250	0.1740	0.3254
0.500	0.6341	2.6993
0.750	0.4767	2.0293
1.000	0.1222	0.5203
1.250	0.0070	0.0317
1.500	0.0000	0.0000
	1.4140	5.6060

After the phenols in geothermal water from well 4667 were adsorbed, the experiments of boron retention on the resin Vionit AS-116 were continued, the results of which are summarized in Table 5.

The resin retained 6.0172 g of boric acid. The calculated adsorption capacity of the resin is 25 mg H_3BO_3/ml resin. The elution of boric acid from the resin column was realized by using a 4% sulphuric acid solution. The boric acid migrates in sulphuric acid at very short intervals. The extracted boric acid from the Vionit AS-116 resin is presented in Table 6 for the waters from the two geothermal wells.

4. CONCLUSIONS

The aim of this paper was to establish a method to recover boron from geothermal waters for use.

Waters with a certain amount of boron determined by spectrophotometry were passed through a column filled with an ionic exchange resin called Vionit AS-116 that is produced in Romania. The adsorption capacities of the Vionit AS-116 resin were found to be 30.48 and 25 mg H_3BO_3/ ml resin for waters from wells 4058 and 4667, respectively.

As the organic content of the water increases, the retention of boric acid decreases. For waters from well 4667 with higher phenol concentrations, a preliminary treatment was necessary. The phenol was retained on a column with a copolymeric resin called CA-30 and then removed with methanol.

The elution of the boric acid from the Vionit AS-116 resin was performed using 4% sulphuric acid, and a good elution was achieved with 750 ml of acid solution. The experimental data showed that all the retained boric acid was eluted.

The obtained boric acid solution with a concentration around 6 g/l may be concentrated to obtain high purity crystals of boric acid.

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