Studies on Boron Recovery

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Abstract: This paper presents the studies made in laboratory in order to recover boron from waters, where boron is found as borate. First it was realised the retention of boric acid from waters on a resin Vionit AS-116 produced in Romania. It was noticed that waters, which content organic compounds like phenol, reduce the retention process of boric acid. For these waters it was applied a retention process of the phenols on a copolymeric resin CA-30 produced in Romania. After that phenol was removed, the retention of boric acid from water on Vionit AS-116 resin was done in good conditions. The retained boric acid was then eluted from the resin with a diluted sulphuric acid solution. In this way it could be recovered boron from solutions with a methaboric acid content around 100 mg/l.

Introduction

In Romania most of boron necessity is supplied from abroad. In these conditions, all resources with boron content must be considered. The western side of Romania has plenty of geothermal resources. In order to recover boron, two of them were taken in this study. Comparative studies of boron recovery from geothermal waters were made by using geothermal waters of low temperature, having comparable boron content, but different phenol content.

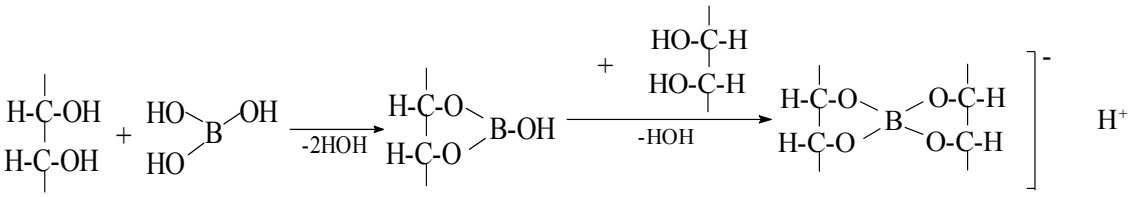
Results and discussion

In order to extract boric acid from geothermal waters there were used waters from the production wells 4058 Săcuieni and 4667 Salonta, which have an arthesian flowrate of about 10 l/s. The results of boron [1] and phenol [2] analysis from these waters are shown in Table 1.

Table 1. Chemical content of boron and phenol, in mg/l

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

Retention of boric acid from waters from the studied wells was experimented [3] by using an ionic exchange resin Vionit AS-116 produced by Romanian. This selective resin has a glucaminic substituent on a divinilbenzenic structure. It is a slight basic anionit. The retention of boric acid is realised by forming a complex between the boric acid and the hydroxilic substituents from the glucaminic rest, as follows:



Through the column with 50 ml Vionit AS-116 they passed geothermal water from well 4058 with a start flowrate of 500 ml/hour. Samples were collected and the methaboric acid concentration was detected by a spectrophotometric method [1]. The resin kept the boric acid from water, the results being indicated in Table 2.

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

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

The resin retained a total of 1.52 g boric acid. Based on data from Table 2 it was calculated the capacity of adsorption of the resin as 30.48 mg H_3BO_3/ml resin.

The experiments made for recovery of boron from geothermal water from well 4667 were not good at all, 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 must be due to a retention of the organic compounds presented into the water. In order to facilitate boric acid retention from waters it was studied the behavior of a copolymeric resin CA-30, that retains the phenols from aqueous solutions [4]. The copolymers from this resin are characterized by the fact that they do not present ionic substituents. They are hydrofobes and the adsorption properties result from the porous structure, large specific surfaces and due to the aromatic character of the basic compound. This kind of resin fits to adsorption from aqueous solutions of organic compounds with rather small molecular mass. A positive aspect is that this resin has a good thermic resistance, being possible to utilize it up to 250ºC. Water from well 4667 passed through the column filled with 50 ml resin CA-30. It happened a repartition of phenols between the aqueous solution and the resin CA-30. The experimental results are summarized in Table 3.

Based on the data from Table 3 it was calculated the adsorption capacity of CA-30 as 6.62 mg phenol / ml resin. The phenol from the CA-30 resin was removed by passing methanol with a flowrate of 500 ml/hour through the column. In Table 4 are presented the results. The elution of the phenol from the column is suggestive illustrated in Figure 1. You can notice a very good efficiency of removing the phenol from the resin, with methanol, with a maximum corresponding to a volume of 125 ml methanol and then the elution process records a suddenly decrease. Even if methanol continues to pass through the column, the extracted phenol from the resin is insignificantly.

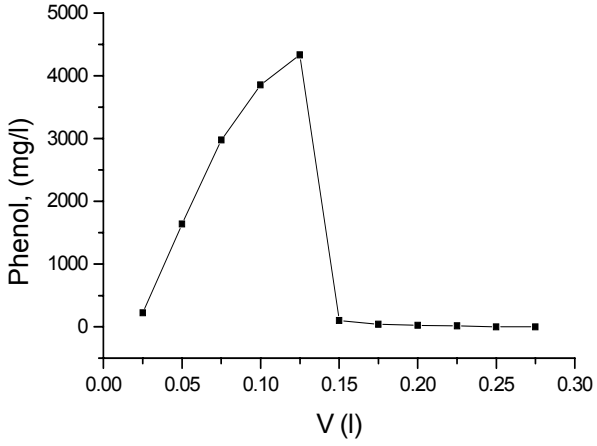


Figure 1. Elution of phenol with methanol.

The experiments for boron recovery were repeated after the phenols were adsorpted on a CA-30 resin. A column with 240 ml resin Vionit AS-116 was used. Geothermal water from well 4667 with 134 mg boric acid/l passed through the resin, the results being summarized in Table 5.

The resin retained 6.0172 g boric acid. The calculated capacity of adsorption of the resin is 25 mg H_3BO_3/ml resin. The elution of boric acid from the resin column was realised by using sulphuric acid solution 4% [5]. The boric acid migrates in sulphuric acid in a very short interval. The extracted boric acid from the resin Vionit AS-116 is presented in Table 6 for the waters from the two geothermal wells.

Conclusions

The aim of this paper was to establish a method to recover a useful mineral compound from waters. Waters with a certain amount of boron determined by spectrophotometry were passed through the column filled with an ionic exchange resin Vionit AS-116 produced in Romania. The capacity of adsorption of the resin Vionit AS-116 was 30.48 mg H_3BO_3/ ml resin for waters from well 4058, respectively 25 mg H_3BO_3/ ml resin for waters from well 4667.

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

The elution of the boric acid from the Vionit AS-116 resin was performed by the use of sulphuric acid 4%, a good elution being done with 750 ml 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 used to be concentrated in order to obtain crystals of boric acid of high purity.

References

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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/l	Extracted phenol, mg
25	222.40	5.56
50	1641.6	41.04
75	2975.2	74.38
100	3852.4	96.31
125	4353.6	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

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

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