

BORON POLLUTION IN THE SIMAV RIVER, TURKEY AND VARIOUS METHODS OF BORON REMOVAL

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Abstract—The present study was undertaken to investigate various methods for boron removal from the drainage waters of the Bigadic boron mines of Turkey. α -Cellulose, magnesium oxide and boron-specific resin Amberlite IRA-743 (Rohm & Haas Co.) were selected for the present work. Experimental results show that both the adsorption method using magnesium oxide and the ion-exchange operations are effective in removing boron from the drainage waters. Cellulose as an adsorbent has a minimum efficiency. MgO can be used effectively at a Mg/B mol ratio of 20 for three cleaning cycles with 85% removal efficiency but must be discharged and refreshed after the third cycle. Consumption of 18,100 tons of MgO per year in the removal system makes this process uneconomical. Boron-specific resin Amberlite IRA-743 in free-amine form is also uneconomical due to expensive regeneration steps. The capacity of this resin in salt-form was found to be 1.5 mg boron ml⁻¹ resin at 10% boron leakage and at a flow rate of 16 l h⁻¹ l⁻¹. The possibility of reuse of 90% of the regenerant and production of 4400 tons of boric acid in the removal system with salt-form boron-specific resin, compensate the annual cost of chemicals and also bring in some profit.

Key words—boron pollution, boron removal, adsorption, ion-exchange, boron-specific resin, waste water treatment, water pollution, irrigation water, discharge waters

INTRODUCTION

This study aims to provide the most cost-effective method for disposal of boron-laden drainage waters from boron mines. The boron mines in question are in the Bigadic district of Turkey where there are colemanite and ulexite reserves. The Bigadic district is important both from the view of agricultural potential and of that borate production. There is a significant amount of drainage water discharged from the boron mines into the Simav River, as a result of borate production. About 33,000 ha of agricultural land, which is irrigated by the Simav River is threatened by boron pollution which is causing a national income loss of 20×10^6 \$ (1981 unit price); a further 35,100 ha of land is under the threat of boron pollution (Onel, 1981).

This paper details the extent of boron pollution in Bigadic district and the results of a literature survey evaluating the technology of boron removal. Experimental work related specifically to the Bigadic boron mines district and treatment systems proposed are also discussed.

BORON POLLUTION IN TURKEY

Turkey possesses approx. 60% of the world's boron reserves. The known borate reserves in Turkey are located in four main districts, namely Emet, Bigadic, Kirka and Mustafakemalpaşa. These four districts frame a rectangular area of approx. 100 km in width and 200 km in length and are all located in the

vicinity of the Simav River (Fig. 1). Consequently boron pollution has reached dangerous dimensions, especially in the Simav River, which is used for irrigation purposes (Onel, 1981).

The boron mines are located 5–10 km to the north of Bigadic town and along the side of the Simav River (Fig. 1). Boron compounds present the main source of chemical pollution of the Simav River water. Previous studies of the region show that the boron concentration of the Simav River is in the range of 0–0.5 mg l⁻¹ before it enters the mining region (Onel, 1981). The boron concentration of the river increases up to 4 mg l⁻¹ after it receives the discharge waters from the mines and may increase up to 7 mg l⁻¹ during the irrigation season. The increase of the boron concentration in the Simav River through the boron mining district is shown in Fig. 2. The relation of the boron concentration to the flow rate of the Simav River measured at the Kaletpe regulator is given in Fig. 3. An annual increase of 150–280% boron was detected in Balıkesir plain which was irrigated by the Simav River.

Previous studies of State Water Works (DSI) show that the boron containing soils excavated from the mines do not cause pollution; the main source of boron pollution in the Simav River is the drainage waters discharged from the boron mines into the river (Onel, 1981). The chemical analyses and the flow rates of the drainage waters are listed in Table 1. The Simav River receives the drainage waters from Avsar, Simav and Yenikoy mines, which contain approx. 135 mg l⁻¹ boron with a flow rate of 230 l s⁻¹. This

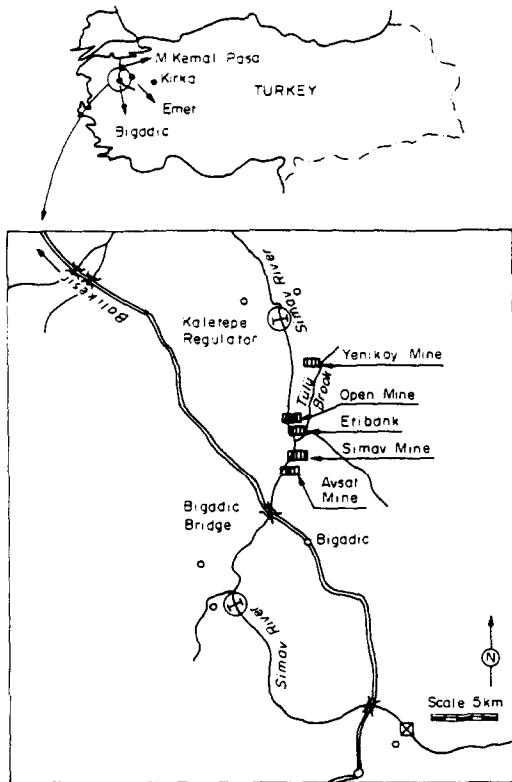


Fig. 1. Map of the Bigadic area showing the Simav River and the boron mines.

is equivalent to 1000 tons of boron per year (or 5500 tons boric acid/year) which is transported by the Simav River to the Marmara Sea.

There are two main alternatives to prevent the boron pollution in the Simav River:

First is to collect the drainage waters from the boron mines in a dam for 11 months and then discharge them into the river at the end of the irrigation season when the flow of the river is maximum. The volume of this dam, planned by DSI (State Water Works) would need to be $25 \times 10^6 \text{ m}^3$. The disadvantage of this solution is that the boron

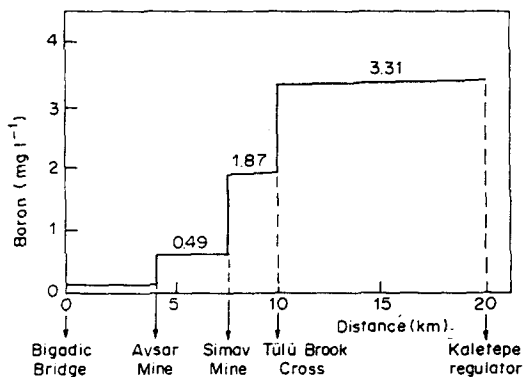


Fig. 2. Increase of the boron concentration in the Simav River through the boron mining district (based on the averages of the analyses done between 15 November 1977—2 April 1979) (Onel, 1981).

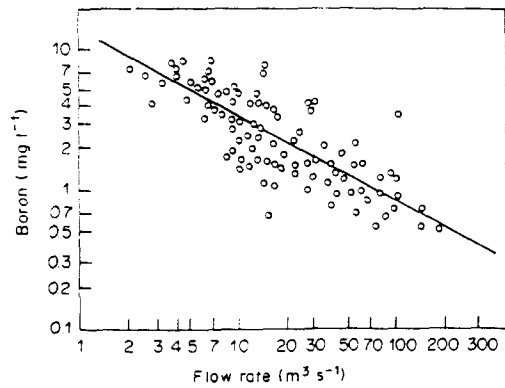


Fig. 3. Relation of the boron concentration to the flow rate of the Simav River (observation point is the Kaletepe regulator on the Simav River) (Onel, 1981).

accumulated in the dam for the whole year which approximates to 1000 tons boron would be discharged into the river during 1 month; this would result in a sudden increase in the boron concentration of the river and could alter the ecological balance of the Marmara Sea.

The second alternative is the removal of boron from the drainage waters by using suitable adsorbing agents or boron-specific resins.

SELECTION OF THE METHODS FOR BORON REMOVAL

There is no easy method for the removal of boron from waters and waste waters. Boron removal by conventional biological treatment and chemical coagulation with lime, ferrous and aluminium salts etc. has proved to be ineffective (Waggott, 1969). The adsorption of boron by clays, soils and other minerals has been extensively studied by many investigators (Metwally *et al.*, 1974; Choi and Chen, 1979; Keren *et al.*, 1981; Keren and Mezuman, 1981; Keren and O'Conner, 1982). Krejcirik (1968) reviewed magnesium oxide as a potential adsorbent for the removal of boron from aqueous solutions, where the activity of the adsorbent was regained by heating. Other widely reported techniques for removing boron from a solution, namely evaporation-crystallization and solvent extraction processes, are effective in high concentration streams and are geared more to the production of boric acid rather than to its removal from boron waters (Garbato 1961; Garrett *et al.*, 1963; Basol and Eren, 1975; Grinstead, 1972).

Ion-exchange processes with strong base anion-exchange resins, are effective for removing boron but all other ionic species are also removed, rendering the operation uneconomical if boron is considered as the only objectional constituent. Boron-specific resin Amberlite IRA-743 with sorbitol functional groups, viz., $\text{R}-\text{CH}_2-\text{N}(\text{CH}_3)-\text{C}_6\text{H}_8(\text{OH})_5$, forms complexes with boron and is highly specific. Using this resin it is possible to reduce the boron concentration below 1 mg l^{-1} in water (Kunin, 1973; Rohm & Haas Co., 1980). Polysaccharides like cellulose and starch,

also form complexes with boron and act as a boron-specific resin (Kane and Anstadt, 1971).

In the present study, α -cellulose, magnesium oxide and boron-specific resin Amberlite IRA-743 were selected for the boron removal tests.

EXPERIMENTAL

Characteristics of the materials

α -Cellulose (Seka Co.), ground. Magnesium oxide (Bozuyuk Chem. Co.), mean particle diameter = 0.10–0.25 mm, total porosity = 74%. Amberlite IRA-743 (Rohm & Haas Co.), boron specific resin, effective particle dia = 0.45 mm.

Experimental parameters and methods

Boric acid (reagent grade) in distilled water and the drainage waters of the Bigadic boron mines were used as the source of boron throughout the study. Boron concentrations were determined by the carminic acid method (Hatcher and Wilcox, 1950). The percentage of boron adsorbed on MgO was determined by titration in the presence of mannitol. The chemical compositions of the drainage waters were determined by flame photometric, atomic absorption and titrimetric methods.

In batch experiments 300 ml of boron contaminated water was taken in 500 ml glass bottles. To these, varying amounts of adsorbent were added. These bottles were stirred for a predetermined contact time at room temperature ($22 \pm 2^\circ\text{C}$) or at a constant temperature. The boron adsorbed was calculated as the difference between the amount added and that found in the solution at equilibrium.

In column experiments, the boron solution was passed with a constant flow rate through the columns which were filled with various adsorbents or resins. Concentration of effluent was determined periodically to obtain the concentration history of the procedure. A glass pipe equipped with various chromatography fittings were used for the column tests. Column tests with boron-specific resin were carried out at a flow rate of 161 h^{-1} . The exhausted beds were backwashed for 10 min at a column expansion of 100%. Regeneration was done at a flow rate of 81 h^{-1} . The volume capacity data is expressed in terms of the free-amine resin form.

RESULTS

Boron adsorption studies using α -cellulose are presented in Fig. 4. The results indicate that the boron retention capacity increases, although the breakthrough capacity decreases with the increasing boron concentration in the solution. The total boron retention capacity of cellulose was found to vary between 0.30–0.54 mg boron g^{-1} cellulose. Boron saturated cellulose can be regenerated with distilled water at room temperature. In laboratory studies using magnesium oxide as the adsorbent for boron, the effects of boron concentration and sorbent concentration in a solution and adsorption temperatures have been examined in order to determine the optimum conditions of adsorption.

As with cellulose, the boron removal efficiency of magnesium oxide increases from 70 to 90% with increasing boron concentration in solution (Fig. 5). The effect of temperature on the rate of boron adsorption on MgO is very significant (Fig. 6). For example at 72°C MgO removes 95% of boron from

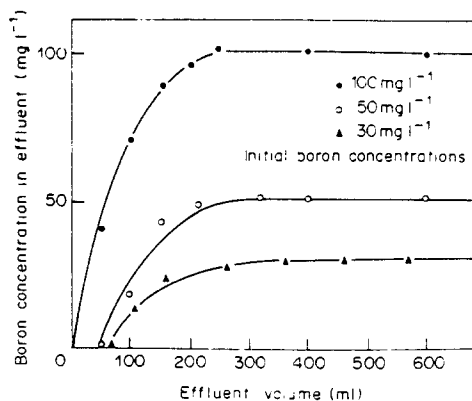


Fig. 4. Concentration history for boron removal from boron-distilled water solutions by α -cellulose (column: height = 42 cm, 3.19 cm i.d., flow rate = 2.64 ml min^{-1} , amount of cellulose = 10 g).

aqueous solutions after a contact time of 20 min, whereas only 10–15% of boron is removed at 20°C during the same contact time.

The effect of the Mg/B mol ratio on the boron removal for various boron concentrations is given in Fig. 7. The results show that the boron removal efficiency increases rapidly with increasing Mg/B ratio until a value of 15–20 is reached. Beyond this critical value, the Mg/B ratio has very little effect on the boron removal efficiency.

In conclusion, for an optimum adsorption process with MgO, the following points must be emphasized:

(1) To remove 70–90% boron from the solution, it is necessary to add 15–20 mol MgO/mol boron to the solution.

(2) The equilibrium time is maximum 2 h for temperatures of 40°C or over, and shows a decrease with the increasing temperature. At room temperature, the equilibrium time is around 10 h; however the same boron retention is observed for constant Mg/B mol ratio at all temperatures.

After the boron adsorption reaches an equilibrium value, the MgO can be filtered and reused as sorbent either with or without regeneration. The results of using MgO several times is shown in Fig. 8. The

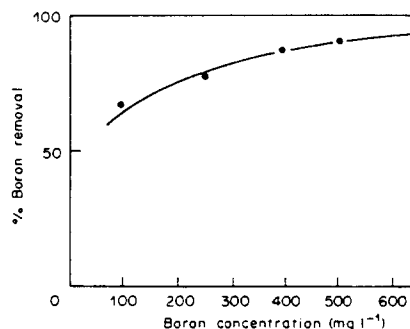


Fig. 5. Concentration history for boron removal from boron-distilled water solutions by magnesium oxide (volume of the solution = 300 ml, amount of MgO = 18 mol Mg/mol B, temp. = $22 \pm 2^\circ\text{C}$, contact time = 24 h).

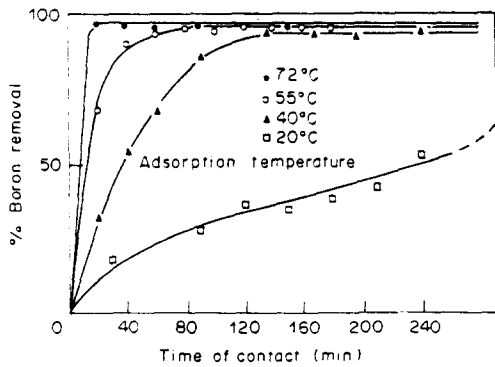


Fig. 6. Effect of temperature on the rate of boron adsorption on magnesium oxide (initial boron concentration = 500 mg l^{-1} , volume = 700 ml, amount of $\text{MgO} = 23 \text{ mol Mg/mol B}$).

boron removal efficiency decreases in successive runs. After regeneration by heating to 500°C , some increase is observed in the efficiency but MgO stays suspended in the solution and does not settle. The analysis of the sorbent after the 5th run shows 3.35% boron ($10.73\% \text{ B}_2\text{O}_3$).

Tests with MgO were also carried out on drainage waters from the Simav and Yenikoy mines. The results revealed that the boron removal efficiency of MgO was not affected by the presence of other ions. The analyses of drainage waters after sorption showed that the boron concentrations of the original samples were reduced by 85%.

As expected, the boron-specific resin Amberlite IRA-743 is also effective for the removal of boron from solution. The breakthrough capacity (at 1 mg l^{-1} boron in effluent) of this resin in free-amine form was found to be $2.25 \text{ mg boron ml}^{-1}$ resin. As shown in Fig. 9(a), this resin is unaffected by the presence of other ions in the drainage waters. Conventionally, the exhausted boron-specific resin is regenerated first with 10% sulphuric acid solution with an amount of $48 \text{ kg H}_2\text{SO}_4 \text{ m}^{-3}$ resin (Rohm & Haas Co., 1980). This strips off the complexed boron and converts the column to the salt form. Since the amine group of the

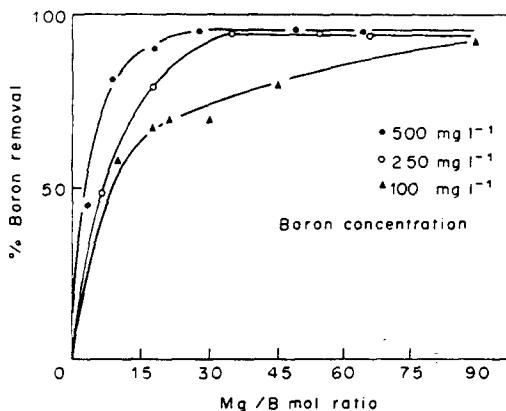


Fig. 7. Effect of the Mg/B mol ratio on the boron removal for various boron concentrations (volume = 300 ml, temp. = $22 \pm 2^\circ\text{C}$, contact time = 24 h).

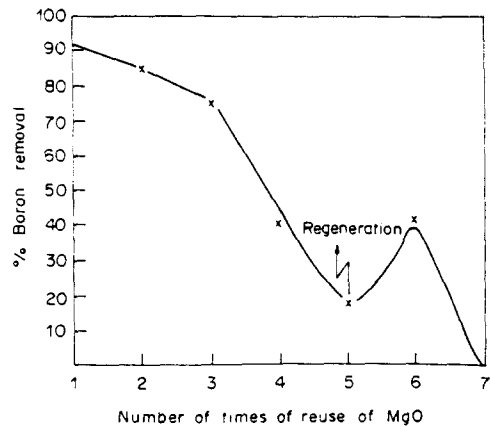


Fig. 8. Effect of the number of times of reuse of MgO to the boron removal efficiency (volume = 300 ml, amount of $\text{MgO} = 18 \text{ mol Mg/mol B}$, temp. = $22 \pm 2^\circ\text{C}$, contact time = 24 h, initial boron concentration = 500 mg l^{-1}).

resin is neutralized during the acid regeneration to form the acid sulphate, hydrolysis of the amine acid sulphate during the subsequent exhaustion cycle results in a very acidic effluent. To avoid this, the resin is then converted back to the free-amine form with 4% NaOH solution with an amount of $64 \text{ kg NaOH m}^{-3}$ resin. The following scheme expresses the load-

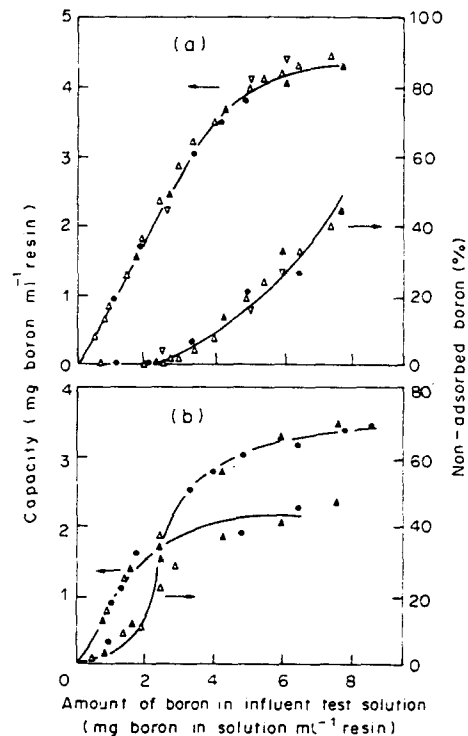
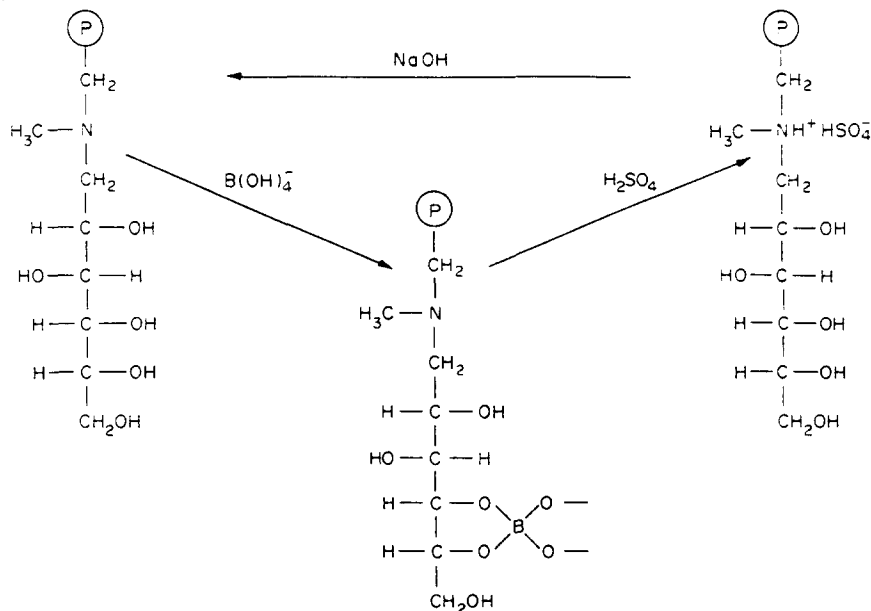


Fig. 9. Boron removal by Amberlite IRA-743 in free-amine form (a) and in salt form (b) for various boron solutions; (∇) boron-distilled water solution ($100 \text{ mg l}^{-1} \text{ B}$); (Δ) boron-distilled water solution (300 mg B l^{-1}); (\blacktriangle) drainage water of the Simav mine (260 mg B l^{-1}); (\bullet) drainage water of the Yenikoy mine (390 mg B l^{-1}); (amount of the resin = 15 ml, column: height = 22 cm, 0.93 cm i.d., flow rate = $16 \text{ l h}^{-1} \text{ l}^{-1}$).

ing and elution of the boron specific resin in free-amine form:



Consequently, this process of boron removal from solutions of high boron concentrations and high flow rate such as the drainage waters of Bigadic boron mines, is totally uneconomical. It has been found that the exhausted beds can be regenerated only with 10% sulphuric acid solution at a level of 30.4 kg $\text{H}_2\text{SO}_4 \text{ m}^{-3}$ resin with a 14% lowering in boron adsorption capacity (Roberts, 1971). The influent boron solution in these experiments exhibited a pH of 7.9 and contained 4890 mg l^{-1} dissolved solids and 10 mg l^{-1} boron.

The results of the exhaustion tests on the boron-specific resin regenerated with 10% sulphuric acid solution only (salt-form resin) are given in Fig. 9(b). The exhaustion run exhibited immediate boron leakage. However, the boron retention capacity at 10% boron leakage was found to be 1.5 mg boron ml^{-1} resin. 10% boron leakage corresponds to the breakthrough capacity for influent solutions containing 10 mg l^{-1} boron and effluent containing 1 mg l^{-1} boron (Kunin and Preuss, 1964; Roberts, 1971). The boron retention capacity of this resin in salt-form is also independent of the pH and the other ions in the solution.

According to Roberts (1971), the regenerant can be used again until it reaches a saturation value of 50% boric acid (2% boric acid in 6% sulphuric acid solution). It is claimed that the exhaustion tests of salt-form resin regenerated with 6% H_2SO_4 containing 2% H_3BO_3 do not show any significant change in the breakthrough capacity.

Studies performed in the laboratory with synthetic reused regenerants gave the following results:

The used acid, containing 6% H_2SO_4 and 2% H_3BO_3 , can be concentrated by evaporation up to 52% H_2SO_4 content. As evaporation continues, the

boric acid precipitates out and can easily be separated by filtration. After filtration, the concentrated acid solution which contains 52% H_2SO_4 and 1.9% H_3BO_3 can be diluted to make 6% H_2SO_4 and 0.2% H_3BO_3 , and can be reused.

DISCUSSION

Laboratory tests showed that boron can be removed from the drainage waters of Bigadic boron mines by magnesium oxide and by ion-exchange. Cellulose as adsorbent has a minimum efficiency.

Table 1, which gives the analyses of the drainage waters, shows that the drainage waters of the Simav and Yenikoy mines are the most important boron pollution sources and these two sources are responsible of 94% of the total boron pollution in the

Table 1. Chemical analyses and the flow rates of the drainage waters

Element	Concentration (mg l^{-1} as ion)		
	Avsar mine	Simav mine	Yeniköy mine
B	16	260	390
SiO_2 (total)	110	17	39
Cl^-	13	18	23
SO_4^{2-}	67	70	60
CO_3^{2-}	—	340	220
HCO_3^-	200	230	420
K^+	2	3	3
Ca^{2+}	10	140	65
Na^+	40	80	170
Mg^{2+}	40	30	40
Li^+	0.4	1.2	1.1
As (total)	0.3	0.07	0.2
Fe (total)	0.05	0.05	0.05
Total solids	430	1625	2270
Suspended solids	40	20	100
pH	7.4	8.8	8.4
Conductivity ($\mu\text{mho cm}^{-1}$)	523	940	1065
Flow rate (l s^{-1})	120	100	7

Simav River. The average flow rate of the river measured between 15 November 1977 and 2 April 1979 is $10 \text{ m}^3 \text{ s}^{-1}$ (Onel, 1981). For this flow rate, 10% boron leakage from Simav and Yenikoy mines in addition to Avsar mine will cause a boron concentration in the river of only 0.5 mg l^{-1} . This level is in the permissible limit of boron in irrigation water for sensitive crops (Wilcox, 1958). Therefore, magnesium oxide with 85% boron removal efficiency and Amberlite IRA-743 in salt-form with 90% boron removal efficiency can be applied for boron removal from the drainage waters of Simav and Yenikoy mines.

MgO can be used effectively for three cleaning cycles but must be discharged and refreshed after the third cycle. This system will use about 2700 tons MgO year⁻¹ for the Yenikoy mine and about 15,400 tons MgO year⁻¹ for the Simav mine (the chosen Mg to B mol ratio is 20). Consumption of 18,100 tons of MgO per year increases the yearly chemical cost of the removal system with MgO to \$4.5 million, based on the cost of MgO of \$245 ton⁻¹ from Bozuyuk Chemical Co. Adaptation of this system may be possible only when the boron bearing MgO can be made into a valuable industrial material (cement, insulation, etc.).

Boron-specific resin Amberlite IRA-743 in free-amine form reduces the boron concentration of the drainage waters below 1 mg l^{-1} . However, the expensive regeneration steps make this process uneconomical. In addition, the regenerant from this system ($2.08 \text{ m}^3 \text{ m}^{-3}$ resin or $0.22 \text{ m}^3 \text{ m}^{-3}$ drainage water of Simav mine) will be another source of boron pollution. The same disadvantages are also valid for an ion-exchange process with the strong base anion-exchange resins.

At 10% boron leakage, the capacity of the boron-specific resin in salt-form was found to be $1.5 \text{ mg boron ml}^{-1}$ resin. The exhausted beds will be regenerated with 10% H_2SO_4 at a level of $30.4 \text{ kg H}_2\text{SO}_4 \text{ m}^{-3}$ resin. The boron bearing regenerant will be recycled for several times and the waste acid will be concentrated to precipitate out as boric acid. The precipitated boric acid will be separated by filtration and the recovered regenerant will be diluted and recycled. The used regenerant will be 10% fresh make-up regenerant and 90% recovered regenerant (Roberts, 1971). The total production of the boric acid will be around 4400 tons year⁻¹. The possibility of the reuse of 90% of regenerant and production of 4400 tons of boric acid per year from the removal system with boron-specific resin in salt-form can overcome the yearly chemical costs and also bring in some profit.

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