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# Boron Removal At Different Temperatures from Kizildere Geothermal Brine by Means of Coprecipitation with $Al_2(SO_4)_3.18H_2O$ and $KAl_3(SO_4)_2.OH$(Natural Alunite)

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## ABSTRACT

Denizli-Kizildere Geothermal Fields is the first geothermal field that suitable for electricity production situated on the Western Anatolia. The first geothermal power plant of 20.4 MW of Turkey was installed in this field. The water disposed away from the power plant has a capacity of 1500 tons/h. High concentrations of boron is particularly detrimental for citrus fruits. Therefore the permitted level of boron in irrigation water is 1 mg/dm$^3$. The wastewater from Kizildere geothermal brine contains boron approximately 30 mg/dm$^3$. The level of boron is high to use this water for irrigation in agricultural areas.

In this research, experimental work was carried out to investigate the optimum conditions of boron removal from Denizli-Kizildere Geothermal wastewater by utilizing co-precipitation method.

Since boron waste accumulates in Buyuk Menderes River day by day, it would be necessary to consider ion exchange process as a potential process for Boron removal. A certain emphasis should be given on searching natural adsorbents or developing cheaper ion exchange resins with better performance for boron removal.

## 1. GENERAL INFORMATION

### 1.1 Chemistry of Boron

Borates are defined as salts or esters of boric acid, a compound containing the radical $B_2O_3$ (Bates, R.L: & Jackson, J.A., 1987).

Boric acid borate buffer mixtures serve as pH standard, occur in natural aqueous systems. It is not surprising, therefore, that the equilibrium which occur in various aqueous solutions of boric acid and borate have been extensively studied. From the results it is clear that, in addition to the mononuclear boric acid and orthoboric ion which have been well established by infrared and Raman spectroscopy to be trigonal ($B(OH)_3$) and ($B(OH)^-{}_4$) species, a number of polyborate ions also are formed (Mesmer, R.E.,Baes, C.F. & Sweeten, F.H., 1972).

$$B(OH)_3 + H_2O \rightarrow B(OH)^-{}_4 + H^+$$

(Xiao, Y., Sun,D., Wang, Y., Qı, H., Jın, L., 1991).

It doesn't have any trivalent cations such as $B_2(SO_4)_3$ or $B(NO_3)_3$ but boron atom forms $BO_3^{-3}$ and $BO_4^{-5}$ groups by reacting three or four oxygen atoms.

During the formation of $B(OH)_3$, $B^{+3}$ cations attract the oxygen and as a result of this attraction effect O-H binding is broken and the $BO_3^{-3}$ anion is formed. The radius of $B^{+3}$ cation is very small (0.23 A°) and therefore it is not found free in nature. In chemical reactions due to its great affinity to oxygen, the oxygen compounds of boron are abundant (etc. $H_3BO_3$, $HBO_2$).

The occurrence of boron is changed depending on the pH of water. In acidic waters (pH<6) orthoboric acid is dominant. Tetra-pentha-hegza and other polyborates are come across in neutral and alkaline natural waters. Dissolution of alkaline metallic borates in aqueous media is faster than the others and dissolution rate of borates in general is increased with increasing temperature. Therefore in hydrothermal media boron migrates quickly. Boric acid dissolves faster in hot waters than cool waters.

Boron ions are adsorbed by clay minerals, thus the soil is enriched with respect to boron.

In chemical degradation, boron is found in waters as $B(OH)^-_4$ and as ionized $B(OH)_3°$ (in seawater).

In underground waters and streams boron might be found a lot especially waters with soda. On the other hand, in waters containing Ca, Mg and Cl it is not found as much. Some thermal waters and volcanic sources bear boron abundantly. In general volcanic gases and precipitates are rich in boron content. Between 4-36 mg/l boron can be traced in such waters. Boron in seawater (4.45 mg/l in average) is fed by rivers, and volcanoes, clay minerals and biological activities cause its precipitation (Sahinci, A. 1991). The concentration of boron in the earth's crust is 3 ppm (Muetterties, E.L., 1967).

### 1.2. Removal of Boron from Geothermal Brine

#### 1.2.1. Removal by Co-Precipitation

Precipitation and coagulation were chosen as the form of treatment for the quench water on the basis of economic considerations.

Pretreatment such as cooling was necessary to reduce the temperature of the waste to levels of safety in handling and that pH adjustment was necessary after treatment (Chang,Y. & Burbank, N., 1977).

The use of hydrous oxide floc for the adsorption of metallic cations and anions as well as co-precipitation of other species has been recognized for many years. Throngdethsri carefully had indicated the efficiency of coagulation and precipitation in the removal of metallic cations from incinerator quench water (Stillwell, C.W., 1938).

Chang and others investigated removal of boron from incinerator water with high hydrous metallic oxides. They used ferrous sulfate, aluminum sulfate and sodiumaluminate for precipitation and coagulation. Boron removal was 30.6 % by ferrous sulfate, 86.7 % by aluminum sulfate, 65.1 % by sodium aluminate. As a result, boron removal was about 30.6 %, which is tolerable for plants when the heavy metals are co-precipitated with iron salts in an alkaline medium (Chang&Burbank, , 199).

### 1.3. Toxicology of Boron

Boron, unlike sodium, is an essential element for plant growth (Chloride is also essential but in such small quantities that it is frequently non-essential). Boron is needed in relatively small amounts, however, and if present in amounts appreciably greater than needed, it becomes toxic. For some crops, if 0.2 mg/l boron in water is essential, 1 to 2 mg/l may be toxic.

Boron toxicity symptoms normally show first on older leaves as a yellowing, spotting, or drying of leaf tissue at the tips and edges. Drying and chlorosis often progress toward the center between the veins (interveinal) as more and more boron accumulates with time. On seriously affected trees, such as almonds and other tree crops, which do not show typical leaf symptoms, a gum or exude on limbs or trunk is often noticeable.

Most crop toxicity symptoms occur after boron concentrations in leaf blades exceed 250-300 mg/kg (dry weight) but not all sensitive crops accumulate boron in leaf blades. For example, stone fruits (peaches, plums, almonds, etc.) and pome fruits (apples, pears and others) are easily damaged by boron but they do not accumulate sufficient boron in the leaf tissue for leaf analysis to be a reliable diagnostic test. With these crops, boron excess must be confirmed from soil and water analysis, tree symptoms and growth characteristics.

Table 1 presents this recent revision data on relative boron tolerance of agricultural crops (Ayers, 1994).

**Table 1 : Relative Boron Tolerance of Agricultural Crops** (Ayers, 1994)

| | |
|---|---|
| Very Sensitive (< 0.5 mg/l) | *Lemon, Blackberry* |
| Sensitive (< 0.5-0.75 mg/l) | *Avocado, Grapefruit, Orange, Apricot, Peach, Cherry , Plum, Persimmon, Fig, Grape, Walnut, Pecan, Onion* |
| Sensitive(< 0.75-1.0 mg/l) | *Garlic, Sweet potato, Wheat, Barley, Sunflower, Bean , Lumping, Strawberry, Artichoke, Peanut* |
| Moderately Sensitive (< 1.0-2.0 mg/l) | *Pepper(red), Pea, Carrot, Radish, Potato, Cucumber* |
| Moderately Tolerant (< 2.0-4.0 mg/l) | *Lettuce, Cabbage, Celery, Turnip, Bluegrass, Oats, Tobacco, Mustard, Squash, Muskmelon* |
| Tolerant (< 4.0-6.0 mg/l) | *Sorghum, Tomato, Alfalfa, Vetch, Parsley, Beet(red), Sugar beet* |
| Very Tolerant (< 6.0-15.0 mg/l) | *Cotton, Asparagus* |

(Levinskas, G.J.)

Since compounds containing boron vary widely in their chemical reactivity, it is not surprising that they also exhibited a wide range of biological activity. Although many references have been made to the high lethality of boric acid and borax, experimental laboratory data indicate that they are only slightly toxic compounds for animal and humans. Widespread use of these materials, including the fact that large intravenous doses have been tolerated by humans, support the view that they have a relatively low order to toxicity (Levinskas, G.J.)

## 2. EXPERIMENTAL STUDIES

### 2.1. Materials

Kizildere geothermal brine was used for the experiments. Its properties have been summarized in Table 2.

**Table 2: The properties of Kizildere Geothermal Brine**

| | |
|---|---|
| pH | : 9.30 |
| Specific Conductivity (μmho/cm) | : 4120 |
| Evaporation Residual (180°C)( mg/dm$^3$) | : 4108 |
| Total hardness (AS°) | : 0.06 |
| Temporary Hardness(AS°) | : 0.06 |
| Permanent Hardness (AS°) | : 0 |
| $K^+$ (mg/dm$^3$) | : 145 |
| $Na^+$ ( mg/dm$^3$) | : 1300 |
| $NH_4^+$ (mg/ dm$^3$) | : 3.5 |
| $Ca^{2+}$(mg/ dm$^3$) | : 0.39 |
| $Mg^{2+}$ (mg/ dm$^3$) | : 0.08 |
| Fe (total) (mg/ dm$^3$) | : <0.05 |
| As (total)(mg/ dm$^3$) | : 0.58 |
| B(total)(mg/ dm$^3$) | : 30.2 |
| $Li^+$ (mg/ dm$^3$) | : 4.8 |
| $Al^{3+}$(mg/ dm$^3$) | : 0.71 |
| $SiO_2$ (mg/ dm$^3$) | : 415 |
| $HCO_3^-$ (mg/ dm$^3$) | : 1037 |
| $CO_3^{2-}$ (mg/ dm$^3$) | : 780 |
| $SO_4^{2-}$ (mg/ dm$^3$) | : 695 |
| $Cl^-$ (mg/ dm$^3$) | : 134 |
| $I^-$ (mg/ dm$^3$) | : 4.6 |
| $F^-$ (mg/ dm$^3$) | : 15 |
| $Br^-$ (mg/ dm$^3$) | : 0.53 |
| $NO_2^-$ (mg/ dm$^3$) | : < 0.01 |
| $NO_3^-$ (mg/ dm$^3$) | : < 1 |
| $PO_4^{3-}$ (mg/ dm$^3$) | : < 0.1 |

### 2.2. Results and Discussions

2.2.1. Coagulation

$Al_2(SO_4)_3.18H_2O$, $MgSO_4.7H_2O$, $AlK(SO_4)_2.18H_2O$ and $KAl_3(SO_4)_2(OH)$ (natural alunite) were used as coagulant; NaOH (caustic soda) and $Ca(OH)_2$ (lime) as pH regulator. Boron concentration was determined by using spectrophotometric method with carmine.

A 5 min rapid mixing (226 1/min), 30 min of flocculation time (32-36 1/min) and a sedimentation period were generally used. To find the optimum pH, NaOH (pH range 10-12) and lime were used for pH adjustments . During the experiments, pH values were kept constant at predetermined levels.

At the end of each run approximately 10 ml of supernatant solution was taken for boron determination by spectrophotometer.

2.2.2. Effect of Coagulant Type

Various coagulants were tried to find the best reagent for boron removal from the geothermal brine. The results are summarized in Table 3.

**Table 3: Effect of Various coagulant**

| **Coagulant** * | **pH** | **Removal of Boron (%)** |
|---|---|---|
| **$Al_2(SO_4)_3.18H_2O$** | 10 | 2.7 |
| | 11 | 7.5 |
| | 12 | 17.5 |
| **$MgSO_4.7H_2O$** | 10 | 0.0 |
| | 11 | 0.0 |
| | 12 | 0.0 |
| **$AlK(SO_4)_2.18H_2O$** | 10 | 0.0 |
| | 11 | 0.0 |
| | 12 | 0.0 |

- 1 g coagulant was used for 1 $dm^3$ of solution

As seen from the Table 3 $Al_2(SO_4)_3.18H_2O$ and $MgSO_4.7H_2O$ coagulants were observed to be promising.

2.2.3. Effect of Amount of Coagulant

Different amounts of $Al_2SO_4.18H_2O$ ( 0, 2, 4, 6, 8, 10 and 15 g/l) were used to determine the effect of coagulant dosage. The results are presented in Figure 1.

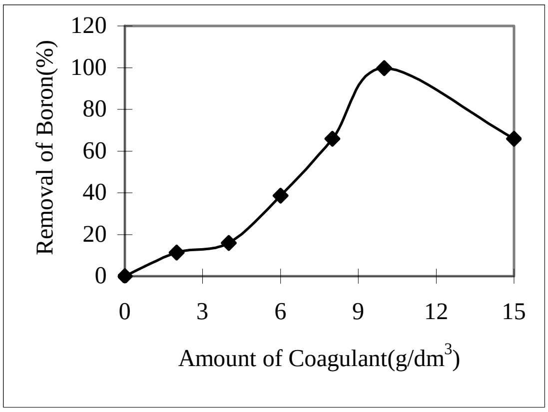

**Figure 1 : Effect of Coagulant Amounts**

The removal of boron increased with the increasing amount of coagulant. This is again due to increasing the amount of $Ca_2Al_2(SO_4)_3(OH)_{12}.25H_2O$ compound within the solution for the adsorption of boron anions resulting in removal of more boron from the solution.

### 2.2.4.Effect of pH

In order to investigate the effect of pH in the removal of boron from geothermal brines a series of experiments were carried out. The results of the experiments are presented in Figure 2. The original pH of the sample solution is around 9.3. Above this pH value, it was observed that removal of boron from the solution by precipitation is enhanced. At pH 12, all the boron in the geothermal brine was completely removed.

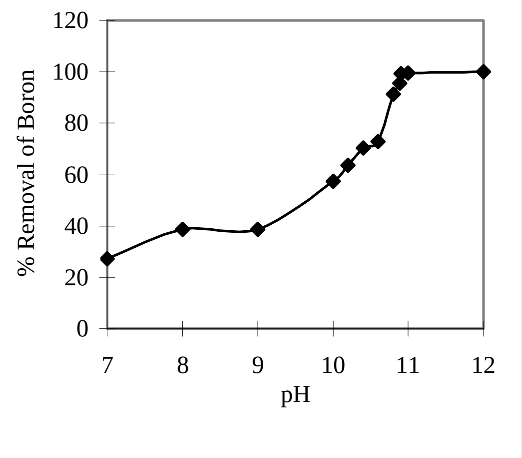

**Figure 2: Effect of pH on Boron removal**

At pH values below the original pH where there is no lime addition, boron removal was still possible with a recovery of about 30 percent.

These results indicate that both $Al_2(SO_4)_3.18H_2O$ and lime are responsible for the precipitation of boron out of the solution.

### 2.3. Experimental Results at Kizildere-Denizli Geothermal Field

Due to approximately $70^0$C of geothermal waste water of power plant is discharged to he Menderes River directly; effect of temperature on removal of boron by co-precipitation using with $Al_2(SO_4)_3.18H_2O$ and

$KAl_3(SO_4)_2.OH$ was examined at different temperature. The results are presented in Figure 3 and 4. The boron concentration of 1 mg/lt in the effluent was accepted as the breakthrough point on the resulting curves. Removal of boron increased with decrease in temperature.

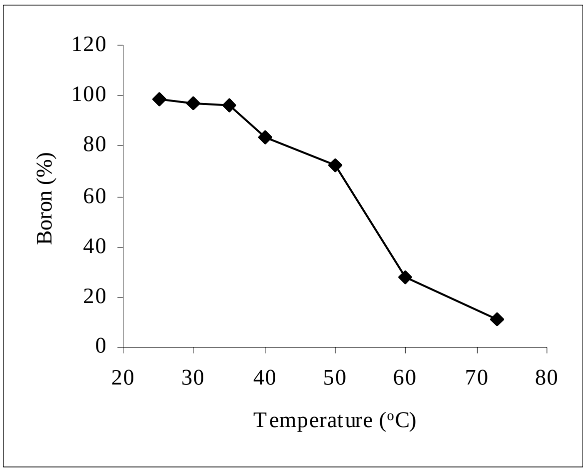

**Figure 3: Boron Removal At Different Temperatures from Kizildere Geothermal Brine with $Al_2(SO_4)_3.18H_2O$**

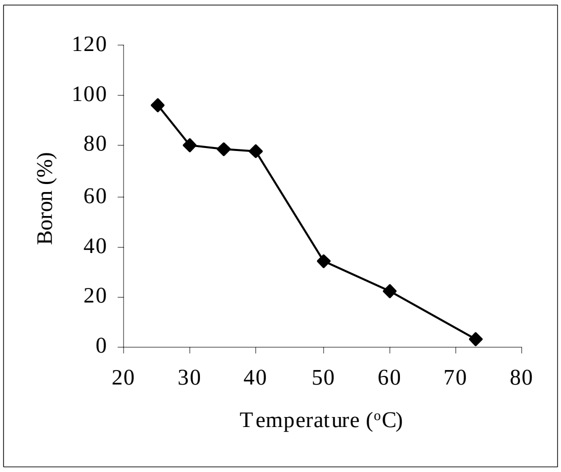

**Figure 4: Boron Removal At Different Temperatures with $KAl_3(SO_4)_2.OH$**

### 2.4. Optimum Conditions

The optimum conditions for co-precipitation are as follows: 10 g/ $dm^3$ $Al_2(SO_4)_3.18H_2O$ or $KAl_3(SO_4)_2.OH$ is added to the brine while the pH is kept constant at around 11-12 using lime. Under these conditions, the Boron removal is approximately 100% and the resulting precipitate is a complex of $Ca_6Al_2(SO_4)_3(OH)_{12}.25H_2O$ and small amount of $CaCO_3$ and $CaSO_4.2H_2O$.

## 3. CONCLUSIONS

The geothermal brine from Kizildere Region contains approximately 30 mgB/$dm^3$. Boron. In order to be able to utilize this brine for irrigation, the maximum content of boron should be reduced below 1 mg/$dm^3$. In this study the necessary conditions for achieving such a low concentration were investigated using such techniques as co-precipitation and ion exchange. The following subjects can be further persuade :

1- During the co-precipitation process pH is kept quite high (about 11-12) which results in a highly basic effluent. Use of this effluent for irrigation requires a reduction in pH to about 9.0 . To achieve this aim the use of $H_2SO_4$ should be investigated.

2- In the same process, a precipitation in the form of $Ca_6Al_2(SO_4)_3(OH)_{12}.25H_2O$ occurs. We suggest that the potential application areas of these precipitates in other industries should be investigated.

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