

Reducing the Amount of Boron in the Wastewater of a Boron Processing Plant by Chemical Precipitation

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ABSTRACT: *The effect of pH and the amount of $\text{Ca}(\text{OH})_2$ on the precipitation of boron from Eti Maden Kırka Boron Operations' wastewater that contained 2752 ppm boron was investigated. It was observed that control of pH was the most important parameter and stepwise addition of $\text{Ca}(\text{OH})_2$ after adjustment of pH improved the precipitation. The best result was obtained in the two-stage addition of $\text{Ca}(\text{OH})_2$ with the initial control of pH and additional use of aluminum sulfate in the second stage which helped both in the reduction of pH and coagulation. Under these conditions, it was possible to lower the boron content in the wastewater to 250 ppm.*

KEYWORDS: *Boron removal; Wastewater treatment; Precipitation; Removal efficiency.*

INTRODUCTION

In Turkey, boron deposits are located in Kırka/Eskişehir, Bigadiç/Balıkesir, Kestelek/Bursa and Emet/Kütahya. The most abundant boron ores in Turkey are tinkle ($\text{Na}_2\text{O} \cdot 2\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$) and colemanite ($2\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$). The tincal deposits are mostly located in Kırka and the colemanite deposits are in Emet, Bigadiç, and Kestelek. Also, there is a small reserve of ulexite in Bigadiç [1].

Boron is an element that is widely used in many industries such as glass, fertilizers, detergents, ceramics, etc. [2-3]. It is a very important element for living beings' regulation about boron concentration in drinking waters

was determined as 0,3 mg/L by WHO in 1993. In 1998, this value was changed to 0.5 mg/L due to poor performance of the processes used in boron removal and today this value is still valid [5]. In Turkey, the boron discharge value of the wastewater from mining and chemical industries is determined as 500 mg/L (maximum) in accordance with the Regulation of Water Pollution Control in 2004 [6].

Kırka boron deposits are the only sodium borate deposits in Turkey and the borax pentahydrate (BPH), borax decahydrate (BDH) and anhydrous borax (AB) are

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produced in Kırka Boron Operations [7]. The wastewaters which are obtained from boron production plants are collected in wastewater ponds. These wastewaters cannot be discharged to the environment directly due to high boron concentration and the occupancy rate of wastewater ponds is increased day after day which necessitates the construction of new ponds [8].

For removal of boron from water and wastewater; adsorption and ion exchange [9-14], solvent extraction [15-17], reverse osmosis [18-22], chemical coagulation-electrocoagulation [23-25], and precipitation [26-31] and membrane electrodialysis [32,33] methods have been used. Chemical precipitation is preferred for the removal of boron at high concentrations due to being a simple and cost-effective process that can be automated easily.

In a conventional chemical precipitation study; precipitants such as MgO, CaO, Ca(OH)₂, MgO-CaO, MgSO₄-NaOH, MgCO₃-NaOH was tested and the maximum boron removal efficiency was obtained from Ca(OH)₂[21,27]. A two-stage precipitation method using Ca(OH)₂ was applied for the removal of boron from synthetically prepared and up to 3000 ppm boron-containing water [30]. Also, co-precipitation methods utilizing lime in combination with sulphuric acid or phosphoric acid have been studied under conventional and microwave heating [34-35].

In aqueous medium boric acid is in equilibrium with borate anions (Reaction-1) and the dominant species is dependent on pH. B(OH)₃ is the dominant species when pH is below 9, above that value it is B(OH)₄⁻ as is also evidenced by the Pourbaix diagram (Fig. 1a). Therefore, studies conducted on the removal of boron from aqueous solutions by lime are strongly dependent on pH, boron concentration and reaction time [26]. The use of lime in excess quantities increases the pH value above 12 and the solid phase contains a mixture of precipitated borate and unreacted lime [26]. Also, above pH 13 Ca(OH)₂ becomes a solid phase not being effective in the reaction as shown in the logarithmic concentration diagram of Fig. 1b. Accordingly, control of the amount of lime addition considering the initial pH of the wastewater and reaction temperature to shorten the reaction time seem to be of prime importance for better results [26,31].

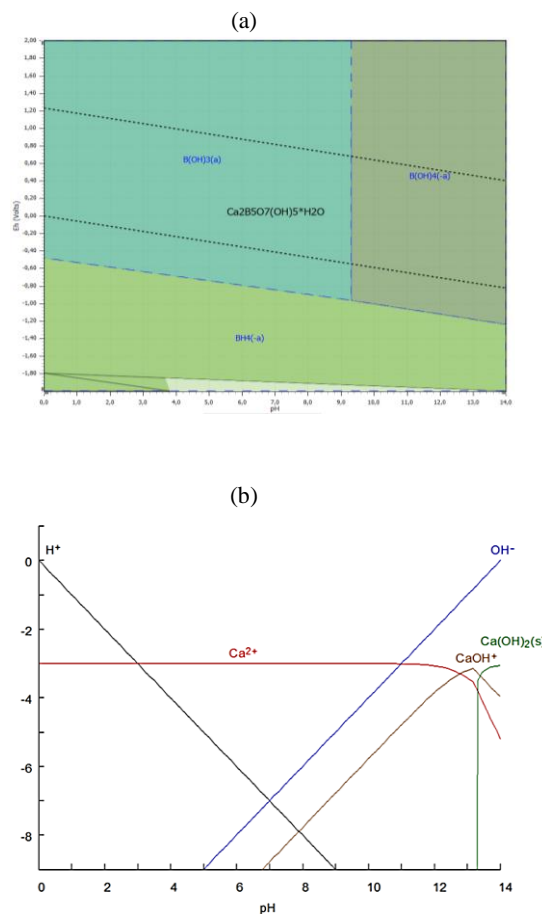
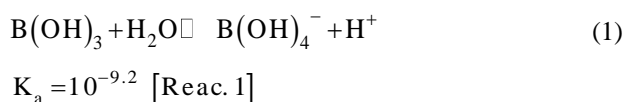


Fig.1: Pourbaix diagram of B-Ca system at 25°C (a) and logarithmic concentration diagram of Ca(OH)₂ (b).

In this study, the parameters that affect the chemical precipitation of boron from Eti Mine Kırka Boron Operations' wastewater with Ca(OH)₂ were examined. Furthermore, it is worth considering that to study with real wastewater instead of synthetic wastewater and the amount of Ca(OH)₂ used is quite low compared to other studies.

EXPERIMENTAL SECTION

Materials and Methods

A wastewater sample was supplied from Eti Maden Kırka Boron Operations' pond and the chemical composition is given in Table 1. The pH of the wastewater was determined as 9.43. Ca(OH)₂ of 99.9% purity was obtained from Adaçal (Turkey), Al₂(SO₄)₃.18H₂O, and nitric acid were Merck grade reagents.

Precipitation experiments were performed using 500 mL of wastewater with varying amounts of Ca(OH)₂ under magnetic stirring conditions at 450 rpm for 60 minutes.

Table 1: Chemical composition of Kurka wastewater.

Element	Na	K	Ca	Mg	Li	B	SO ₄	Cl
mg/L	5765	142.2	10.74	23.87	109.3	2752	1442	524.7

Then, the precipitate was separated by filtration using black filter paper, and the filtrates were analyzed for boron by volumetric analysis [36]. These experiments were done as a single and two-stage precipitation using only Ca(OH)₂ and as a two-stage precipitation by addition of Al₂(SO₄)₃.18H₂O in the final stage. The boron removal efficiency was calculated using Eq. (1).

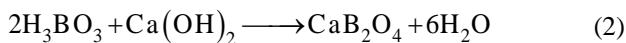
$$\text{Boron Reoval Efficiency (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C₀ is the initial boron concentration (mg/L) and C_e is the boron concentration (mg/L) at the end of the experiment.

RESULTS AND DISCUSSION

The concentrations of boron species could be much less than the borate ions in solutions since the pH value of the samples was greater than 11. The presence of calcium and borate ions in the solutions could lead to the formation of Ca–B ionic pairs, [CaB(OH)₄]⁺ under the basic medium at the beginning of the reaction. As a result, [CaB(OH)₄]⁺ is the minor predominant soluble boron species in solutions with respect to the borate ion (B(OH)₄⁻) [37].

Experiments were done considering the effects of reagent additions (Ca(OH)₂ and Al₂(SO₄)₃.18H₂O) and pH as the basic parameters. Experiments were done both at the natural pH of wastewater (9.43) and by adjustment of pH using nitric acid whenever needed. The amount of Ca(OH)₂ additions was determined considering Reaction (2).



The stoichiometric amount of Ca(OH)₂ was calculated as 10.09 g/L for wastewater by using Eq. (2). An optimum value of 20 g Ca(OH)₂/L was given for a chemical precipitation study [10]. In this series of precipitation experiments, the amount of Ca(OH)₂ addition was kept at values between 5-40 g/L.

The results of the use of Ca(OH)₂ between 5-15 g/L for the precipitation of boron are given in Fig. 2. As shown in Fig. 2, the initial boron concentration of 2752 ppm in wastewater was reduced to 1700, 1300, 1200 ppm

by use of 5, 10, and 20 g Ca(OH)₂, respectively. Upon the addition of 5 g of Ca(OH)₂ pH value is increased to 12.37 and a decrease of 1090.4 ppm of boron is obtained in the wastewater. By doubling the amount of Ca(OH)₂, pH value reached 12.66 and the extra increase in boron removal was only 388.7 ppm. Even further increase of Ca(OH)₂ to 20 g caused no significant changes in boron removal. The results given in Fig. 3 show that the pH of the wastewater when increased above 12 is not suitable for the precipitation of boron. Also, the stepwise addition of 5+5 g of Ca(OH)₂ did not cause any difference from the addition 10 g of Ca(OH)₂ (Fig.3).

In order to see the effect of pH on precipitation, the initial pH of the wastewater was adjusted to 6 using nitric acid (%50 v/v), 5 grams of Ca(OH)₂ was added and the pH was increased to 12 with a decrease of boron content to 1200 ppm (Fig. 3). Then, after adjustment of the pH to 6 additional 5 g of Ca(OH)₂ was added and the better result was obtained as boron content was reduced to 530 ppm (Fig. 4).

Finally, two-stage precipitation using Ca(OH)₂ (Fig. 5) with pH adjustment using nitric acid initially and then adding aluminum sulfate as a coagulant which also lowers the pH. Tests showed that after adjusting the initial pH value to 6 with nitric acid, 7.5 g of Ca(OH)₂ was just enough to increase the pH to 12 during the precipitation of boron. In this first stage, boron in wastewater was reduced to 630 ppm. The addition of 6 g of Al₂(SO₄)₃.18H₂O lowered the pH to 4.08 and then further addition of 3.5 g of Ca(OH)₂ was more effective for the removal of boron, the final boron in wastewater being reduced to 250 ppm.

As shown from previous studies 7.5 g of Ca(OH)₂ was found enough to reach pH 12 after adjusting the initial pH value to 6 with nitric acid. In another two-stage precipitation experiment, 7.5 g Ca(OH)₂ with pH adjustment using nitric acid at the first stage was used and then at the second stage, 4 g Al₂(SO₄)₃.18H₂O and 2 g of Ca(OH)₂ were added as a coagulant-pH adjustment agent and precipitant, respectively. As it can be seen from Fig. 6, boron concentration in wastewater was reduced to 530 ppm in the first stage and reduced to 280 ppm in the second stage. It is seen that the boron removal efficiency is 81% in the first stage and approximately 90% in the second stage.

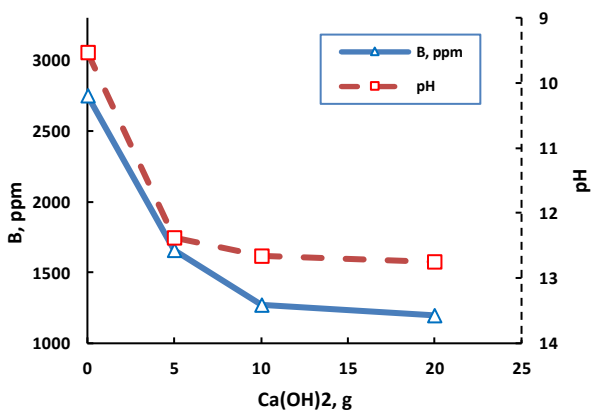


Fig. 2: Effect of $\text{Ca}(\text{OH})_2$ on precipitation.

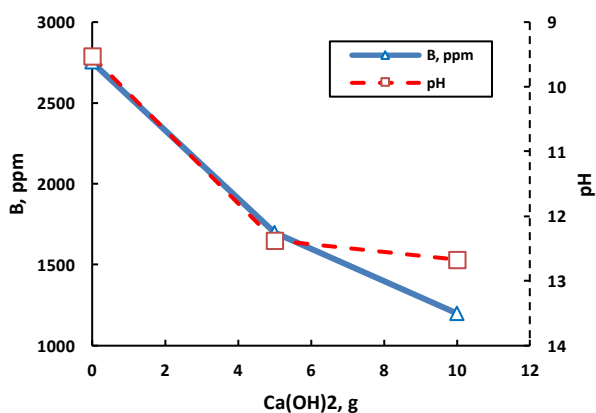


Fig. 3: Effect of two-stage addition of $\text{Ca}(\text{OH})_2$ on precipitation.

It is considered that these values can compete with extraction processes, which are more complex processes. [38]

It was shown that a lower amount of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ than in literature was enough to reach pH 6 and less $\text{Ca}(\text{OH})_2$ amount was found as adequate to reach pH 12 due to adding less amount of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ during chemical precipitation. Final boron concentrations of the experiments in which 11 g $\text{Ca}(\text{OH})_2$ 6 g $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and 9.5 g $\text{Ca}(\text{OH})_2$ 4 g $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ were used respectively were found to be close to each other and pH was shown the same trend in both experiments and in the lighting of this information by using less amount of precipitant and coagulant makes the study more economic.

In addition, the zero charge point of $\text{Ca}(\text{OH})_2$ is around 12.9, which is higher than the final pH of the solutions in this study (12.2-12.7). This meant that the surface of $\text{Ca}(\text{OH})_2$ particle may have less positive charge and that could facilitate the adsorption of negatively charged ions.

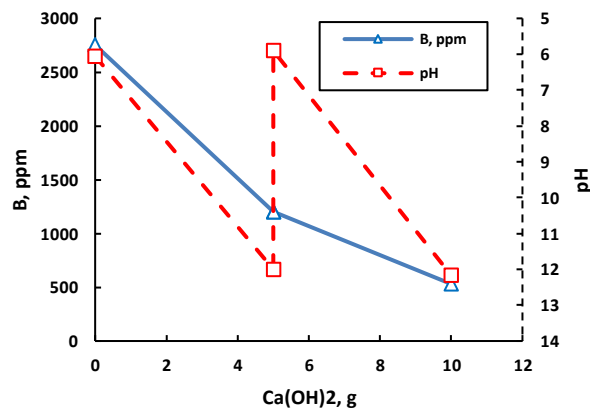


Fig. 4: Effect of pH adjustment before $\text{Ca}(\text{OH})_2$ addition.

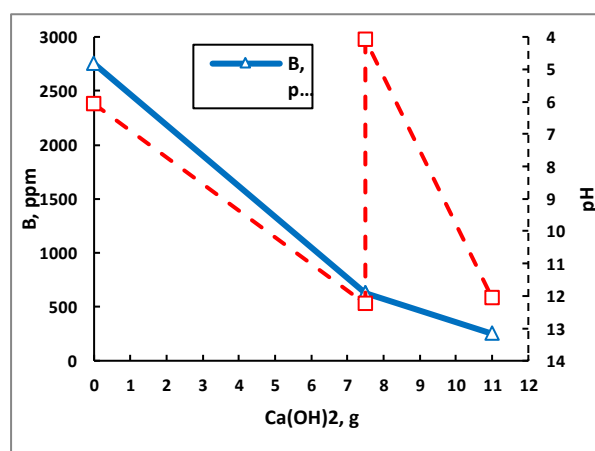


Fig. 5: Effect of pH adjustment and $\text{Al}_2(\text{SO}_4)_3$ addition on precipitation.

For the real wastewater study, the formation of calcium borate may be inhibited by the lower pH values [37].

CONCLUSIONS

A single-stage precipitation with 10 grams of $\text{Ca}(\text{OH})_2$ proceeds until the pH of the solution is increased from 9.4 to 12.7 and the boron content is only lowered from 2752 ppm to 1273 ppm. When $\text{Ca}(\text{OH})_2$ was added in two stages (5+5 g), a slightly better result was obtained and the final value of the boron content was reduced to 1200 ppm. But, when the two-stage precipitation was repeated after adjustment of pH value to 6 using nitric acid, boron in solution was reduced to 530 ppm. Two-stage precipitation was performed with the extra use of aluminum sulfate in the second stage. 7.5 g of $\text{Ca}(\text{OH})_2$ was found to be a suitable amount to increase the pH from 6 to 12.2 in the first stage and then the addition of 6 g of aluminum sulfate in the second stage reduced the pH to 4.1. Finally, addition

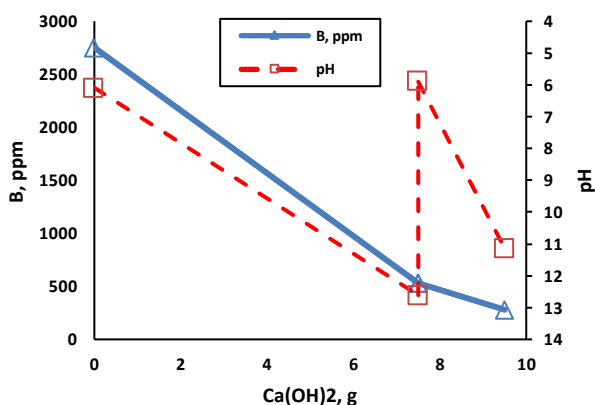


Fig. 6: Effect of pH adjustment and $Al_2(SO_4)_3$ addition on precipitation.

of 3.5 grams of $Ca(OH)_2$ increased the pH to 12 and the final value of boron in the wastewater was decreased to 250 ppm.

Thermodynamic evaluation of Ca-B system using pH-Potential and logarithmic concentration diagrams (Fig. 1) shows that the most important parameter for the removal of boron from wastewaters by precipitation with $Ca(OH)_2$ is pH. As the natural pH of the wastewater is 9.43, boron is in the form of $B(OH)_4^-$. Upon addition of $Ca(OH)_2$ to wastewater, pH increases rapidly and above 13 the system is buffered which causes the precipitant to lose its effectiveness as it is transferred to a solid phase. Thus, experimental findings are in good agreement with the thermodynamic considerations. To conclude;

--- For the removal of boron from wastewater by precipitating with $Ca(OH)_2$, the acidity of the medium should be controlled between $6 \leq pH \leq 12$.

--- Since the control of pH in a single-stage precipitation is very difficult, stepwise addition of $Ca(OH)_2$ should be preferred which gives a chance to adjust the pH for the precipitation to be more effective.

--- Use of additional reagents, like aluminum sulfate, that lower the pH and help for coagulation of the precipitated phase seems to increase the efficiency of the reaction.

--- Although better results could be obtained by strict control of pH and temperature, complete removal of boron from wastewater by only precipitation does not seem possible and the use of other methods in conjunction is required.

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