



Precipitation of boron from waste water of Kirka borax plant

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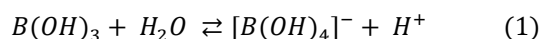
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ABSTRACT

Kirka Boron Inc., which is the largest boron processing plant in Turkey, produces tincal from the run of mine ore and sodium penta borax in the same complex. However, the deficiency of the tailings ponds causes significant problems, since approximately 75 % of the current pond volume is filled with waste water, which consists 3 g/L boron. The boron content of this water should be decreased for its usage in the plant again, meanwhile about concentration of 3 g/L boron creates an environmental risk. In this study, the boron in the effluents of the Kirka Boron Inc. was precipitated using $\text{Ca}(\text{OH})_2$ and Al_2SO_4 . The effects of several parameters such as $\text{Ca}(\text{OH})_2$ dosage, initial pH, agitation duration, and settling duration were investigated. It was found that, the precipitation was strongly related to the Ca^{2+} concentration. Therefore, when the initial pH was proceeded towards acidic values, boron precipitation was increased. In conclusion, 97 % of the boron could be precipitated from the solution by two stages and a precipitate assaying 38 % B_2O_3 was obtained.

1. Introduction

Boron has an important role in manufacturing different types of products such as glass, ceramics, high quality steel, catalysts, cosmetics, and flame retardants (Yılmaz et al., 2008a). Boron is found in the crust of earth as salts (borates) or boro-silicate (Parks et al., 2005; Yılmaz et al., 2008a); acid can easily be dissolved in water (solubility of 55 g/L at 298 K) according to following reaction (Yılmaz et al., 2008a):



In some cases, boron is desired to be removed from water. These cases can be classified as: a) environmental issues, b) technological issues, which maintain a recyclable water for the beneficiation plant and diminish some kind of precipitates in tailing

ponds so it is provided new volumes for the tailings.

Today, there is not any specific boron removal technology, which leads to the utilization of the methods in conjunction with the other target parameters. These involve coagulation-electrocoagulation, adsorption (on oxides and activated carbon), chemical precipitation, ion exchange, solvent extraction, electro dialysis, membrane filtration, thermal treatment, and use of resins. When the boron concentration in the solution is relatively high, chemical precipitation is preferred, while milk of lime, oxides of manganese, copper, cobalt and magnesium are the precipitants used (Frütwirth et al., 1891; Boryta, 1995; Yamada and Eto, 1995; Kalafatoğlu, 1997; Hasenmuller and Criss, 2013). Large boron reserves in Turkey require tailings ponds with large volumes. However, the management of large volume tailings ponds imposes some difficulties. Kirka Boron Inc. encounters a number of problems and will probably

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encounters a number of problems and will probably face in the future, related to its capacity.

Kirka Borax Plant is located 70 km away from Eskisehir near the town of Kirka. It is the largest boron plant in Turkey with 1,000,000 tons of run-of-mine ore processing capacity producing borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$). Tailings are pumped to 14,000,000 m^3 capacity tailing ponds that are mostly filled up. The shortage of waste ponds creates a serious problem in terms of environment. Currently, tailing ponds hold about 12,000,000 m^3 of material of which 11,500,000 m^3 is waste water containing about 3 g/L of boron.

There are 5 tailings ponds in Kirka, 4 of which are used for the tailings of the borax concentrator and the remaining one is used for the tailings of the sodium penta borax plant. Concentrator tailings contain 5-10 % solids by weight. The tailings are fed to the ponds in a cascading fashion, therefore, solids are primarily settle out in the first pond. The last tailings pond primarily contains boron rich solutions from the tailings of the concentrator and the penta borax plant. One of the most important problems faced in boron minerals processing plants is tailing ponds. Tailings of those plants have to be kept in well-constructed leakage free ponds. Although trace amounts of boron are needed for living organisms and the habitat, higher concentrations become environmentally hazardous (Adams, 1964; Wong, 1984; Börekçi, 1986; EPA, 1986). Therefore, concentrator tailings containing high amounts of boron must be strictly kept under control to prevent environmental pollution and urgent precautions must be taken. This investigation aims to remove boron from the liquid phase of the vast Tailings Ponds of Kirka for both economic and environmental reasons. Because of the boron concentration of 1 mg/L more in the water used for agricultural activities, it can cause problems (Ayers and Westcot, 1976; Uygan and Çetin, 2004). But water containing 3 mg/L boron can be used for dilution of durable plants (Uygan and Çetin, 2004). The drinking water in Turkey up to 1 mg/L B comprises is allowed (Official Gazette, 2013).

2. Materials and method

2.1. Material

Boron containing effluents used in the experimental studies were collected from the tailings pond of Kirka Borax plant. A homogenous solution was prepared by mixing 30 L lots. The chemical composition of the blended test solution is given in Table 1. According to the analysis, 3.93 g/L B, 6.38 g/L Na, and 675 mg/L SO_4 was determined, while the pH of the solution was 9.44. Boron analyzes were carried out using volumetric titration method and other analyzes were carried out using atomic absorption spectrometry.

Table 1
The chemical composition of the test solution

Component	Concentration	Component	Concentration
B	3.93 g/L	Ca	6.28 mg/L
Na	6.38 g/L	Fe	0.42 mg/L
K	102.8 mg/L	SO_4	675 mg/L
Al	0.52 mg/L	Cl	536 mg/L
Mg	19.1 mg/L	As	0.52 mg/L

2.2. Method

This study investigates the removal of boron from the waste solutions in order to obtain a solution, which contains below environmentally acceptable average level of 2 mg/L B (Uygan and Çetin, 2004). The boron removal tests were performed by utilizing the chemical precipitation method in two steps (preliminary and basic tests). With reference to the results obtained from the preliminary tests, basic tests were conducted in two stages. The parameters given below were examined in the first stage:

- The amount of $\text{Ca}(\text{OH})_2$ – initial pH,
- Agitation duration,
- Settling duration.

Following the first stage basic precipitation, the solution was subjected to second stage precipitation, in which the effect of $\text{Ca}(\text{OH})_2$ usage only and $\text{Ca}(\text{OH})_2$ usage with $\text{Al}_2(\text{SO}_4)_3$ as precipitants were observed.

The precipitation tests were performed in a 400 mL beaker using 100 mL of solution. The solution was agitated with a magnetic stirrer. During the precipitation tests, $\text{Ca}(\text{OH})_2$ and $\text{Al}_2(\text{SO}_4)_3$ were used, while HNO_3 was utilized to decrease the pH. The reason for the use of HNO_3 is that the damage and toxic effects of chlorine and sulfate anions on the water and the environment are more than nitrate ions.

After the agitation test, the solution was let to stand for the particles to settle out and then some amount of aliquot was taken. The boron analyses were performed with titration method. Besides, all of the reagents used in the experiments were analytical grade. The parameters and ranges of the precipitation tests are shown in Table 2.

Table 2
The parameters tested in precipitation experiments

Parameters	Ranges
$\text{Ca}(\text{OH})_2$ dosage (g/L)	10, 20, 40, 60, 80
Initial pH	3, 6, 8, 9.44
Agitation duration (min)	5, 15, 30, 45, 60
Settling duration (min)	5, 10, 20 30, 60, 120, 240,480

3. Results and discussion

3.1. The Preliminary Precipitation Tests

The preliminary tests revealed that the maximum Ca^{2+} solubility in the waste solution at the original pH (9.44)

was 300 mg/L. Above this pH, reaction between boron and calcium cannot develop. However, if the initial pH is decreased, then the Ca^{2+} concentration in the solution increases, which promotes the reaction between calcium and boron. At the first stage, preliminary tests were carried out in order to observe the effect of solution temperature on precipitation. As a result, it was found that an increase in solution temperature did not provide an enhancement in precipitation reaction. Therefore, following tests were decided to be performed at the temperature of 20 °C. Preliminary tests indicated that reaction kinetics of calcium-boron compound formation was found to be slow. Even after the agitation stopped, the formation of calcium-boron compound continued, which led to an enhancement in the efficiency of boron precipitation. Test results revealed that the discharge of one stage precipitation was inadequate in terms of environmental issues. Therefore, a second stage precipitation process was decided to be necessary.

3.2. The Basic Precipitation Tests

3.2.1. One Stage Precipitation

The Effects of $\text{Ca}(\text{OH})_2$ Dosage and Initial pH

In the first part of the experiments, the effect of $\text{Ca}(\text{OH})_2$ was examined at different dosages, where different initial pH values were tested under the following conditions:

- Agitation duration: 30 min,
- Solution temperature: 22 ± 2 °C,
- Settling duration: 60 min.

The results of the tests carried out at this conditions are given in Table 3. According to the results given in Table 3, the precipitation of boron increased almost linearly, when the initial pH value decreased, particularly at low $\text{Ca}(\text{OH})_2$ additions. The increase in boron precipitation at decreasing initial pH values could be related to the increasing solubility of Ca^{2+} ions. Boron precipitation efficiencies showed similar values at $\text{Ca}(\text{OH})_2$ dosages exceeding 20 g/L. About efficiency of 87 % boron precipitation could be reached at this group tests, but boron concentration at the solution discharged to the tailings pond was inadequate in terms of environmental issues. Therefore, a second stage precipitation process was needed. It was found that the solubility of Ca^{2+} ions strongly depended on the solution pH, which can be confirmed by Figure 1. These indications show that initial pH of the solution has a significant effect on calcium-boron interaction. Increasing the initial pH from 6 to 9 prevents the dissolution of $\text{Ca}(\text{OH})_2$ in the solution and therefore calcium-boron interaction cannot develop because of insufficient Ca^{2+} ions concentration.

Table 3
The effects of $\text{Ca}(\text{OH})_2$ dosage and initial pH on boron precipitation

$\text{Ca}(\text{OH})_2$ Dosage (g/L)	Initial pH	Final Boron Concentration (g/L)	Precipitation Efficiency (%)
10	9.4	2.64	32.8
	8.0	2.50	36.5
	6.0	2.35	40.1
	2.6	2.20	44.0
	9.4	1.17	70.3
20	8.0	0.71	81.8
	6.0	0.59	84.9
	2.9	0.52	86.7
	9.4	1.07	72.8
	8.0	0.69	82.5
40	6.0	0.56	85.8
	2.8	0.50	87.3
	9.4	1.04	73.5
	8.0	0.70	82.1
	6.0	0.55	86.2
60	2.8	0.50	87.4
	9.4	1.01	74.3
	8.0	0.74	81.2
	6.0	0.54	86.4
	2.8	0.49	87.5

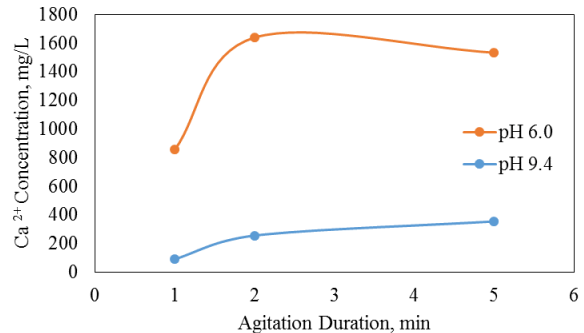


Figure 1. The variation in Ca^{2+} concentration with respect to pH and agitation duration

The Effect of Agitation Duration

In these tests, the effect of agitation duration on the precipitation was investigated by adding varying dosages of $\text{Ca}(\text{OH})_2$ under following conditions:

- Initial pH: 6,
- Solution temperature: 22 ± 2 °C,
- Settling duration: 60 min.

The results in Figure 2 show that even 5 minutes agitation duration would be enough for more than 80 % precipitation. When the agitation duration was increased from 5 to 15 minutes, 5 % marginal increase in the precipitation efficiency was observed.

15 minutes agitation duration was found to be sufficient as an optimum the precipitation time. The reaction between boron ions and Ca ions takes place in two stages.

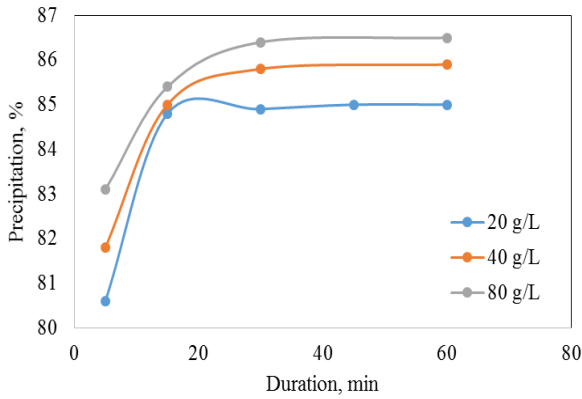


Figure 2. The effect of agitation duration on boron precipitation with different Ca(OH)_2 dosages

During the first 15 minutes of agitation, the reaction kinetics was very fast, but slows down suddenly at later times. However, the second phase also continued in the settling duration.

The Effect of Settling Duration

Precipitation tests were performed under the following conditions, in order to observe the effect of settling duration:

- Ca(OH)_2 dosage: 20 g/L,
- Agitation duration: 15 min,
- Initial pH: 6,
- Solution temperature: 22 ± 2 °C.

These tests are particularly important in terms of the solid-liquid separation, since this process requires particular space and equipment in industrial scale operations.

According to Figure 3, it is seen that the precipitates could readily settle out with 85 % efficiency even in 30 minutes. Thus, there is no need for prolonged durations.

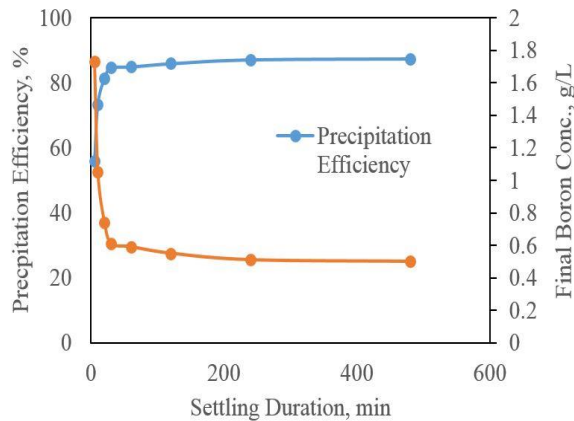


Figure 3. The effect of settling duration on boron precipitation

3.2.2. The Second Stage Precipitation Tests

As a result of one stage precipitation, 87 % of boron could be removed using 20 g/L Ca(OH)_2 , agitation duration of 30 min, solution temperature of 22 ± 2 °C and settling duration of 60 min. However, the residual boron concentration obtained under optimum conditions was found to be 0.61 g/L, which was not close to the environmental limitations (2 mg/L).

While the initial pH was 6, agitation duration was determined to be 15 min. The final pH of the solution was measured as 12.4. On the other hand, in this group of tests, the effects of Ca(OH)_2 addition only and $\text{Ca(OH)}_2 + \text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ were investigated.

The Effect of Ca(OH)_2 Addition Only

During the tests, Ca(OH)_2 dosage was changed from 2.5 to 20 g/L. HNO_3 was used to decrease the pH of the solution, under the experimental conditions:

- Initial pH: 6,
- Agitation duration: 15 min,
- Solution temperature: 22 ± 2 °C,
- Settling duration: 30 min.

It could be concluded from Figure 4 that the increase in Ca(OH)_2 dosage had a slightly positive effect on the precipitation. 0.44 g/L boron content was obtained by 20 g/L Ca(OH)_2 usage, which is unsatisfactory.

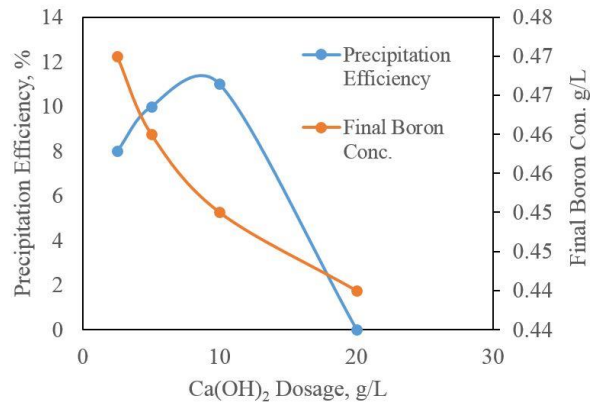


Figure 4. The effect of Ca(OH)_2 dosage on boron precipitation in the second stage

The Effect of $\text{Ca(OH)}_2 + \text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$

In these tests, varying dosages of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ from 40 to 120 g/L was added in the presence of 10 and 20 g/L of Ca(OH)_2 . The reason for $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ addition is to decrease pH to facilitate the reaction of Ca^{2+} ions (Yamada and Eto, 1995).

Table 4The effect of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ addition on boron precipitation in the second stage

Ca(OH) ₂ Dosage (g/L)	Al ₂ (SO ₄) ₃ ·18H ₂ O Dosage (g/L)	Initial pH	Final pH	Final Boron Concentration (g/L)	Precipitation Efficiency (%)	Total Precipitation Efficiency (%)
10	40	3.7	8.0	0.20	61.0	94.9
	60	3.5	3.7	0.14	71.8	96.3
	80	3.4	3.6	0.12	75.8	96.9
	100	3.3	3.5	0.12	76.2	96.9
	120	3.2	3.4	0.12	77.4	97.1
20	40	3.7	10.2	0.16	69.5	96.0
	60	3.5	7.4	0.13	74.5	96.7
	80	3.4	4.1	0.11	77.7	97.1
	100	3.3	3.8	0.11	78.5	97.2
	120	3.2	3.5	0.11	79.0	97.3

Following conditions were kept constant in the tests:

- Agitation duration: 15 min,
- Solution temperature: 22 ± 2 °C,
- Settling duration: 30 min.

During the tests, it was observed that pH decreased from 12.4 to lower levels. These can be seen in Table 4 as the initial pH values. However, the final pH values changed depending on the reagent addition.

According to the results given in Table 4, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ greatly affected the precipitation efficiency of boron. The precipitation efficiency in the second stage increased up to nearly 75 % with elevating $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ dosages than the levels off. The ultimate boron precipitation efficiency obtained was 97 % as a result of two stages of treatment. The final boron concentration in the effluents was about 110 mg/L, which was still too high for safe environmental discharge.

4. Conclusion

The boron in the effluents of the Kirka Boron Inc. contained 3.93 mg/L B, 6.38 g/L Na, and 675 mg/L SO₄.

The effluents could be precipitated at its natural pH 9.44 up to 74.3 %. However, when initial pH was lowered by HNO₃, the precipitation efficiency increased up to 87 %.

It was found that the boron precipitation is strongly related to the Ca²⁺ concentration in the solution. As the pH proceeded towards acidic values, Ca²⁺ concentration in the solution increased to from 300 mg/L to around 1600 mg/L.

Second stage precipitation using $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ in addition to Ca(OH)₂ increased the precipitation efficiency yet remained ineffective to reach the environmentally accepted values of around 2 mg/L discharge concentration.

In conclusion, when the pulp was agitated for 15 min with 20 g/L Ca(OH)₂ and let to settle 30 min, 84.8 % boron could be precipitated. After solid-liquid separation,

the remaining solution was subjected to second stage precipitation, in which the solution was agitated for 15 min with 20 g/L Ca(OH)₂ and 80 g/L $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ for 15 min and then settled for 30 min. As a result, 97 % boron precipitation was achieved. Yet, 0.11 g/L B remained in the solution.

After one stage precipitation, 38 % B₂O₃ was determined in the solid fraction. The XRD analysis on the precipitant showed the chemical composition is in the form of 2CaO·3B₂O₃·13H₂O, which is suitable for boric acid production.

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Izdvajanje bora iz otpadnih voda postrojenja Kirka boraks

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I Z V O D

Kirka Boron Inc. je najveće postrojenje za preradu i dobijanje bora u Turskoj, proizvodi "tincal" (borax) iz rudnika i natrijum penta boraksa u istom kompleksu. Međutim, jalovište predstavlja značajan problem, jer aproksimativno 75 % zapremine postojećih bazena je ispunjeno otpadnom vodom koja sadrži 3 g/L bora. Udeo bora u ovoj vodi mora da se smanji kako bi se ona ponovno koristila u postrojenju. Pri tome koncentracija od 3 g/L bora predstavlja i rizik za životno okruženje. U ovom radu, bor iz vode koja se izliva iz Kirka Boron Inc. postrojenja je istaložen pomoću $\text{Ca}(\text{OH})_2$ i Al_2SO_4 . Praćen je uticaj nekoliko parametara kao što su količina $\text{Ca}(\text{OH})_2$, polazna pH, vreme mešanja i vreme taloženja. Može se reći da koncentracija Ca^{2+} jona ima veliki uticaj na proces precipitacije i da je stepen precipitacije veći ukoliko polazna pH teži kiselim vrednostima. Istraživanja su pokazala da 97 % bora se može istaložiti iz rastvora kroz dva stepena, i pri tome je utvrđeno da se pri taloženju dobije 38 % B_2O_3 .