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Acceleration of Probertite Precipitation in Borax Solutions by Polyelectrolytes

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ABSTRACT

In this study, the importance of surface charge in the precipitation of probertite ($NaCaB_5O_9 \cdot 5H_2O$) in borax solution was shown. By controlling the surface charge with polyelectrolytes, the removal of calcium ions from the borax solution in the form of probertite, which is the most difficult impurity to remove, was studied. The use of only 5 ppm cationic polyelectrolyte and 0.2% of probertite seed crystals was sufficient to reduce the calcium ion concentration to the 200 ppm level in 2 hours. By comparison with the 50–60 hours precipitation time from clear solution to the same level of calcium concentration, it was concluded that polyelectrolytes can be used as tailor-made additives to control precipitation.

Key Words. Probertite; Borax; Polyelectrolyte; Zeta potential

INTRODUCTION

The most important water-soluble boron mineral is tincal ($Na_2B_4O_7 \cdot 10H_2O$) which is used in the production of borax decahydrate, borax pentahydrate, and other boron compounds. The biggest borax reserve in the world is in Kirka (Eskisehir-Turkey) (1). Tincal ore in the Kirka basin contains 60–80% tincal mineral, the rest being mainly dolomite and montmorillonite and to a lesser extent other water-insoluble boron minerals

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such as ulexite, colemanite, inyoite, meyerhofferite, hydroboracite, kurnakovite, and tunellite (2).

The tincal content of this ore is increased to about 88–95% in a concentrator by washing under a mechanical effect, and then it is used as a raw material in a borax refinery plant. In this plant the borax concentrate is dissolved in the recycling mother liquor at about 95°C, and then the insoluble parts are removed by flocculation. The clear borax solution is crystallized at 65°C to obtain borax pentahydrate (3), and the mother liquor of this stage is sent to the borax decahydrate crystallizer working at 45°C (4–6).

Although the production process of borax salts is not complex, the impurity behavior is not very simple. It is well known that borax solutions give complex ion formation with alkaline-earth metals, especially with calcium salts. This property is used for the analytical determination of the boron oxide content of the sample (7).

In borax plants the final refined borax salts always contain some insoluble impurities, mainly in the form of probertite. The precipitation of probertite is not controlled and, depending on many factors, it precipitates in the tubes, in other equipment, and in the product (8–10).

The necessary calcium ion to form probertite comes from calcium-containing minerals in the ore through dissolution and a complexation mechanism (10). The solubilities of calcium-containing minerals in the ore are higher in the borax solution than in water. The higher the borax concentration and temperature, the higher the calcium solubility. In a borax refinery plant, high temperature and borax content lead to dissolution of 300–1000 ppm calcium; this is higher than the equilibrium value of probertite (8–10). Therefore, probertite formation is inevitable. The precipitation rate of probertite is very slow in clear solutions and uncontrolled in the same borax solutions containing suspended matter of different minerals. Clear borax solutions containing about 600–800 ppm calcium at 92°C and 30% $Na_2B_4O_7$ reach the equilibrium solubility of probertite by precipitation in more than 5 days (10). The rate of precipitation is a function of the initial calcium concentration and the kind of solid mineral in the bulk. The precipitation process becomes more complex during the crystallization of borax salts, since the temperature and $Na_2B_4O_7$ content of the solution decrease simultaneously.

This uncontrolled precipitation can be prevented by decreasing the calcium concentration in borax solutions before crystallization starts. Three different methods can be used to control the calcium content in the borax solutions. Any source of carbonate, such as sodium carbonate, CO_2, sodium bicarbonate, and sodium sesquicarbonate, can be used to precipitate calcium ions as $CaCO_3$ in the borax solutions. Carbonate ion concentration must be 0.5–2.5% of the solution by weight, depending on the borax concentration. Under these conditions, calcium is precipitated as calcium carbonate, and it is possible to reduce the calcium concentration to the 150–90 ppm level at which no more probertite precipitation can be observed (9, 10). The carbonate ion concentration needed to precipitate as $CaCO_3$ is extremely high compared to the stochiometric requirement.

A more effective method for the removal of calcium from borax production solutions is to use an ion exchanger. However, this is an expensive method because of the initial investment costs. There is a temperature problem when the solution at 95–100°C is contacted with an ion exchanger having lower temperature stability limits.

The best method for inducing crystallization is to inoculate a supersaturated solution with small particles of the material to be precipitated. Deliberate addition of small quantities of fine particles has been found helpful for inducing crystallization in specific cases (11). A way to accelerate probertite precipitation before the crystallization step is based on the addition of probertite seed crystals to borax production solutions containing calcium ions. For this method, the probertite seed crystals must be at least 5–15% of the solution (8). However, this large amount of seed crystals causes filtration problems.

The aim of this study is to investigate the precipitation mechanism of probertite, to understand the reason why such a large amount of seed crystals is needed to accelerate precipitation, and to provide a method for removing calcium ions from borax production solutions which is efficient and economically desirable.

EXPERIMENTAL

Pure borax decahydrate crystals used in the experiments were obtained from recrystallization of technical grade borax pentahydrate crystals produced in the Kirka Borax Plant in Turkey.

Probertite seed crystals added to the solution were obtained by adding $CaCl_2$ solution to give 1000 ppm calcium ions to a borax solution containing 28% $Na_2B_4O_7$ at 90°C. The precipitated probertite was filtered, washed, dried, analyzed, and used as the seed crystal. The polyelectrolytes used in this study were commercial products, and their trade names and chemical compositions are given in Table 1. Other chemicals used for the analysis were all analytical grade.

In order to determine the effects of the polyelectrolyte concentration and the amount of probertite seed crystals on probertite precipitation, 200 mL borax solutions containing 28% $Na_2B_4O_7$ and 580 ppm calcium ion at 90°C were put into flasks with different probertite and polyelectrolyte

TABLE I
Polyelectrolytes Used in This Study

Trade name	Company	Chemical	Charge
Cat Floc TL	Calgon	Dimethyl diallyl ammonium chloride (DADMAC)	Cationic (100%)
WT 2479	Calgon	Methacryloxy trimethyl ammonium chloride (METAC)	Cationic (~80%)
N100	Cyanamid	Polyacrylamide (PAM)	Nonionic

contents. These flasks were shaked in a thermostated bath for a definite time to follow changes in the calcium ion concentration in the clear solution.

The zeta potential measurements were made with a Zeta Meter. In each test, 0.5 g probertite (<38 μm) was suspended in 200 mL distilled water (conductance of 1.2×10^{-6} ohm·s^{-1}·cm) and in different concentrations of borax solutions. The reagent additions were continuously carried out using the AST (Automatic Sample Transfer) unit of a Zeta Meter 3.0. Polyelectrolyte solutions with 100 ppm stock concentration were added dropwise into the suspension.

$Na_2B_4O_7$ concentration in the solution was determined by a well-known complexation method with mannitol followed by titration with dilute NaOH (12). Calcium ion concentration was determined by a EDTA titration method (13). Precipitation of probertite was followed by calcium ion determination. The chemical composition of the precipitate was also determined by analytical methods.

RESULTS AND DISCUSSION

Calcium ions in borax production solutions containing 3, 8, 18, and 30% $Na_2B_4O_7$ form calcium borate complexes of high solubilities. These complexes reach a maximum concentration, and then calcium starts to precipitate very slowly in the form of probertite ($NaCaB_5O_9 \cdot 5H_2O$) (10).

The mechanism of calcium ion removal by probertite addition can be explained as "the seed crystal role" of the added probertite crystals to the system. To investigate the reason for very large amount of probertite seed crystal required in the probertite precipitation mechanism, the surface charge of probertite particles in pure water and in borax solutions with different $Na_2B_4O_7$ concentrations was measured. The change in the zeta potential of probertite versus borax concentration is shown in Fig. 1.

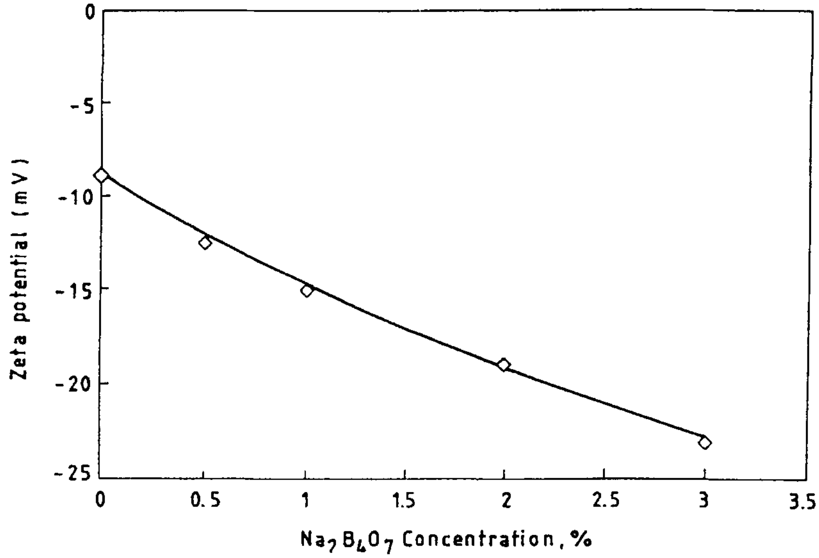

FIG. 1 Variation of the zeta potential of probertite with $Na_2B_4O_7$ concentration.

It is seen from Fig. 1 that probertite gives a −8.92 mV zeta potential in distilled water. The zeta potential of probertite becomes more negative with increasing $Na_2B_4O_7$ concentration in the solution. The zeta potential of probertite cannot be measured in borax solutions containing higher than 3% $Na_2B_4O_7$ because of the high conductivity of the solution. The trend of the curve shows that at higher $Na_2B_4O_7$ concentrations the zeta potential of the probertite surface approaches a high negative asymptotic value. The high negative surface charge of probertite particles in borax solution explains its inability to precipitate spontaneous.

To accelerate the precipitation of probertite, it is necessary to form a critical nucleus upon which further growth can occur thermodynamically. Particles with the critical nuclei size form embryos in the solution. This is possible because of collisions of the required number of embryos (11). Repulsive electrical forces arising from the electromagnetic interactions of the charged layer surrounding the particles, the so-called electrical double layer, prevent the incorporation of embryos in the lattice. Embryos which have the same surface charge cannot contact each other because surfaces of particles with the same charge are repulsive. This results in the formation of invisible embryos in the bulk, and practically no precipitation can be observed. This indicates that probertite should be formed in the amorphous state by a coagulation mechanism. X-ray studies of probertite precipitation prove the existence of the amorphous state. For this reason the spontaneous precipitation of probertite is very slow.

Classical DLVO theory, developed by Deryagin, Landau, Verwey, and Overbeek, defines the total potential energy of the interaction between two charged particles (14–16). This theory states that coagulation time is inversely proportional with the number of stable nuclei and proportional to the stability coefficient, which provide a quantitative measure of the stability of the dispersion. The high stability coefficient of probertite can only be used to explain the time necessary for precipitation from clear borax solutions. This stability can only be broken down by increasing the number of particles. Therefore, an excess amount of seed particles, such as 5–15% by weight of the solution, is necessary for a precipitate to form in a shorter time.

In order to accelerate probertite precipitation, the probertite negative surface charge must be neutralized by using a cationic polyelectrolyte. To accomplish this, nonionic and cationic polyelectrolytes were used in a 3% $Na_2B_4O_7$ borax solution. From 5 to 50 ppm concentrations of polyelectrolyte were added to the suspension, and then the zeta potential of probertite was measured. The change of zeta potential of probertite at these conditions is given in Table 2.

It is clear from Table 2 that nonionic polyelectrolyte N100 did not affect the probertite surface charge, but cationic polyelectrolytes (WT 2479 and Cat Floc TL) neutralized the negative surface charge of probertite and gave an opposite charge. Changes in the zeta potential of probertite as a function of cationic polyelectrolyte WT 2479 concentration are given in Fig. 2.

TABLE 2
The Effect of Polyelectrolytes on the Probertite Surface Charge in Borax Solution (3% $Na_2B_4O_7$)

Trade name	Company	Charge	Concentration (ppm)	Zeta potential (mV)
None	—	—	—	−23.5[a]
N100	Cyanamid	Nonionic	10	−27.0
			25	−27.0
WT 2479	Calgon	Strongly cationic	5	−22.9
			10	−15.6
			25	+14.0
			50	+14.0
Cat Floc TL	Calgon	100% Cationic	10	+16.4

[a] No polyelectrolyte was used in this experiment.

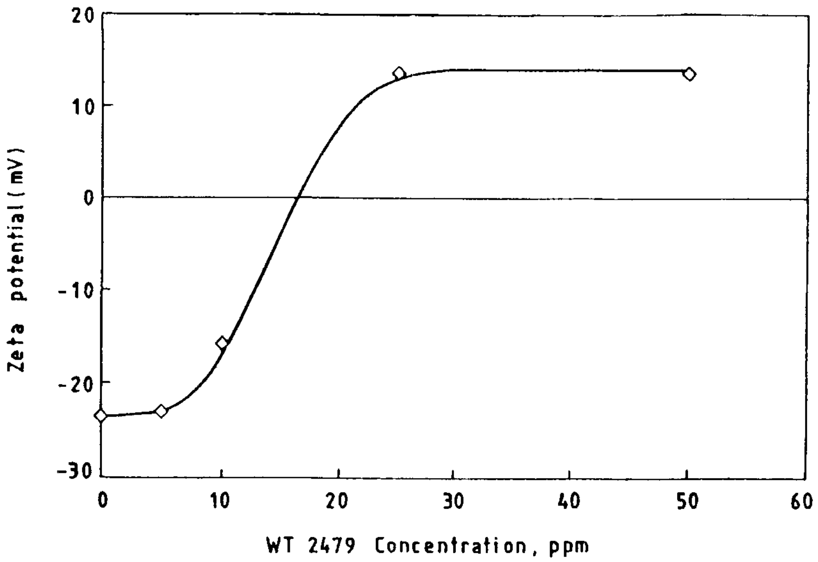

FIG. 2 Variation of the zeta potential of probertite with polyelectrolyte WT 2479 concentration.

Another cationic polyelectrolyte, Cat Floc TL, was also used in the experiments. It neutralized the surface charge of probertite at concentrations lower than WT 2479.

The polyelectrolyte WT 2479 has a polyacrylamide group in its chemical structure which undergoes hydrolysis with temperature and borax concentration, and loses its cationic charge over time. It also has a higher molecular weight and viscosity. The polyelectrolyte Cat Floc TL, on the other hand, is completely stable at high pH values and has a lower viscosity. This is an advantage compared to WT 2479 polyelectrolyte's high viscosity and low physical stability. A 10 ppm concentration of Cat Floc TL is sufficient to change the negative surface charge of probertite to a positive value. For this reason, Cat Floc TL was used for neutralization of the probertite surface charge in the precipitation experiments.

Precipitation experiments were done to examine the effect of the probertite seed crystal ratio and polyelectrolyte concentration on the probertite precipitation rate. The changes in calcium ion concentration in solutions treated with 5, 10, and 25 ppm Cat Floc TL polyelectrolyte and different amounts of probertite seed crystals (0.1–0.5%) are shown in Figs. 3 and 4.

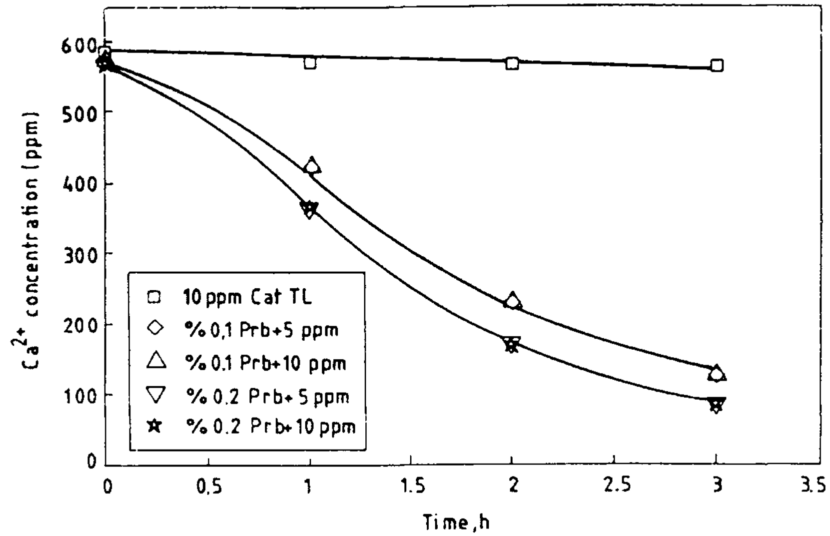

FIG. 3 Variation of the calcium ion concentration as a function of time. (90°C, 28% $Na_2B_4O_7$, Cat Floc TL).

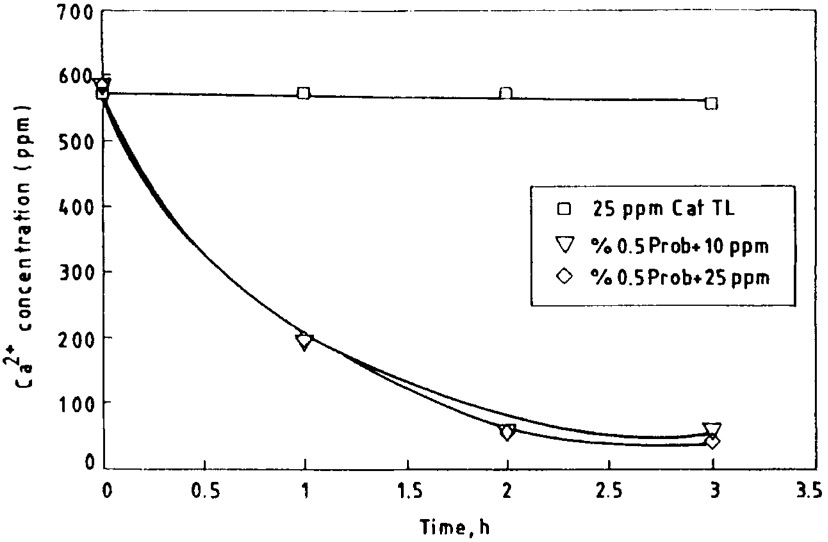

FIG. 4 Variation of the calcium ion concentration as a function of time. (90°C, 28% $Na_2B_4O_7$, Cat Floc TL).

In these figures the change of calcium concentration in the solution is given as the function of time. It is clear from these figures that polyelectrolyte has no effect on the probertite precipitation alone. However, when the solution contains at least 0.1% probertite as seed crystal, there is no difference between 5 and 10 ppm polyelectrolyte additions. This means that 5 ppm Cat Floc TL polyelectrolyte is sufficient to precipitate calcium ions as probertite in 3 hours in a solution which has 0.1% probertite seed crystal. With the addition of 0.2% probertite and 5 ppm Cat Floc TL polyelectrolyte, it is possible to reduce the calcium ion concentration to under 200 ppm in less than 2 hours. In the presence of 0.5% probertite and 5 ppm Cat Floc TL, the calcium ion concentration decreases to under 200 ppm in 1 hour. Without probertite addition, on the other hand, the polyelectrolyte has no effect because the embryos probably cannot reach the critical nuclei size. The results obtained are consistent with DLVO theory, since polyelectrolyte addition eliminates the repulsive forces and the total potential energy of interaction between particles become the van der Waals attractive forces.

CONCLUSION

Surface charge is the dominant factor in the precipitation of highly charged probertite particles. The surface charge and the precipitation kinetics of probertite can be controlled by the addition of polyelectrolytes. Therefore, this group of materials can be looked upon as tailor-made additives for precipitation and crystallization. These results made it possible to find the kind of additive needed for precipitation by using zeta potential measurements.

As a result of this idea, a new technological method was developed to control the calcium ion concentration in a borax solution. By using probertite seed crystals in the amount of 0.2–0.5% of the solution together with 5 ppm Cat Floc TL, the precipitation of calcium ions in the form of probertite was accelerated and the precipitation time was decreased from 60–70 hours down to 1 hour.

REFERENCES

1. D. J. Doonan and L. D. Lower, "Boron Compounds (oxides, acid, borates)," in *Encyclopedia of Chemical Technology*, Vol. 4, 3rd ed. (F. H. Mark, F. D. Othmer, G. C. Overberger, and T. G. Seaborg, Eds.), Wiley-Interscience, New York, 1978.
2. K. Inan, A. C. Dunham, and J. Esson, "Mineralogy, Chemistry and Origin of Kirka Borate Deposit, Eskisehir Province, Turkey," *Chem. Abstr.*, *80*, 62110w (1974).
3. R. A. Smith, "Boric Oxide, Boric Acid, and Borates," in *Ullmanns Encyclopaedia of Industrial Chemistry*, Vol. A4 (W. Gerhartz, Executive Ed.). VCH Verlagsgeselschaft, Weinheim, 1985.

4. A. N. Bulutcu, S. Turkay, H. Gurbuz, and N. Yavasoglu, "Effect of Organic Materials on the Concentration of Tincal Ore," in *2nd. Int. Miner. Process. Symp.* (Y. Aytekin, Ed.), p. 529 (1988).
5. H. Gurbuz, N. Yavasoglu, S. Turkay, and A. N. Bulutcu, "Effect of Two-Stage Washing on the Concentration of Tincal Ore," in *3rd. Int. Miner. Process. Symp.* (G. Onal, Ed.), p. 476 (1990).
6. A. N. Bulutcu, "Crystallisation Problems of Boric-Compounds," in *Bremer International Workshop for Industrial Crystallisation* (J. Ulrich, Ed.), p. 74 (1990).
7. N. P. Nies and G. W. Campbell, "Inorganic Boron-Oxygen Chemistry," in *Boron Metallo Boron Compounds and Boranes* (R. M. Adams, Ed.), Wiley-Interscience, New York, 1964.
8. N. P. Nies and L. Beach, "Production of Sodium Borates," US Patent 3,000,701 (1961).
9. N. P. Nies, L. Beach, and K. K. Kendall Jr., "Production of Sodium Borates," US Patent 3,069,229 (1962).
10. N. Yavasoglu, "The Investigation of the Sources and Removal of Impurities in the Borax Salts Production Process from Tincal Ore," Ph.D. Thesis, Istanbul Technical University, Institute Science and Technology, Maslak-Istanbul, 1993.
11. J. W. Mullin, *Crystallisation*, Butterworths, London, 1972.
12. R. S. Braman, "Boron," in *Encyclopedia of Industrial Chemical Analysis*, Vol. 7 (F. D. Snell and C. L. Hilton, Eds.), Wiley-Interscience, New York, 1968, p. 405.
13. J. B. Bodkin, G. O. Schetty, W. C. Mandell, and C. Wiener, in *Encyclopedia of Industrial Chemical Analysis*, Vol. 8 (F. D. Snell and L. S. Ettre, Eds.), Wiley-Interscience, New York, 1969, p. 104.
14. J. S. Laskowski and J. Ralston, *Colloid Chemistry in Mineral Processing*, Elsevier, Amsterdam, 1992.
15. J. Gregory, "Fundamentals of Flocculation," *CRC Crit. Rev. Environ. Control*, *19*(3), 185 (1989).
16. J. N. Israelachvili, *Intermolecular and Surface Forces*, Academic Press, London, 1985.

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