Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Mechanism of Selective Flotation of Sodium-Calcium Borates with Anionic and Cationic Collectors

M. S. Celik[a]; R. Bulut[a]
[a] MINERAL PROCESSING SECTION MINING ENGINEERING DEPARTMENT, ISTANBUL TECHNICAL UNIVERSITY, ISTANBUL, TURKEY

To cite this Article Celik, M. S. and Bulut, R.(1996) 'Mechanism of Selective Flotation of Sodium-Calcium Borates with Anionic and Cationic Collectors', Separation Science and Technology, 31: 13, 1817 — 1829
To link to this Article: DOI: 10.1080/01496399608001012
URL: http://dx.doi.org/10.1080/01496399608001012

SEPARATION SCIENCE AND TECHNOLOGY, **31**(13), pp. 1817–1829, 1996

Mechanism of Selective Flotation of Sodium-Calcium Borates with Anionic and Cationic Collectors

M. S. CELIK and R. BULUT
MINERAL PROCESSING SECTION
MINING ENGINEERING DEPARTMENT
ISTANBUL TECHNICAL UNIVERSITY
AYAZAGA, 80626 ISTANBUL, TURKEY

ABSTRACT

The major boron minerals, colemanite and ulexite, are frequently found together in boron deposits. Similarities in their chemical compositions create problems in the selective flotation of these minerals. The surface properties of the above boron minerals have been determined by solubility, microflotation, and zeta potential measurements using typical anionic and cationic surfactants. The isoelectric point (iep) of colemanite is 10.5, while ulexite exhibits no iep in a practical pH. Anionic surfactants thus easily float colemanite but fail to float ulexite at a natural pH. This knowledge is used to find the optimum conditions for the selective separation of colemanite from ulexite at a natural pH of 9.3. Cationic surfactants work well but are adversely affected by the presence of clay-type minerals in the boron ore which hinder the floatability of borates by the formation of a slime coating. The mechanism of slime coating onto boron minerals is also elucidated.

Key Words. Colemanite; Ulexite; Boron minerals; Borates flotation; Separation; Collectors

INTRODUCTION

Boron minerals are extensively used in the chemical, metallurgical and nuclear industries with an annual consumption of over one million tons of equivalent B_2O_3. Among over 150 boron minerals identified, only a few of them, notably borax, colemanite, and ulexite, are of commercial importance. The major impurities associated with boron minerals are montmorillonite-type clay minerals expressed with the general formula $(Al,Mg,Fe)_4(Si,Al)_8O_{20}(OH)_4 \cdot nH_2O$. These clay minerals are generally found in the form of hectorite (lithium montmorillonite) and saponite (magnesium montmorillonite). Beneficiation processes at coarse sizes usually involve scrubbing followed by classification to remove the unwanted clay minerals. However, as boron minerals are rather friable, they tend to become finer and are eventually lost in the tailings. Recovery of these fines is possible only through beneficiation processes such as flotation. Fundamental information on the flotation of boron minerals is rather scarce in the literature. Most studies to date have dwelled on colemanite (1–3) and to some extent on borax (4, 5). However, there is no information on ulexite.

Since flotation is usually done in aqueous solutions, the solubility of minerals and the interaction of dissolved species with the solid surface are of considerable importance in determining the final state of charge generation at the solid surface. When a mixture of minerals in water containing different ions is present with flotation collectors, the situation becomes more complex. The interactions of flotation collectors with dissolved species and charged surfaces govern the adsorption of collectors at the surface. It is this adsorption that determines both the hydrophobicity of the solid and its amenability to particle/bubble interactions. Zeta potential is an additional indicator of the ability of ions to be incorporated in the electrical double layer and helps to understand the level of adsorption of flotation reagents.

Colemanite ($Ca_2B_6O_{11} \cdot 5H_2O$) and ulexite ($NaCaB_5O_9 \cdot 8H_2O$) are frequently found together in large reserves in Turkey. Similarities in their chemical structures pose problems in their selective flotation. The objective of this study is therefore to determine the surface properties of ulexite, to compare them with previously published work on colemanite, and to identify a mechanism for adsorbing flotation reagents onto these minerals. Toward this aim, the flotation and zeta potential of colemanite and ulexite have been determined using anionic and cationic surfactants. The presence of clay-type minerals in the boron ore, however, hinders the floatability of borates with cationic collectors because of the formation of a slime coating. The mechanism of slime coating is also elucidated with the help of flotation and zeta potential measurements.

EXPERIMENTAL

Materials

Ulexite and colemanite samples were handpicked from the Bigadic boron deposit in the form of ultrapure crystals. The lump-sized crystals were crushed by a hammer and then ground in an agate mortar to obtain a sample 150 × 210 μm in size for microflotation studies. The finer fractions were used for zeta potential measurements. High purity sodium dodecylsulfate (SDS) and dodecylamine hydrochloride (DAH) were purchased from Fluka and Eastman Kodak, respectively, and used as received. The pH was adjusted by adding HCl or NaOH. Distilled water was used in all experiments.

Methods

Microflotation tests were conducted in a 150-mL all-glass column cell (25 × 220 mm) with a 15-μm fine fritt and a magnetic stirrer. The samples were conditioned in 150 mL of a solution containing the desired reagent for 10 minutes and then were floated for 1 minute using nitrogen at a flow rate of 50 cm^3/min. An automatically controlled apparatus designed in our laboratories was used to control the nitrogen flow rate and the flotation time (2). Calcium ion concentration measurements were made with a Shimadzu 640-12 Model Atomic Absorption Spectrometer. The zeta potential measurements were carried out with a Zeta Meter 3.0 equipped with a microprocessor unit to calculate the zeta potential directly. The procedure used for zeta potential measurements is described elsewhere (4).

RESULTS AND DISCUSSION

Solubility Measurements

Ulexite is a boron mineral with a natural light transmission fiber property (6). The structural formula of ulexite is $NaCa[B_5O_6(OH)_6]\cdot 5H_2O$. The pentaborate fundamental building block (FBB) is found isolated and fully hydrated in the structure of ulexite (6). The structure of colemanite is $Ca[B_3O_4(OH)_3]\cdot H_2O$ and it has a FBB of triborates (7). While colemanite has a monoclinic crystal structure, ulexite has a triclinic structure. Differences in the crystal chemistry and polyanion formation are expected to be reflected in the solubility, electrokinetic, and adsorption behaviors of surfactants on boron minerals.

Boron minerals undergo acid–base reactions in the vicinity of pH 9.3. The dissolution process of colemanite in the presence of CO_2 can be represented as (8)

$$2CaO\cdot 3B_2O_3\cdot 5H_2O + 4CO_2 + 6H_2O \Leftrightarrow 2Ca^{2+} + 6H_3BO_3 + 4HCO_3^- \quad (1)$$

Similarly, ulexite undergoes dissolution in a system open to the atmosphere (9):

$$\begin{aligned} &NaCaB_5O_9{\cdot}8H_2O + 3CO_2 + 6H_2O \\ &\Leftrightarrow Na^+ + Ca^{2+} + 5H_3BO_3 + 3HCO_3^- + 5H_2O \end{aligned} \tag{2}$$

The presence of sodium in ulexite imparts high solubility to the mineral compared with that of Ca^{2+} in colemanite. Figure 1 illustrates the effect of solids concentration on the dissolution of colemanite, ulexite, and calcite. Colemanite and ulexite have solubilities of 0.81 and 4.63 g/L at 20°C, respectively. The solubility of colemanite is in fair agreement with that reported by Yarar (1) at 25°C. The solubility value has an important implication for flotation because it dictates the release of multivalent ions and also the interaction of collectors with oppositely charged electrolytes.

Zeta Potential Measurements

Zeta potential measurements are presented in Fig. 2 as a function of pH. Colemanite has an isoelectric point (iep) at pH 10.5 whereas ulexite yields no iep in the pH range of 7 to 11 (10). This indicates that colemanite is positively charged over this pH range whereas ulexite is negatively charged in the entire pH range. The zeta potential measurements as a

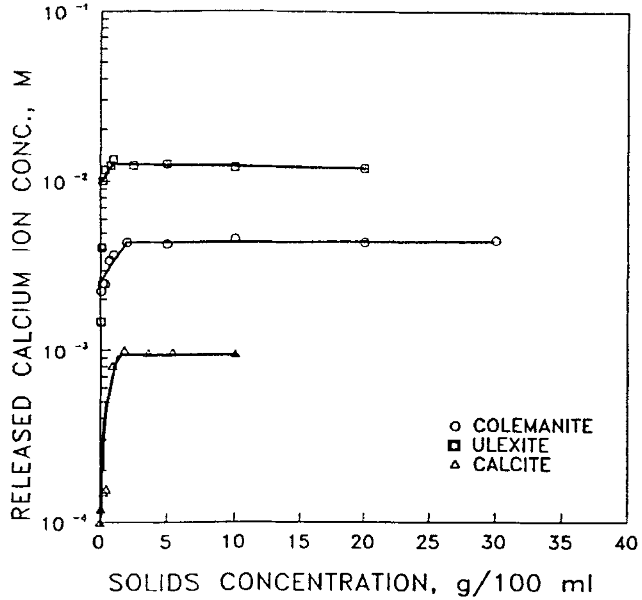

FIG. 1 Solubility of calcite, colemanite, and ulexite as a function of solids concentration at 20°C and a natural pH of 9.6 for calcite and 9.3 for boron minerals.

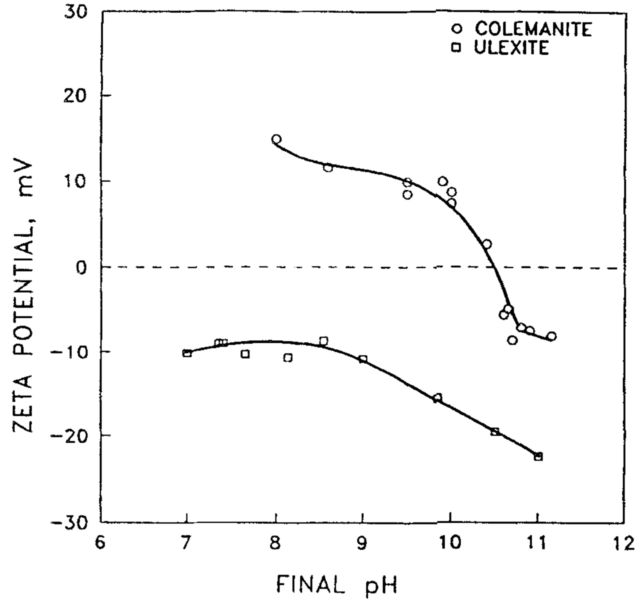

FIG. 2 Variation of zeta potential of colemanite and ulexite with pH in water.

function of various ion concentrations reveal that the potential-determining ions for colemanite and ulexite are Ca^{2+}, $B_4O_7^{2-}$, H^+, and OH^-, which dictate the HCO_3^-/CO_3^{2-} ratio (10). The effect of ionic strength on the zeta potential of colemanite and ulexite has been addressed elsewhere (11). While salts of monovalent cations decrease the charge of colemanite, ulexite is affected in the opposite manner. This is ascribed to the compression of the electrical double layer in the former case and the decrease of the solubility of calcium in the latter case (11).

Flotation of Colemanite and Ulexite

Figure 3 presents the effect of conditioning time on flotation recoveries of ulexite in the presence of anionic (SDS) and cationic (DAH) reagents. Ulexite mineral with both surfactants reaches constant flotation recoveries at approximately 10 minutes of conditioning time. Other boron minerals such as colemanite and borax required the same conditioning time for establishing equilibrium (4). This may indicate that both anionic and cationic surfactants generally adsorb on boron minerals via a physical adsorption mechanism.

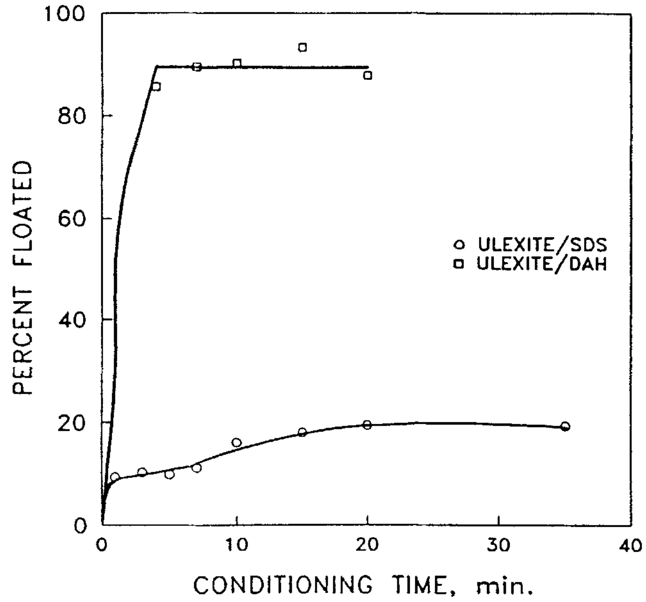

FIG. 3 Effect of conditioning time on flotation recoveries of ulexite with anionic (6.7×10^{-5} M SDS) and cationic (1.0×10^{-4} M DAH) collectors at a natural pH of 9.3.

Figure 4 shows the effect of anionic surfactant (SDS) on floatability of colemanite and ulexite. While SDS is capable of floating colemanite at concentrations above 10^{-5} M, percent recoveries with ulexite are only about 40% at concentrations as high as 5×10^{-4} M. An explanation can be offered if the electrokinetic data given in Figure 2 are reviewed. The iep of colemanite is 10.5; below this pH the surface is positively charged. Since the natural pH of the system occurs at pH 9.3 ± 0.1, SDS can easily float colemanite in most of the pH range. Contrary to this, ulexite is negatively charged in the entire pH range and thus is marginally conducive to electrostatic interaction with anionic SDS.

Unlike SDS, the interaction of cationic surfactant (DAH) with ulexite is lower than that obtained in the colemanite/SDS system. Although at pH 9.3 the net charge on colemanite is positive and that on ulexite is negative, colemanite floats better with the cationic reagent (4). This interesting behavior will be described further when discussing the role of pH in the ulexite/DAH system. The zeta potential measurements given in Fig. 5 support the data for ulexite given in Fig. 4. Interestingly, the zeta potential of ulexite with SDS remains constant with negative charges throughout the concentration range whereas it undergoes a charge reversal with DAH

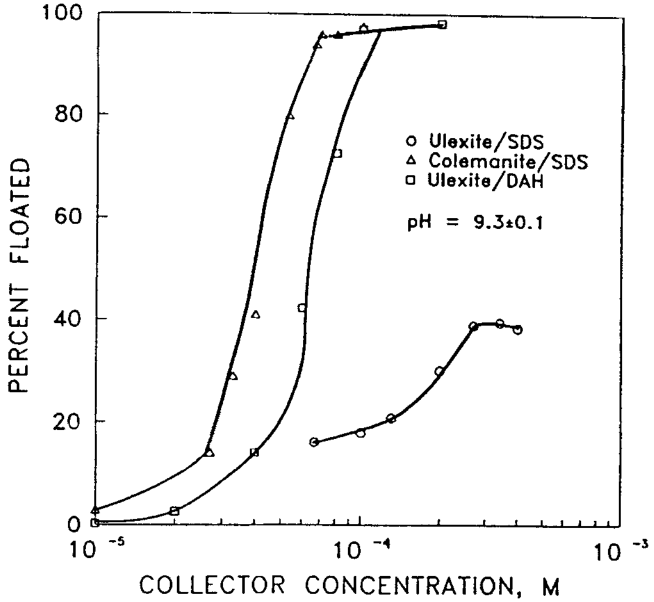

FIG. 4 Floatability of colemanite and ulexite as a function of collector concentration.

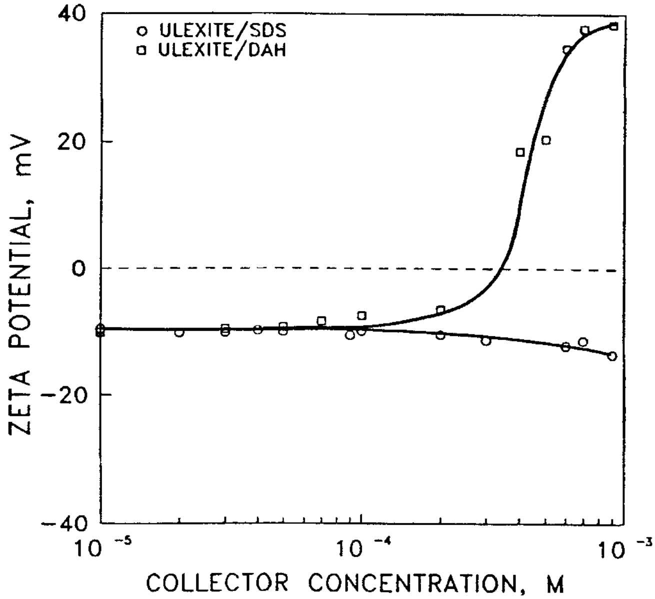

FIG. 5 Zeta potential variation of ulexite in the presence of anionic and cationic collectors at a natural pH of 9.3.

above 2 × 10^{-4} M which approximately corresponds to the solubility limit of DAH at this pH (12).

The flotation recoveries of ulexite and colemanite with SDS as a function of pH are shown in Fig. 6. It should be noted, however, that due to differences in the iep values, the initial concentrations of SDS were selected differently. The flotability of colemanite and ulexite decreases with increasing pH. This is again attributed to the magnitude of electrostatic interactions in this pH range for the respective minerals. The decreasing flotation trend with pH indicates that the adsorption of SDS on colemanite and ulexite is governed via an electrostatic attraction mechanism.

In the same figure (Fig. 6), the flotability of ulexite with two different DAH concentrations is illustrated as a function of pH. At low DAH levels, the flotation recoveries exhibit a sharp decrease with increasing pH. At high DAH levels, where precipitation of DAH is observed, the decrease in the floatability of ulexite with pH is marginal. This is contrary to the behavior observed in the quartz/DAH system where a mirror-image trend in the floatability of quartz is reported (13). It appears that the role of ion–molecular complexes responsible in the quartz/amine system is not evident in the ulexite/amine system. These results are corroborated by

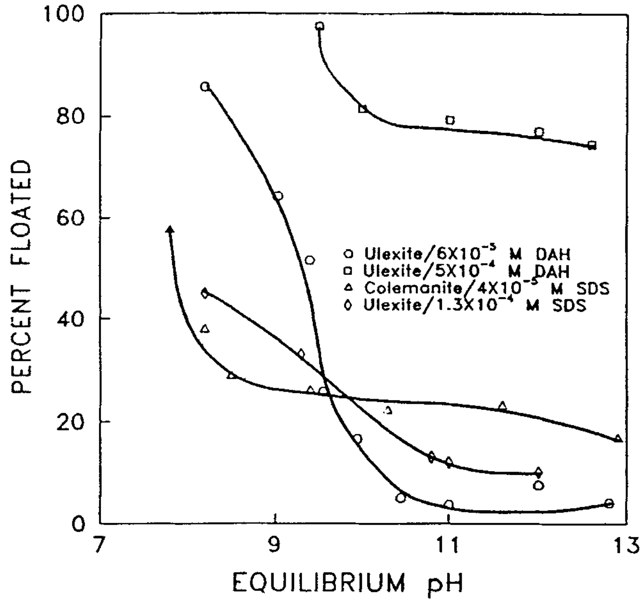

FIG. 6 Floatability of colemanite and ulexite as a function of pH with different collectors.

the data presented in Fig. 7. While the zeta potential of ulexite is negative at low DAH levels in all practical pH range, positive charges persist at high DAH levels.

It should be noted that the flotation conditions proposed based on microflotation results can only be a guide. Implementation of these data in either bench scale, i.e., Denver cell, or pilot scale tests requires more elaborate results on both hydrodynamics and physicochemical parameters. Therefore, microflotation can indicate whether a certain reagent can selectively separate two or more minerals and also provide fundamental information by which one can predict or explain the results of actual tests. However, it is well known that there are always interferences from various minerals in an ore and also from dissolved species in the pulp. Flotation results thus need to be repeated with actual ores and commercial reagents.

Effect of Clay Minerals on Floatability of Ulexite

Previous studies have shown that the addition of as little as 10 mg (0.5% by weight of the total solids) clay mineral is capable of lowering the flotation recoveries of borax to below 30% (14). As with borax, clay minerals are the major impurity associated with ulexite. Figure 8 illustrates the

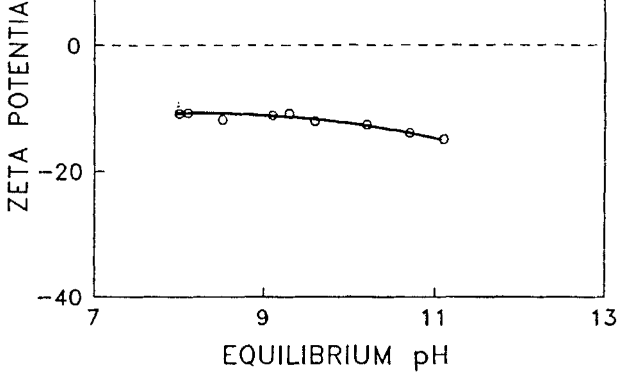

FIG. 7 Zeta potential of ulexite versus pH with two levels of cationic collector addition.

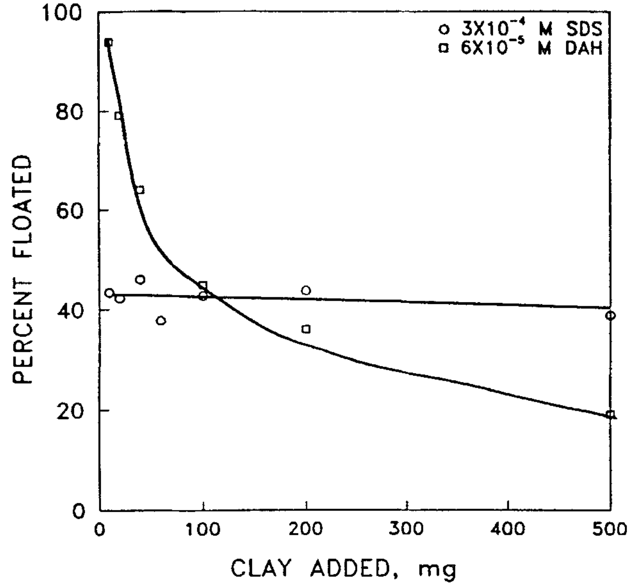

FIG. 8 Effect of added slime on the floatability of ulexite with two different collectors at a natural pH of 9.3.

effect of added clay on the floatability of ulexite with SDS and DAH. Interestingly, while the floatability of ulexite with SDS is not affected by the presence of clay, the addition of clay to a system floated with DAH gradually lowers the recoveries significantly. The indifference of clay mineral to the ulexite surface vividly shows the weak electrostatic attraction in the system. Conversely, the compatibility of electrostatic interactions in ulexite/DAH/clay is again a good example of the presence of electrostatic interaction in the system. Previous studies conducted with colemanite revealed that clay minerals are very active on oppositely charged surfaces and can easily accumulate on positively charged colemanite surfaces by electrostatic attraction.

Figure 9 shows that it is possible to improve the floatability of clay-coated ulexite at higher DAH concentrations. The recoveries reach over 90% at 4×10^{-4} M DAH concentration. However, SDS appears to have no affinity for ulexite at concentrations even as high as 10^{-3} M; this is attributed to the negative charges predominating on ulexite at all SDS levels, as shown in Fig. 7.

Based on the above results, it is possible to formulate some optimum conditions for the selective separation of colemanite from ulexite. An

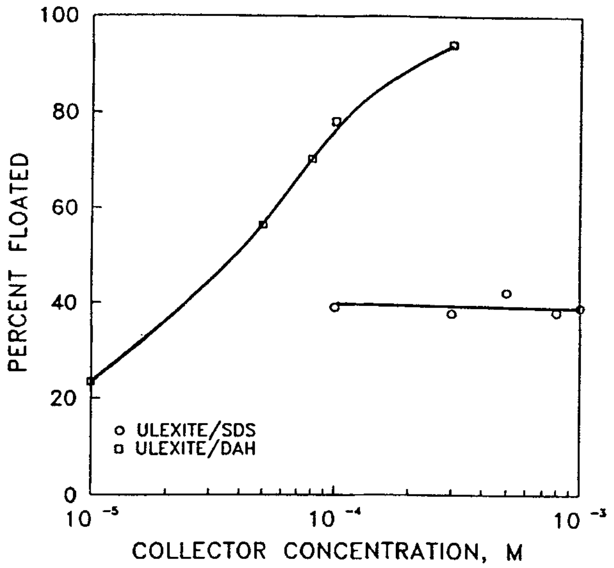

FIG. 9 Effect of increasing collector concentration on the floatability of ulexite in the presence of 60 mg clay at a natural pH of 9.3.

anionic collector floats colemanite at low collector concentrations at which ulexite is not significantly floatable. Also, an anionic collector is not affected significantly by a slime coating. This window of selectivity can be utilized for their selective separation. However, this flotation scheme needs to be repeated in a bench-scale flotation cell.

Mechanism of Slime Coating

The mechanism of slime coating can be explained in the following manner. The clays associated with boron minerals have been shown to be of the montmorillonite type and to exhibit negative charges in the entire pH region with no iep values. This feature gives the boron clays a high affinity for interaction with positively charged boron minerals. Except for ulexite, the boron minerals, i.e., colemanite, borax, inderite, and tunellite, are similar in their clay uptake. The low charge character on these minerals makes slime coating particularly amenable. However, it is difficult to generalize the order of uptake of slime and collector molecules. Studies with colemanite show that the order of addition is not critical. The most important criteria are the concentration of the collector and the surface charge of the mineral. It is possible to induce competition between the collector molecule and slime by increasing the collector concentration. As shown in Fig. 9, flotation recoveries increase rapidly with increasing collector concentration. Whether this is due to the competition of the slime and DAH molecules for the ulexite surface or the uptake of further DAH molecules on the ulexite surface still needs to be investigated. Another equally plausible alternative is the adsorption of DAH onto slime-coated sites on the ulexite surface.

CONCLUSIONS

The solubility of boron minerals is generally dictated by the constituent lattice ions. While sodium-calcium-containing ulexite at 20°C has a solubility of 4.63 g/L, calcium-containing colemanite has a solubility of 0.81 g/L. Colemanite has an iep value of 10.5, whereas ulexite has no iep value in the entire practical pH range. The potential-determining ions for these minerals are Ca^{2+}, $B_4O_7^{2-}$, and H^+ (and thus OH^-) ions which dictate the ratio of HCO_3^-/CO_3^{2-}.

Because of differences in the electrokinetic behaviors of colemanite and ulexite, the anionic reagent SDS easily floats colemanite but fails to float ulexite. This behavior enables the selective separation of colemanite from ulexite at a natural pH of 9.3. Slime coating does not adversely affect the selective separation of colemanite from ulexite in the presence of an anionic collector. Cationic surfactants float both colemanite and ulexite similarly, and thus are not effective in separating them. Also, the presence of slime coating hinders the floatability of both minerals with a cationic collector.

The mechanism of slime coating is ascribed to physical uptake of negatively charged clay minerals on the positive sites of boron minerals. While this prevents the adsorption of cationic collectors, adsorption of anionic collectors is affected only marginally.

REFERENCES

1. B. Yarar, "The Surface Chemical Mechanism of Colemanite–Calcite Separation by Flotation," in *Borates: Economic Geology and Production* (S. J. Barker and J. Lefond, (Eds.), AIME Publishers, New York, 1985, pp. 221–233.
2. M. Hancer and M. S. Celik, "Flotation Mechanisms of Boron Minerals," *Sep. Sci. Technol.*, *28*, 1703–1714 (1993).
3. M. S. Celik, M. Hancer, G. Atesok, and F. Emrullahoglu, "Activation Mechanisms of Multivalent Ions in the Flotation of Boron Minerals," in *Beneficiation of Phosphates: Theory and Practice*, (H. El-Shall, B. M. Moudgil, and R. Wiegel, Eds.), SME Publishers, New York, 1993, pp. 57–65.
4. M. S. Celik, S. Atak, and G. Onal, "Flotation of Boron Minerals," *Miner. Metall. Process.*, *10*, 149–153 (1993).

5. R. Yalamanchili and J. D. Miller, "Discussion to Flotation of Boron Minerals," *Ibid.*, *11*, 121–123 (1994).
6. S. Ghose, C. Wan, and J. R. Clark, "Crystal Structure of Ulexite, a Natural Light Transmission Fiber," *Am. Cryst. Assoc., Winter Meet. Abstr.*, *5*, 39 (1977).
7. C. L. Christ, and R. Clark, "A Crystal-Chemical Classification of Borate Structures with Emphasis on Hydrated Borates," *Phys. Chem. Miner.*, *2*, 59–87 (1977).
8. M. Alkan, M. Oktay, M. M. Kocakerim, and Z. Karagolge, "Dissolution Kinetics of Some Borate Minerals in CO_2-Saturated Water," *Hydrometallurgy*, *26*, 255–262 (1991).
9. M. Alkan and M. Kocakerim, "Dissolution Kinetics of Ulexite in Water Saturated by Sulfur Dioxide," *J. Chem. Tech. Biotechnol.*, *40*, 215–222 (1987).
10. E. Yasar, I. Gulgonul, Y. Kaytaz, and M. S. Celik, "Electrokinetic Properties of Boron Minerals," Demirel, H. (Ed.), in *Proceedings of V International Mineral Processing Symposium, Cappadocia, Turkey* (H. Demiral, Ed.), Balkema Publishers, 1994, pp. 131–134.
11. M. S. Celik, Y. Akin, and M. Hancer, *Decompression of Electrical Doublelayer with Monovalent Cations*, Presented at the SME Annual Meeting, Phoenix, Arizona, March 11–14, 1996.
12. J. S. Laskowski, J. L. Yordan, and R. H. Yoon, "Electrokinetic Potential of Microbubbles Generated in Aqueous Solutions of Weak Electrolyte Type Surfactants," *Langmuir*, *5*, 373–376 (1989).
13. R. W. Smith and J. L. Scott, "Mechanism of Dodecylamine Flotation of Quartz," *Miner. Process. extr. Metall. Rev.*, *7*, 81–94 (1990).
14. M. Hancer, Y. Kaytaz, and M. S. Celik, "Flotation of Borax with Cationic and Anionic Collectors in Saturated Solutions," in *Proceedings of XIII Mining Congress of Turkey, Istanbul*, May 1993, pp. 519–528.

Received by editor November 2, 1994
First revision received May 3, 1995
Second revision received September 14, 1995