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Characterization of clay rock samples of a borax ore in relation to their problematical flocculation behavior

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ABSTRACT

Beneficiation process in the Kırka Borax Concentrator in Turkey generates a tailings effluent containing 3–10% solids that are composed mainly of colloidal particles of clay-rock-type gangue minerals and some unrecoverable borax fines. These colloidal particles form very stable aqueous suspensions in the tailings, hindering solid/liquid separation and clean water recovery. This leads to difficulties in the sustainable and environmentally acceptable operation of the concentrator. Flocculation studies on these colloidal suspensions had shown that the particles of the gangue minerals presented significant resistance to destabilization and remained in suspension forming high-turbidity supernatants in settling tests. For this reason, this study was undertaken to characterize the nature of such gangue particles with the intention of understanding the reason for their extreme colloidal stability and poor performance in polyethylene oxide (PEO)-induced flocculation tests. Particle size and zeta potential measurements elucidated the suspension stability with $d_{80} \leq 5$ μm and ζ-potential ≤ −70.1 mV. XRF and XRD studies showed that the problematical particles were rich in Mg-minerals (dolomite and trioctahedral smectite). A plausible explanation of the insufficient destabilization might be that the surface Mg ions have very high hydration energy and hold the water molecules very tightly by blocking the surface for the polymer adsorption and particle–particle interaction. FTIR spectra indicated the lack of isolated hydroxyl groups on the particle surfaces. Due to this vital drawback, the polymer chains could not be adsorbed through hydrogen bonding mechanism and this highly turbid suspension could not be flocculated.

1. Introduction

The Kırka deposit in western Turkey is presently the largest borax deposit known in the world. The main boron mineral in the deposit is borax (sodium borate) with lesser amounts of colemanite, ulexite, and many other varieties of borate minerals. The gangue material associated with borax is made up of mainly a smectite-group mineral and dolomite with varying proportions, and relatively low amounts of other silicates [17]. The enrichment of borax ore in the Kırka borax concentrator is comprised of washing the crushed and scrubbed ore [1,27] at ambient temperatures to remove insoluble impurities, mainly clay minerals and dolomite. This physical separation process generates a borax-saturated tailings effluent containing 3–10% clay-sized particles of colloidal behavior, which is directly discharged [9] to the tailing ponds without any physicochemical treatment. However, it takes seven to ten days for the sedimentation of the colloidal particles in the tailings effluent [19] because the increase in the clay concentration decreases the sedimentation rate [2]. This long period of sedimentation is not acceptable for a sustainable plant operation as the waste effluents are gradually filling up the tailing ponds, necessitating ever increasing pond areas. Some mechanical dewatering systems, like successive thickeners and centrifugal decanters were tried to remedy the problem but it was seen that effective polymer-induced flocculation was needed for a satisfactory dewatering process even in the case of centrifuge decanter trials [5]. Using Al- or Fe-based inorganic coagulants prior to polymeric flocculants to increase the efficacy of flocculation is not suitable in this case since the presence of dissolved borax in the effluents buffers the pH about 9.4. Such inorganic coagulants, however, are effective at pH values about 5 to 6. Based on this fact, the flocculants alone were generally preferred and suggested instead of inorganic coagulants in the wastewater treatment of the boron industry [13]. Some studies have been directed towards understanding the flocculation behavior of Kırka borax slimes with various flocculants. Gür et al. [16] tested the performance of various conventional polyacrylamide (PAM)-based polymers of different ionic character and polyethylene oxide (PEO) in reducing the turbidity of flocculated suspensions prepared in borax solutions using various types of clays selected from the Kırka open-pit mine. They reported that either PAM- or PEO-based polymers could flocculate the clay dispersions having different borax and solids concentrations, but the PEO-based flocculant produced clearer supernatants, particularly in the flocculation of dolomite rich suspensions. Their

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flocculation tests with smectite-rich samples at 65 °C indicated lower supernatant turbidity and lower optimal polymer consumption with increasing borax concentration (3%, 8% and 15%) in solution. Sabah and Yesilkaya [30] studied the settling behavior of Kırka borax concentrator tailings, testing one non-ionic and two anionic PAM-based flocculants, both in the presence and absence of coagulants (aluminum sulfate and ferric chloride) at pH 9, the natural pH of the waste water samples taken from the plant. The anionic flocculants performed much better than the non-ionic flocculant in terms of the settling rate, but still at quite a high flocculant consumption of 1176 g/ton solids, and no data were reported with regard to supernatant clarity. Use of coagulants together with the better performing anionic flocculant or increasing the borax concentration in solution both resulted in slower sedimentation rates. More recently, the authors [6–8,18] investigated the performance of conventional medium anionic PAM- and nonionic PEO-type flocculants (2-D linear structure) as well as non-conventional anionic PAM-type flocculants (3-D branched structure) in the settling tests of dolomite/clay/borax-containing suspensions, using the clay samples taken from the Kırka Borax mine. Their work revealed that the nonionic PEO performed better than the other conventional and nonconventional PAM-type flocculants in reducing the supernatant turbidity.

The abovementioned studies focused mostly on the flocculation performance of different polymers without giving much consideration to characterization of the colloidal particles of the tested suspensions. Therefore, this paper attempts to give a detailed characterization of two major clay rock types of the Kırka borax deposit. These rock types, as the major gangue material of the ore, generate slow-settling aqueous colloidal dispersions in the plant tailings which do not respond well to flocculation. To ascertain the underlying particle-induced problem(s) in the flocculation of these colloidal dispersions, chemical and mineralogical constituents of the samples of the two major rock types were firstly determined in a qualitative and quantitative manner. The colloidal property of the mineral phases in the samples was explained with the fineness of the particles and the zeta potential of their surfaces. Finally, the active groups on the particle surfaces, which were called the isolated hydroxyls, were tried to be identified via FTIR studies. With the help of these characterization studies, the main causes of the flocculation problem specific to these two samples were identified, and the technical requirements to efficiently destabilize their dispersions were proposed.

2. Materials and methods

Samples of two clay rock types, locally named green clay and white clay, according to their natural color, were collected from the Kırka open-pit mine in western Turkey. These rock types reflect the general characteristics of the non-flocculatable gangue particles of the borax formation and frequently used [7,16] as test materials in previous laboratory work.

Prior to the characterization studies, colloidal dispersions of the test samples were subjected to flocculation tests with a non-ionic high-molecular-weight (M_W: 8,000,000) polyethylene oxide (PEO) flocculant to show the resistance of the dispersions to flocculation. The free-flowing white powder (100% ≤ 1000 μm) of PEO with the repeating unit of $[—CH_2—CH_2—O—]_n$ was used as flocculant. The required amount of PEO was added into the distilled water and mixed for 1-hour in magnetic stirrer to prepare 0.05% (w/w) feed solution. Due to the behavioral change of the flocculant chains after 24 h, the flocculant solutions were prepared freshly on a daily basis. The dispersions were prepared with distilled water containing 3% solids and 3% dissolved borax by weight to resemble the tailings stream of the Kırka Borax Concentrator. Due to the buffering property of borax, pH of the solution was fixed about 9.40 throughout the flocculation experiments. The suspensions in 800 ml beakers were conditioned with standard flat blades of a Jar Test apparatus, in which the polymer-injected suspensions were mixed at 10 rpm by adjusting automatic timing unit to 120 s. The assessment of flocculation efficiency was reported as the supernatant turbidity in units of nephelometric turbidity (NTU) after sedimentation of flocculated dispersions. Turbidity was measured with a Lamotte Model Portable Turbidimeter.

Chemical analyses of the clay rock samples were performed using Spectro IQ X-ray Fluorescence (XRF) spectrometer. The samples were firstly subjected to pressure under a press to obtain disk-shaped pellets and the XRF spectra of these pellets were analyzed via the equipment software.

X-ray diffraction studies were carried out by a Rigaku X-ray diffractometer, operating at 40 kV and 20 mA using CuKα radiation at a scanning speed of 2°/min. Bulk mineralogy of the whole samples was determined with randomly ordered mounts of the powdered samples. However, some preparation steps were applied to identify clay minerals with the use of the oriented samples. Since the samples were rich in dolomite, dilute hydrochloric acid (0.1 M) solution, rather than acetic acid, was used to remove dolomite from the sample, as suggested by Ostrom [26]. The acid-treated suspension was rinsed as soon as all the carbonate had been dissolved and left to settle for 8 h. The unsettled part of the dispersion was collected and centrifuged at 1500 rpm for 10 min to sediment the clay-size solids. The sediment was then redispersed and homogenized in distilled water. This clay suspension was drawn into a dropper. Four or five drops of the suspension were poured on each of three glass slides placed on a ceramic tile so as to completely cover the surfaces of the glass slides with the clay–water suspension. Then, the glass slides were dried at room temperature to obtain oriented clay platelets. One of the oriented clay samples was subjected to ethylene glycol vapor for 12 h at 60 °C. This treatment was used for defining the degree of swelling of the contained clay mineral in the samples. The remaining two of the oriented samples were subjected to heat treatment at 300 °C and 550 °C, respectively. These samples were used to define collapsing behavior of the swelling clay.

Quantitative mineralogical analyses of the samples were accomplished using the Rietveld method via the computer program MAUD (Material Analysis Using Diffraction) [21]. The Rietveld method, which is known as whole-pattern fitting structure refinement, uses all intensity data in the XRD pattern rather than a few of the most intense peaks [33]. In the Rietveld analysis, refinement is done by minimizing the sum of the weighted squared differences between observed and calculated intensities in the XRD pattern. The calculated intensity at a given step (yic) is determined by summing the contributions from background and all neighboring Bragg reflections (k) for all phases (p). Hence, the Rietveld method can be considered as an iterative computation technique as summarized by Bish & Post [3] with a given formula:

$$y_{ic} = \sum_{p}^{\backslash} S_p \sum_{k}^{\backslash} p_k L_k |F_k|^2 G(\Delta\theta_{ik}) P_k + y_{ib}(c)$$

where S is the scale factor; L_k is the Lorentz and polarization factors for the k-th Bragg reflection; F_k is the structure factor; p_k is the multiplicity factor; P_k is the preferred orientation function; is the Bragg reflection angle for the kth reflection; is the reflection profile function; and is the refined background.

A Malvern Mastersizer 2000 instrument utilizing the light scattering technique with the help of a laser beam was used for particle size measurements. For this purpose, the clay rock samples were completely dispersed in 250 ml distilled water with the help of mechanical agitation and ultra-sonication. For the ultra-sonication, Vibra Cell Product of Sonics & Materials Inc. was used with a standard probe and a power output of 200 W. Since these measurements refer to volume-based particle size distributions, it should be noted that the smectitic components of the samples might cause small deviations in the results due to their swelling property.

The actual solid concentration of 3% w/w could not be measured in the zetameter due to the very high particle counting levels, which exceeds the upper limit of the detection. To limit the particle count