An Investigation of the Phase Transformation of Brownmillerite in Chromite Ore Processing Residue

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ABSTRACT

Chromite ore processing residue (COPR) is a hazardous waste generated by a high lime process for Chromium (Cr) extraction. Brownmillerite is the main mineral phase in COPR and it is unstable in aqueous environments. Katoite and calcium aluminum chromium oxide hydrates (CAC) are the main reaction products of brownmillerite with water and soluble chromate, respectively. Millions tons of COPR have been deposited at two sites in USA that are currently under investigation, with regard both to heaving phenomena observed at the sites, as well as with Cr(VI) speciation, leaching behavior and treatment. In order to elucidate the reaction pathway of COPR, a kinetic study of CAC and katoite formation was conducted at ambient temperature by preparing slurry samples with both synthetic brownmillerite and actual COPR samples with high brownmillerite content, Slurry samples were prepared with deionized water and with a potassium chromate solution on a 2:1 liquid-to-solid ratio in order to investigate the transformation of brownmillerite to katoite and CAC compound, respectively. The concentration of chromate was calculated based on 1% w/w of the dry sample to represent an average Cr(VI) concentration in COPR. Subsamples were drawn after an aging time of 1 hour, 8 hours, 1 day, 2 days and 7 days. All samples were analyzed by X-Ray Powder Diffraction (XRPD). Scanning Electron Microscopy (SEM)/Energy Dispersive Spectroscopy (EDS) was also utilized to support XRPD results. The pH of the mixture was also monitored. Overall, by using synthetic brownmillerite, the transformation of brownmillerite to katoite was very fast (less than 1 hour) and was complete within 7 days. CAC formation was also thermodynamically favored

upon chromate influx, as it was observed in the XRPD pattern within one hour of reaction. The XRPD patterns of formed katoite and CAC are shown in Figure 1 and 2, respectively. Also, SEM images of synthetic brownmillerite, transformed katoite and CAC phases are presented in Figures 3 and 4. However, employing actual COPR samples as opposed to synthetic brownmillerite, katoite and CAC formation were not observed in the reported experimental period of time; no major phase transformation was observed in these samples This indicates that the dissolution of brownmillerite identified in COPR materials is very slow, so that katoite and CAC formation is kinetically inhibited.

Key words: COPR, Brownmillerite, Katoite, CAC, XRPD, SEM/EDS

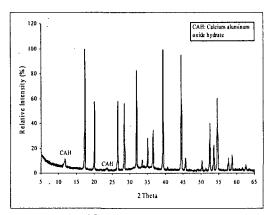


Figure 1. XRPD pattern of synthetic brownmillerite, hydrated to form katoite

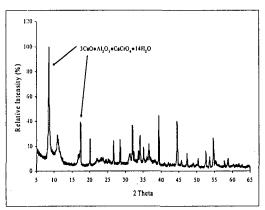


Figure 2. XRPD pattern of synthetic brownmillerite, reacted with chromate to form CAC.

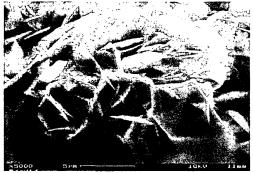


Figure 3. SEM image of katoite (hexagonal in shape) formed from synthetic brownmillerite upon hydration.

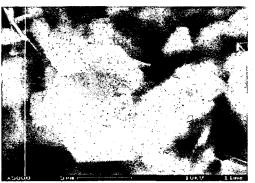


Figure 4. SEM image of CAC (hexagonal in shape) formed from synthetic brownmillerite upon chromate addition.