

Crystallization of hydroxide cobalt carbonates during aging processes at ambient temperature: Evolution during thermal treatment.

J. González López (1), A. Jiménez (2), and A. Fernández González (3)

(1) Spain, Fac. Geology, University of Oviedo (jgonzalez@geol.uniovi.es), (2) Spain, Fac. Geology, University of Oviedo (amalia.jimenez@geol.uniovi.es), (3) Spain, Fac Geology, University of Oviedo (mafernan @ geol.uniovi.es)

Cobalt carbonates are rare in nature but typical in hydrothermal cobalt bearing mineral deposits (Anthony et al., 2003). At environmental conditions, the presence of low concentrations of aqueous Co^{2+} are responsible of morphological changes in calcite crystals at both macroscopic and nanoscopic scales (Fernandez Diaz et al., 2006; Freij et al., 2004). Moreover, previous studies have demonstrated that the formation of Co-bearing calcite, Co-bearing aragonite and Co-rich low crystallinity phases are involved at ambient conditions (Katsikopoulos et al., 2008). The crystallization behaviour of Co-carbonates seems to be complex and needs to be studied in depth. The objective of this work is: a) Synthesise Co-bearing carbonates and study its evolution during aging processes at ambient temperature. b) Study the evolution of the phases previously obtained by applying a thermal treatment. With this aim, a set of 9 experiments (all of them from a mutual parent solution) were carried out by mixing aqueous solutions of CoCl_2 (0.05M) and Na_2CO_3 (0.05M) with increasing reactions times (5 minutes and 1, 5, 24, 48, 96, 168, 720 and 1440 hours). These experiments were performed at 25°C and the solutions were kept at constant agitation during the entire reaction period. The final solid phase obtained by precipitation was then heated at 500°C in air atmosphere during 240 minutes. All the solid phases were analyzed by X-ray powder diffraction (XRD) and the crystallinity degree was followed by the intensity and the full width at high medium (FWHM) of the main peaks. The precipitates were examined by Scanning Electron Microscopy (SEM) and by Transmission Electron Microscopy (TEM).

In the early stages of the experiments, a low crystallinity phase was obtained. With increasing time, this phase evolves progressively to form hydroxide carbonate cobalt ($\text{Co}_2\text{CO}_3(\text{OH})_2$) which crystallize with the spatial group P21/a (monoclinic system). Although a slight increasing degree of crystallinity of hydroxide carbonate cobalt is observed with aging, the peaks shows low intensity and high FWHM values. This phase is isostructural with minerals Rosasite group. TEM results confirm the low crystallinity of the hydroxide carbonate cobalt obtained at the end of the aging processes. The hydroxide carbonate cobalt evolves to the most stable cobalt oxide (Co_3O_4) after heating. Cobaltic oxide crystallise in the spatial group Fd3m (cubic system) with a spinel structure. These results show that the crystallization behaviour of Co-bearing carbonates involves the formation of a low crystallinity phase, which evolves to hydroxide carbonate cobalt during aging process and then to cobaltic oxide after heating.

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