



Crystallization behaviour of hydroxide cobalt carbonates by aging: Environmental implications.

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Cobalt is a naturally occurring element widely distributed in water, sediments and air that is essential for living species, since it is a component of B12 vitamin and it is also a strategic and critical element used in a number of commercial, industrial and military applications. However, relatively high accumulations of cobalt in environment can be toxic for human and animal health. Cobalt usually occurs as Co^{2+} and Co^{3+} in aqueous solutions, where Co^{2+} is the most soluble and hence its mobility in water is higher. The study of the precipitation of cobalt carbonates is of great interest due to the abundance of carbonate minerals in contact with surface water and groundwater which can be polluted with Co^{2+} . Previous works have demonstrated that the formation of Co-bearing calcium carbonates and Co-rich low crystallinity phases takes place at ambient conditions.

With the aim of investigating the crystallization behavior of Co-bearing carbonates at ambient temperature, macroscopic batch-type experiments have been carried out by mixing aqueous solutions of CoCl_2 (0.05M) and Na_2CO_3 (0.05M) during increasing reaction times (5 minutes and 1, 5, 24, 48, 96, 168, 720 and 1440 hours). The main goals of this work were (i) to analyse the physicochemical evolution of the system and (ii) to study the evolution of the crystallinity of the solid phases during aging. After a given reaction period, pH, alkalinity and dissolved Co^{2+} in the aqueous solutions were analysed. The evolution of the morphology and chemical composition of the solids with aging time was examined by SEM and TEM. The precipitates were also 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 results show that a low crystallinity phase was obtained at the very beginning of aging. 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) after about 4 days. At the same time, the most important fall of cobalt content takes place, but pH and alkalinity values do not show significant changes. The evolution of the aqueous solutions is closely related to the increases of crystallinity degree. TEM study confirms the evolution of the shape of crystals, which exhibit platelet morphology at the end of aging time.