

Precipitation of Co^{2+} carbonates from aqueous solution: insights on the amorphous to crystalline transformation.

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Cobalt is toxic metal that is present only as a trace in the Earth crust. However, Co might concentrate on specific areas due to both natural and anthropogenic factors and thus, soils and groundwater can be contaminated. It is from this perspective that we are interested in the precipitation of cobalt carbonates, since co-precipitation with minerals phases is a well-known method for metal immobilization in the environment. In particular, the carbonates are widely used due to its reactivity and natural abundance.

In order to evaluate the cobalt carbonate precipitation at room temperature, a simple experimental work was carried out in this work. The precipitation occurred via reaction of two common salts: 0.05M of CoCl_2 and 0.05M of Na_2CO_3 in aqueous solution. After reaction, the precipitated solid was kept in the remaining water at 25 °C and under constant stirring for different aging times of 5 min, 1 and 5 hours, 1, 2, 4, 7, 30 and 60 days. In addition to the aging and precipitation experiments, we carried out experiments to determine the solubility of the solids. In these experiments each precipitate was dissolved in Milli-Q water until equilibrium was reached and then the aqueous solution was analyzed regarding Co^{2+} and total alkalinity. Furthermore, acid solution calorimetry of the products were attained. Finally, we modeled the results using the PHREEQC code. Solid and aqueous phase identification and characterization have been extensively reported in a previous work (González-López et al., 2015).

The main results of our investigation were the initial precipitation of an amorphous cobalt carbonate that evolve towards a poorly crystalline cobalt hydroxide carbonate with aging treatment. Solubility of both phases have been calculated under two different approaches: precipitation and dissolution. Values of solubility from each approach were obtained with a general error due to differences in experiment conditions, for instance, ionic strength, temperature and water content. It was surprising the low solubility product (K_{sp}) of the new phase $\text{Co}_2\text{CO}_3(\text{OH})_2$ in the order of 10^{-30} and this could explain its appearance only after 7 days of aging. On the other hand, the high solubility product of amorphous is consistent with its instantaneous precipitation at the beginning of the reaction. Solution calorimetry shows a higher value of exothermic solution enthalpy for crystalline cobalt hydroxide carbonate and hence, the solubility result are confirmed. Although geochemical models indicated that aqueous solution was supersaturated with respect both phases, the sequence of obtained phases (first amorphous and next crystalline) indicate that the evolution of the saturation index has to be dropped with respect to amorphous phase with time. These results points towards a simultaneous dissolution of the amorphous and the precipitation of crystalline phase $\text{Co}_2\text{CO}_3(\text{OH})_2$ at the first stages of the reaction.

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