Use of zirconium-based MOFs to enhance silicate carbonation

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Organisms arrange complex aminoacidic sequences to obtain enzymes able to catalyse specific reactions with high energetic barriers. Despite the organic nature of the enzymes, the active sites are commonly based on the presence of transition metals. Metal Organic Frameworks (MOFs) offer the possibility to emulate the catalytic effect of the enzymes, with several advantages of using MOF instead of enzymes: (i) MOFs have an easier chemical structure that allows these materials to be suitable for large scale applications; (ii) MOFs have low prizes compared with the high costs necessaries for enzyme purification, and (iii) MOFs have a wider physical-chemical resistance to non-ambient conditions (pH, temperature, presence of chemicals, etc.). [1]

We performed a comparative study to assess the potential of Zr-based MOFs in catalysing the carbonation of silicates, a geochemical process of great interest for geological carbon storage. Our study presents a comparison between the catalytic effect of Carbonic Anhydrase (CA) and that exerted by 4 different types of MOFs (UiO-66, MOF-808, and the analogues doped with $Mg(OH)_2$) on the reaction of carbonation that transforms wollastonite ($CaSiO_3$) into calcite ($CaCO_3$). Experiments were performed at 40 °C and neutral pH to preserve the enzyme from denaturation. We compared the catalytic effect of these compounds on both the dissolution and carbonation of wollastonite.

After the reaction, the solids were filtered, observed with electron microscopy and analysed by XRD; the aqueous phase was analysed by ICP-OES to determine the total concentration of Ca, Si and Al and to test the ions released by the catalysts. Further experiments were performed using a titration system equipped for continuous monitoring of the evolution of free calcium (ISE) and pH during the carbonation process. Our experiments show an enhacement in the carbonation achieved during the reaction in the presence of MOFs, thus suggesting that Zr-based MOFs could be suitable catalysts to enhance the performance of silicate carbonation reactions.

[1] Nath, Chakraborty & Verpoort (2016) *Chem. Soc. Rev.* 45, 4127-4170.