

Carbonation of minerals and industrial residues for CO₂ storage: perspectives of application in energy generation systems.

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The most accredited CO₂ storage options rely on in-situ technologies, which consist in injecting CO₂ into deep saline aquifers, coal bed seams (enhanced coal bed methane recovery), oil reservoirs (enhanced oil recovery), and potentially into deep oceans (ocean storage). Although a few pilot-scale in-situ storage facilities are running, still many doubts are raised on how to assess the fate of CO₂ after injection reliably, and to avoid leakage back to the atmosphere. Besides, it is possible that several CO₂ point sources are located too far from available storage sites, or that the size of the plant is too small to make feasible the construction of a dedicated pipeline. In these cases, an alternative to the in-situ CO₂ storage approach can be found in an ex-situ process based on the chemical reaction with alkaline materials bearing either calcium or magnesium. This process, known as mineral carbonation, mimics natural weathering, where CO₂ reacts exothermically with alkaline elements present in natural metal-oxide bearing material, forming thermodynamically stable and benign carbonates. Minerals containing Ca and Mg silicates, such as olivine, serpentine or wollastonite, have been proposed as suitable candidates for large scale mineral carbonation plants, due to their wide availability. The most promising approach on mineral carbonation developed so far is based on the so-called aqueous route. The two limiting steps of the process are in this case the alkaline mineral dissolution, releasing either Ca or Mg ions in solution, and the precipitation step, where CO₂ is converted into the corresponding carbonate. A one-step process has been proposed, where dissolution and precipitation take place in the same reactor, but severe operating conditions (185°C and 130 bar for olivine) and mechanical and/or thermal pre-treatment are required to get a reasonably fast and effective process. Two-steps processes, where dissolution and precipitation take place in two different reactors, have also been proposed. This approach allows to optimize each of the two steps, by performing dissolution at acidic pH values and precipitation at alkaline ones. This requires a swing of operating conditions, with a consequent consumption of chemicals, unless a way of recycling them is found. An alternative to the use of natural minerals is represented by the alkaline residues from different industrial activities such as pulverized fuel ash produced by coal fired power stations, ground granulated blast furnace and stainless steel slags from the steel manufacturing industry, bottom and fly municipal solid waste incineration ashes, as well as deinking ash, resulting from the waste produced during the recycling of paper. These materials contain alkaline elements in a more readily available form, so that carbonation could in principle take place at less severe operative conditions than the ones needed for silicate minerals. The main advantage of this application is that CO₂ and the residue are produced at the same site, with no need of transportation. Although the amount of available alkaline residues is of a scale which will never allow to solve the global CO₂ problem, the process can have a reasonable impact on specific industrial sectors (e.g. cement or steel industry) and can be a way to introduce the carbonation technology. Moreover, carbonation might improve the environmental behaviour of the residues allowing either for their reuse or make their disposal less expensive.

The carbonation routes proposed so far (aqueous, gas-solid and wet) and their applications to different starting materials will be presented and discussed in this paper, making reference to the results obtained by our research groups in the last few years. Namely, investigation on dissolution of olivine and Mg-carbonates precipitation kinetics, obtained by the ETH group, will be

summarized, together with the results on the carbonation of alkaline residues (stainless steel slags and incineration residues) collected by the two universities in Rome. The available data will be used to provide a preliminary estimate on the feasibility of carbonation as CO₂ storage option for energy generation systems, outlining the integration options. A more detailed feasibility study will be the outcome of a research project, funded by ENEA and specifically aimed to small-medium energy generation systems (< 20 MW), which is supposed to start within mid-2009