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Assessment of the energy requirements for CO₂ storage by carbonation of industrial residues. Part 1: Definition of the process layout

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Abstract

Mineral carbonation is an ex situ CO₂ storage option that could allow to fix large amounts of CO₂ in a solid and thermodynamically stable form. Its feasibility has been proven at lab-scale both employing natural minerals or alkaline industrial residues. However the energy requirements of this process can be quite significant depending on the type of material and operating conditions adopted and thus represent a crucial factor for its full scale applicability. The focus of this paper is the assessment of the energy requirements of CO₂ storage by accelerated carbonation of alkaline materials applying the direct aqueous route. From the analysis of the main studies on energy penalties associated to the carbonation process large differences were observed on the assumptions made, the selected layout and operating conditions, in particular for alkaline residues. In addition most of the evaluations were carried out considering only experimental tests performed with high liquid to solid ratios (slurry phase route) while specific evaluations for tests with liquid to solid ratios lower than 1 (wet route) were not carried out. The overall aim of this study is to estimate the energy duties required to store the CO₂ emissions of a small-medium size power plant (20 MW) by carbonation of different types of residues (steel slags and waste incineration residues) applying either the slurry phase or wet routes. In this paper the layouts of the proposed carbonation processes are presented and discussed.

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1. Introduction

Mineral carbonation is an exothermic reaction that occurs spontaneously in nature, although on geological time scales, and is based on the reaction between CO₂ and mineralogical phases containing calcium and magnesium silicates or oxides. Mineral carbonation can be also considered an ex situ CO₂ storage option that could allow to fix large amounts of CO₂ in a solid and stable form, avoiding the need of long term monitoring required for other more investigated options such as in situ geological storage. In addition, mineral carbon sequestration can be used in areas where other storage techniques, such as geologic carbon sequestration, are either not available or not feasible [1]. Nevertheless, one of the main issues which has hindered so far its application for carbon dioxide storage consists in the high energy requirements of this technology compared to in-situ options. In particular, in order to enhance reaction kinetics, both mechanical and thermal pre-treatments of the minerals and energy-intensive operating conditions are necessary (e.g.: T=100-200 °C and p_{CO2} = 10-100 bar), e.g. [2]-[3].

Accelerated carbonation can be also applied to several types of alkaline industrial residues, characterized by significant contents of reactive metal oxides, i.e. CaO and MgO. These materials require a lower degree of pre-treatment and less energy intensive operating conditions than minerals. In addition, although their total amount is quite limited when compared to silicate minerals, they are typically available at CO₂ point-source emission locations, such as coal-fired power plants, waste to energy facilities and steel manufacturing plants [4]. Thus, these materials could be employed in niche applications in order to store at least part of the CO₂ emissions of the same industries from which they are produced. Besides, another important advantage that could be achieved applying the carbonation treatment to industrial residues is the improvement of the environmental behavior of the residues, thus making their reuse or disposal easier, e.g. [5], [6] and [7].

The main types of alkaline residues that have been selected and tested for accelerated carbonation, due to their availability and chemical and mineralogical composition, are steelmaking slag, bottom ash and air pollution control (APC) residues generated by municipal solid waste incineration and cement kiln dust [8]. Most of the recent studies carried out in this field assessed the reactivity of the above mentioned residues applying the direct aqueous carbonation route ([3], [9] and [10]). This reaction route involves the dissolution of the reactive phases and the precipitation of carbonates in a single stage and has been performed using two different process layouts: slurry phase route at liquid-to-solid (L/S) ratios higher than 1 l/kg (typical operating conditions: T=100-150 °C and p_{CO2} = 1-20 bar) [9]; wet route, using L/S ratios below 1 l/kg (typical operating conditions: T=20-50 °C and p_{CO2} = 1-10 bar) [11]. This latter type of process avoids the treatment and disposal of the processing liquid, and has been also indicated to favor the dissolution kinetics of hydroxide and silicate phases under mild operating conditions, which may allow to more easily reach saturation conditions of carbonate mineral phases. [11].

Although the feasibility of CO₂ storage by carbonation of alkaline residues, as mentioned, has been proven at lab-scale, pilot and full scale applications of this process are currently missing. One of the key factors for the implementation of the investigated accelerated carbonation processes at industrial scale is the associated requirement of materials and energy. Part of the thermal duties of the CO₂ storage process may be potentially covered by integrating accelerated carbonation with existing energy generation systems and utilizing the waste heat of the plant. Recently several studies have focused on the evaluation of the energy penalties related to mineral carbonation adopting the slurry phase route scheme ([2], [9], [12] and [13]). The aim of this work is to develop a specific model that can allow to assess the material and energy requirements for the storage of the CO₂ emissions of a small-medium size power plant by direct carbonation of different types of industrial residues using either the slurry phase or the wet route. Specifically, the influence of the characteristics of the residues (i.e. main mineralogy and particles size)

and of the applied operating conditions (i.e. temperature, CO₂ pressure and liquid to solid ratio) on the sustainability of the process in terms of material and energy requirements at industrial scale was analyzed. In this paper, after a short review of the main findings regarding the energy penalties of the carbonation process reported in literature, the process schemes used as reference for our specific model of the slurry phase and wet routes are presented and discussed.

2. State of the art

In the last few years several studies have addressed the issue of the energy penalties associated to carbonation processes in view of the assessment of the feasibility of their application at full scale.

The Albany Research Centre (ARC) presented a preliminary study aimed at developing an ex-situ aqueous process to convert magnesium silicate-rich ultramafic rocks and minerals, such as olivine and serpentine, to magnesium carbonates by contact with gaseous CO₂ in an aqueous solution [2]. In this study seven kinds of ultramafic minerals were analyzed considering various pre-treatment options and operating conditions for the carbonation reaction and based on the results of lab-scale tests the feasibility of the process at large scale was investigated. In this study it was concluded that an energy requirement of 352 MW was determined for a process scaled for the storage of 100% of the CO₂ emissions from a 1.3 GW coal-fired electric generation plant (1100 t CO₂/h). The energy demand of this process in terms of CO₂ emissions was estimated to be around 28 % of the total amount of carbon dioxide sequestered for olivine (L/S = 2.33 kg/kg and a reaction time of 120 min at 185 °C, 150 bar CO₂ and a particle size of <37 μm) [2].

Huijgen and co-workers evaluated the energetic performance of CO₂ sequestration by aqueous carbonation of Ca-silicates ores and industrial residues [9]. Specifically they considered data obtained from carbonation experiments carried out at lab-scale using both a wollastonite and steel slag feedstock and on this basis they have designed a mineral carbonation process determining the CO₂ sequestration efficiency at various operating conditions. The minimum energy penalty in terms of CO₂ emissions determined for wollastonite and steel slag was 16% and 17 % respectively (at a reaction time of 15 min at 200 °C, 20 bar CO₂, and a particle size of <38 μm, assuming L/S=5 kg/kg). For L/S = 2 kg/kg higher energy penalties resulted for wollastonite and in particular for steel slag (i.e. 25 % and 31% respectively). The grinding of the feedstock and the compression of the carbon dioxide were identified as the main energy-consuming process steps. In addition, a sensitivity analysis has shown that further grinding (particularly for wollastonite) or reducing the CO₂ partial pressure (in the case of steel slag) can potentially improve the process efficiency [9].

Kelly et al. [12] performed a preliminary energy balance for three CO₂ mineralization pathways at industrial scale, i.e. industrial caustics, naturally occurring minerals and industrial wastes. The basis for this evaluation is a theoretical 1 GW coal-fired power plant emitting 8×10^6 t CO₂/y, which is captured by one of the considered mineral carbonation pathways. The estimation of the energy penalties for the carbonation of olivine and wollastonite was performed on the basis of previous works ([2], [9]) taking also into account the requirements for mining and CO₂ separation. The resulting energy penalties ranged between 55-69 % for olivine and were over 100% for wollastonite [12]. Regarding the industrial residues Kelly et al. [9] concluded that the energy penalty associated with CO₂ mineralization of iron slag proposed by Huijgen et al. [9] is greater than 100%, making this process unlikely to be feasible. It should be noted that in the evaluations developed by Kelly and co-authors the energy recovered from the carbonation reaction was not accounted for. Furthermore, the significant differences in the energy penalties for the different materials can be ascribed to the assumption made for the heating stage (i.e. heating required only for T>185°C). However the CO₂ mineralization process with fly ash described by Reddy et al. [14], carried

out in a fluidized bed contacting coal fly ash with flue gas for 1.5-2 h at 60°C, was indicated to present a much lower energy penalty (9 to 22%). These results may be mainly related to the avoidance of CO₂ capture and compression and mechanical pre-treatment of the fly ash.

Recently Kirchofer et al [13] evaluated by LCA the performance of different aqueous mineral carbonation processes using both natural silicate minerals (i.e. olivine and serpentine) and industrial by products, such as cement kiln dust[15], coal fly ash [16] and steel making slag [9]. Referring to data available in literature for these materials the authors analyzed a hypothetical mineral carbonation process to treat 1000 t CO₂/d. In that study the minimum energy requirement expressed in terms of CO₂ (i.e. 14 %) was obtained for cement kiln dust at ambient temperature and pressure conditions. The results obtained for the other considered residues are: 25 % for olivine, 75% for serpentine, 34% for steel slag and 45% for fly ash. Furthermore within the range of operating conditions considered, heating provided the most relevant contribution, followed by mixing and grinding. It should be noted that in this study the energy requirements for CO₂ capture were not considered while those related to mining and transportation of reactants and products were accounted for. Regarding the carbonation of minerals, in this study the energy penalties were estimated on the basis of the experimental results obtained in dissolution tests, assuming that all the dissolved cations react with CO₂ in the precipitation stage. This may explain the observed differences in the considered operating conditions and resulting energy requirement compared to the previously mentioned studies. As for the carbonation of residues, it is worth mentioning that the same process scheme was applied for all of the tested materials regardless of the applied L/S ratio.

On the basis of this review, it can be concluded that the process layout, the operating conditions selected for each unit and the type of materials considered greatly affect the resulting energy requirements of the considered carbonation process. Furthermore for residues, a detailed evaluation of the energy requirements for the wet route process is missing since the effect of the variation of the operating conditions was evaluated only for steel slag applying the slurry-phase route [9].

3. Methods and assumptions

In this work the energy penalties associated to a process for carbonation of industrial residues, both by the slurry phase route or the wet one, were estimated considering the CO₂ emissions of a small-medium size power plant (20 MW). On the basis of this assumption the energy requirements of an hypothetical carbonation process was determined considering data available in the literature and results of specific experimental tests.

From an energetic point of view, as mentioned above, the use of alkaline industrial residues instead of minerals in the carbonation processes presents some advantages. These materials indeed are more reactive compared to natural minerals hence, generally, high CO₂ uptakes can be achieved applying less energy intensive operating conditions even using diluted CO₂ streams thus avoiding the capture step. Furthermore, in many cases these materials present a particle size suitable for the carbonation process allowing to reduce or avoid the need of a grinding step, that represents one of the most energy intensive stages. The kinds of residues most investigated so far in carbonation lab-scale experiments are steelmaking slags, concrete wastes, mining and mineral processing wastes and waste incineration residues. In this study we focused in particular on steelmaking slag and waste incineration residues.

Steelmaking industries are responsible for 6-7% of total CO₂ emissions worldwide [17] and from the different applied processes various types of slags are produced (e.g. blast furnace (BF), basic oxygen furnace (BOF), electric arc furnace (EAF) and ladle slags). Based on current steel production data and on the amounts of slags resulting from each specific process, it can be estimated that around 100 Mt/y of BOF slags and over 55 Mt/y of EAF slags are produced worldwide ([18]-[19]). The chemical and

mineralogical composition of steelmaking slags is strongly affected by the specific industrial process from which they are produced but generally presents a high content of calcium, iron, silicon, aluminum, magnesium and manganese oxides [17].

The solid residues produced by a waste incineration plant consist mainly of two waste streams: bottom ash (80%) and air pollution control (APC) residues (less than 15%). Accelerated carbonation has been applied as a treatment technique prior to reutilization or final disposal of waste incineration bottom ash with the purpose of producing a chemically stable material with improved leaching behavior, while in the case of APC residues, this method has been proposed as a possible CO₂ storage technique, due to the typically higher CO₂ uptake potential of these types of residues [20]. Hence in this work we have considered only the results of experiments carried on APC residues that show a high reactivity with CO₂ at mild operating conditions owing to their fine particle size and high calcium (hydr)oxides content [21].

In this work the experimental results obtained for 5 different kinds of industrial residues under wet and slurry phase conditions were considered in order to develop the process layout of each carbonation route. In particular four types of steel making slags were considered: two kinds of BOF slags, EAF slags from stainless steel making plant and ladle slags produced at the outlet of the argon oxygen decarburization and desulfurization unit in a stainless steel making plant (AOD slags). In addition the results obtained in carbonation lab-scale tests carried out using Air Pollution Control residues (APC residues) collected from the baghouse section of a hospital waste incineration plant were considered. Furthermore data from the experiments carried out by Huijgen and co-workers [9] in the slurry route phase using BOF steel slags were considered.

For all the considered types of residues used in the slurry phase and wet route, the chemical composition of the alkaline material and the operating condition applied in the carbonation experiments are reported in [6], [7], [9], [11] and [22]

4. Results: Proposed processes layout

In the present work two direct carbonation route were considered, i.e. the slurry phase and the wet route, and for each one, the mass and energy balance for all the operation units of the process was performed, allowing to evaluate the corresponding energy requirements. In particular the main process stages that can affect the energy penalties were considered, i.e. the grinding of the solid material, CO₂ separation from the power plant flue gas, pumping of the slurries, compression of gas to the required pressure, mixing and heating of the solid and liquid flows.

4.1. Slurry phase Route

In the slurry phase route, the industrial residues, after being grinded to a specific particle size (unit A), are mixed with water at a fixed liquid-to-solid ratio (unit B) and the resulting slurry is pumped (unit C) to the heat exchanger (unit D). In this unit the slurry is heated to 30 °C below the reactor temperature and then is fed to the carbonation reactor (unit F) after a heater (unit E) required to reach the desired reaction temperature. The CO₂ is pressurized in a multiple stage compressor (unit G) to reach the established pressure and fed to the reactor in which the carbonation reaction takes place. After the carbonation reaction, the heat of the slurry is recovered in the unit D and then the solid product is separated from the liquid (unit H) that is fed again to unit B. This process layout (see Figure 1) is quite similar to those proposed by [2] and [9].

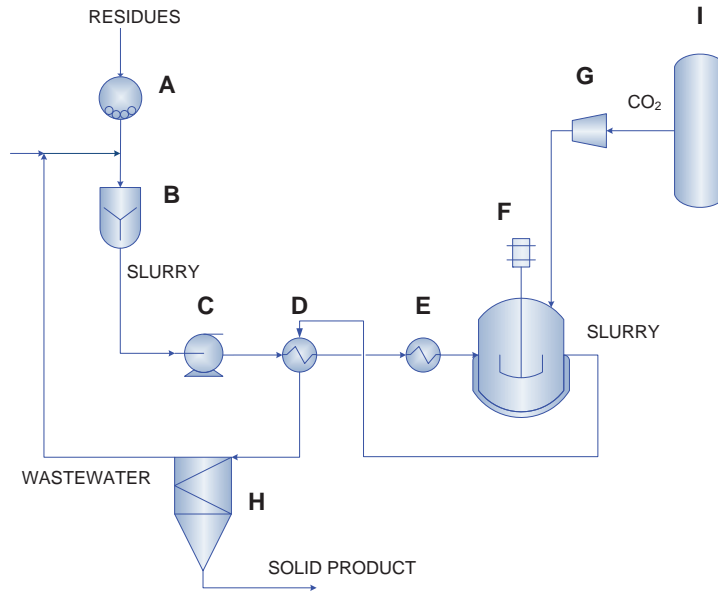


Fig. 1. Scheme of the carbonation process for the slurry phase route

4.2. Wet Route

For the wet route a different process layout was considered since, as reported by Huijgen et al [9], for L/S lower than 2 kg/kg pumping and stirring problems might arise; hence, a different type of reactor should be used. In addition the process layout for the wet route is simplified (see Figure 2) since the number of required unit operations is lower and the energy consumption is mainly associated to CO₂ separation from the flue gas (unit I), CO₂ compression (unit G), milling of the residues (unit A) and the operation of the carbonation reactor (unit K) envisioned for this application as a rotary drum.

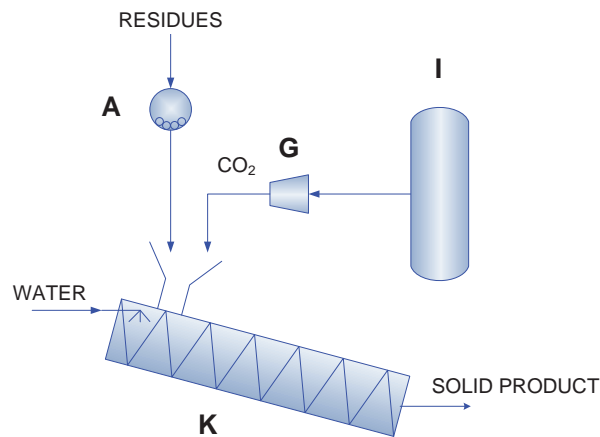


Fig. 2. Scheme of the carbonation process for the wet route

5. Conclusions

The material and energy requirements of accelerated carbonation represent a crucial factor for the full-scale applicability of this process as a CO₂ storage technique. Several studies have tried to evaluate the energy penalties associated to the carbonation of minerals and of some types of industrial residues. However the results differ considerably from one study to the other also when the evaluation was based on the same experimental data due to the differences in the assumption made and in the selected process layout. The differences in the energy penalties found for the alkaline residues are also related to the fact that for each type of material different operating conditions were considered and hence the results cannot be directly compared. Furthermore, for the wet route a specific process layout at industrial scale was not considered. The aim of this study is thus to perform a systematic study of the influence of the composition of the residues and of the applied operating conditions for both the slurry-phase and the wet routes.

In this paper the schemes developed for the two routes are presented and discussed. The detailed explanation of the main assumptions and of the equations used to carry out the estimation of the energy penalties of the carbonation process is reported, together with the main results, in a paper in preparation [23].

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