



Ultrasound-intensified mineral carbonation



Rafael M. Santos^a, Davy François^a, Gilles Mertens^b, Jan Elsen^b, Tom Van Gerven^{a,*}

^a Department of Chemical Engineering, Katholieke Universiteit Leuven, Willem de Croylaan 46, 3001 Leuven, Belgium

^b Department of Earth and Environmental Sciences, Katholieke Universiteit Leuven, 3001 Leuven, Belgium

ARTICLE INFO

Article history:

Received 10 September 2011

Accepted 21 March 2012

Available online 29 March 2012

Keywords:

Mineral carbonation
Ultrasound
Process intensification
Stainless steel slag
Shrinking core
Carbon sink

ABSTRACT

Several aspects of ultrasound-assisted mineral carbonation were investigated in this work. The objectives were to intensify the CO₂ sequestration process to improve reaction kinetics and maximal conversion. Stainless steel slags, derived from the Argon Oxygen Decarburization (AOD) and Continuous Casting/Ladle Metallurgy (CC/LM) refining steps, were used for assessing the technical feasibility of this concept, as they are potential carbon sinks and can benefit from reduction in alkalinity (pH) by mineral carbonation. Ultrasound was applied by use of an ultrasound horn into the reaction slurry, where mineral carbonation reaction took place at 50 °C for up to 4 h; comparison was made to solely mechanically mixed process. It was found that sonication increases the reaction rate after the initial stage, and permits achieving higher carbonate conversion and lower pH. AOD slag conversion increased from 30% to 49%, and pH decreased from 10.6 to 10.1; CC slag conversion increased from 61% to 73% and pH decreased from 10.8 to 9.9. The enhancement effect of ultrasound was attributed to the removal of passivating layers (precipitated calcium carbonate and depleted silica) that surround the unreacted particle core and inhibit mass transfer. Significant particle size reduction was observed for sonicated powders, compared to particle size growth in the case of stirring-only; *D*[4,3] values increased without sonication by 74% and 50%, and decreased with sonication by 64% and 52%, respectively for AOD and CC slags. Considerations on scale-up of this technology, particularly with regards to energy efficiency, are also discussed.

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1. Introduction

To overcome inefficiencies faced by current technologies and feasibility barriers that hinder the applicability of new technologies, process intensification (PI) promises to be a key facet of engineering development for years to come. Stankiewicz and Moulijn [1] defined PI as “any chemical engineering development that leads to a substantially smaller, cleaner, and more energy efficient technology”. Consequently, process intensification seeks to bring together fundamental aspects of process engineering technology (spatial, thermodynamic, functional, and temporal) and find the most optimum balance between them [2]. In particular, Reay [3] has identified that process intensification offers significant opportunities for reduction of greenhouse gas emissions. With this framework in place, an intensification route for mineral carbonation is explored herein.

Mineral carbonation involves the transformation or capture of carbon dioxide in a mineral form. The principal aims and advantages of this approach are the chemical stability and storage safety

of mineral carbonates, the opportunities for process integration offered, and the potential for valorization of otherwise low-value resources (virgin or waste) into useful products. The main barriers to its deployment in industry are: high energy intensity, slow reaction kinetics, low reaction conversion, complexities of the production chain and process adaptability, and competition for attention with alternative carbon capture technologies [4].

A potential intensification route for mineral carbonation involves the application of ultrasound as a source of focused energy capable of enhancing convective mass transfer, reducing diffusion barriers, activating precipitation sites and controlling crystal growth and morphology [4]. These aspects were studied in the present work in view of enhancing the carbonation of raw materials (calcium oxide) and alkaline waste materials (stainless steel slags), both with respect to conversion extent and pH stabilization.

2. Background

2.1. Mineral carbonation

Mineral carbonation is the reaction of carbon dioxide with alkaline solids. It is a natural process in the global carbon cycle, producing carbonate minerals that are stable over geologic

* Corresponding author. Tel.: +32 16 322342; fax: +32 16 322991.

E-mail addresses: Rafael.Santos@cit.kuleuven.be (R.M. Santos), Tom.VanGerven@cit.kuleuven.be (T. Van Gerven).

timescales, consequently having potential to sequester carbon dioxide in the effort to reduce greenhouse gas emissions and slow down climate change [5]. The reaction is also important for the production of solid particles in the paper, polymer, environmental protection and fertilizing industries [6,7]. Mineral carbonation can be performed with pure oxides (e.g. CaO, MgO), as well as virgin minerals (e.g. olivine $(\text{Mg,Fe})_2\text{SiO}_4$, serpentine $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$, wollastonite CaSiO_3) and alkaline waste materials (e.g. steel slags [7,8], incinerator and power plant fly ashes [9,10], paper mill waste [11], cement kiln dust [12], air pollution control residue [13], municipal waste incinerator bottom ash [14]). These waste materials can be used for carbonation due to the presence of alkaline oxides, hydroxides and silicates in their composition.

The carbonation process is an example of a gas-solid-liquid system and consists of several steps that can be illustrated in a simple system as follows:

1. Solvation: $\text{CO}_{2(\text{g})} \rightleftharpoons \text{CO}_{2(\text{l})}$
2. Reaction:
 $\text{CO}_{2(\text{l})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{H}_2\text{CO}_{3(\text{l})} \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \rightleftharpoons 2\text{H}^+ + \text{CO}_3^{2-}$
3. Hydration: $\text{CaO}_{(\text{s})} + \text{H}_2\text{O}_{(\text{l})} \rightleftharpoons \text{Ca}(\text{OH})_{2(\text{s})}$
4. Ionization: $\text{Ca}(\text{OH})_{2(\text{s})} \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$
5. Precipitation:
 $\text{Ca}^{2+} + 2\text{OH}^- + 2\text{H}^+ + \text{CO}_3^{2-} \Rightarrow \text{CaCO}_{3(\text{s})} + 2\text{H}_2\text{O}_{(\text{l})}$

Kinetics of calcium carbonate precipitation in slurry can be approximated by a pseudo-second order rate law of the form of Eq. (1) [15], where Conv_{Ca} is the percent conversion of calcium from calcium-bearing minerals to calcium carbonate, t is reaction time, and k_p is the rate constant.

$$\text{Conv}_{\text{Ca},t} = \frac{\text{Conv}_{\text{Ca,max}} \times t}{(1/(k_p \times \text{Conv}_{\text{Ca,max}})) + t} \quad (1)$$

A challenge of mineral carbonation reactions is the formation of an increasingly thick and dense carbonate layer surrounding the shrinking unreacted core of the solid particle [8]. This phenomenon, illustrated in Fig. 1, creates three rate limiting steps: (i) hydration of oxides/silicates; (ii) leaching of cations; and (iii) diffusion to reaction zone. The result is a limiting of the maximum calcium conversion to calcium carbonate ($\text{Conv}_{\text{Ca,max}}$, Eq. (1)), below 100%.

2.2. Ultrasound

To intensify the mineral carbonation process, in view of removing diffusion limiting layers and breaking particles, ultrasound was applied in this work. The use of ultrasound in chemical processes, also termed sonochemistry, applies sound waves in the range of 16–100 kHz, based on the premise that as frequency is lowered, the power delivered increases. Power is delivered to a solution by inducing cavitation, that is, the formation of small

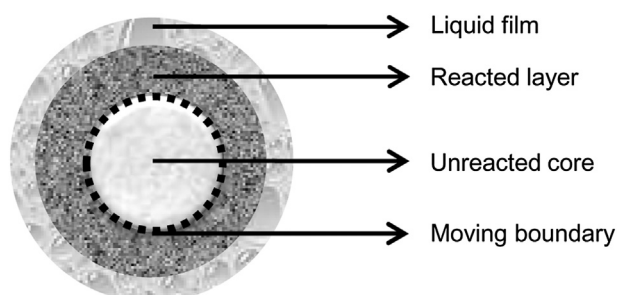


Fig. 1. Shrinking core model of wet particle carbonation.

cavities or microbubbles that grow and collapse rapidly. Cavitation generates turbulence/circulation by acoustic streaming, producing fluid flow pattern similar to a jet loop reactor with higher axial velocities than radial velocities; these effects result in enhanced mixing and mass transfer, including dissolution of gases such as CO_2 [16]. The collapsing microbubbles produce high local temperatures, pressures and shear forces, including the formation of microjets. These effects cause solid surface erosion and interparticle collisions, leading to the removal of passivating layers or to the eventual breakage of particles [17].

Several methods exist to induce cavitation, the most common of which use: ultrasound horn, ultrasound bath, or hydrodynamic cavitation. The hydrodynamic method has been found more energy efficient and easier to scale-up compared to horns and baths, of which the latter is reportedly more energy efficient due to greater irradiating surface area [18]. Conversely, acoustic equipment have been found to generate more intense/rigorous cavitation as indicated by greater collapse pressures ($O(10^7-10^8 \text{ atm})$) [18]. Gogate et al. [19] found, by use of a hydrophone to measure collapse pressure as a function of distance from an ultrasound horn tip, that the cavitation field is nonuniform, having spatial variation both in the axial and radial directions. Improvement of acoustic equipment efficiency has been suggested to be possible by geometric reactor configuration optimization, including use of multiple ultrasound transducers and combination of sonication and mechanical mixing [16]. Moreover, several process parameters are known to influence cavitation, both positively and negatively: for example, solids concentrations and gas sparging can contribute to generation of additional nuclei for cavitation, but also cause, respectively, cushioning effect resulting in decreased collapse pressure, and scattering of sound waves decreasing net energy delivery [20].

Ultrasound-mediated particle size reduction has been reported for powders of calcium carbonate [21], silica [22], clay [23], kaolinite [24], and aluminum oxide [25], and on activated sludge [26]. Experimental work is also reported on the use of an ultrasound horn to speed up carbonation and increase conversion. Nishida [27] tested the effect of sonication on the precipitation rate from a supersaturated solution of calcium and carbonate salts ($[\text{Ca}^{2+}] + [\text{HCO}_3^-]$). Ultrasonic irradiation, proportionally to ultrasound intensity and horn tip diameter, was observed to accelerate the precipitation rate of calcium carbonate, which was optimized as a function of horn immersion depth. The physical mixing effect, macrostreaming, was suggested to cause the enhancement, more so than cavitation induced microstreaming. Morphology and size of calcium carbonate crystals were unaffected. Rao et al. [28] compared stirring versus horn ultrasonic slurry carbonation of fluidized bed combustion ashes. Conversions of CaO were reported to have increased from 23% to 62% at 15 min, and from 27% to 83% at 40 min. Particle size reduction achieved by sonication was attributed to cause the enhancement, allowing access to unreacted calcium oxide in the ash core. Sonawane et al. [29] passed CO_2 gas through a hole drilled along an ultrasound horn probe into a calcium hydroxide slurry, and found improved mixing and greater reduction of calcium carbonate particle size (from 104 nm to 35 nm), resulting from reduction in induction time (from 110 min to 20 min). López-Periago et al. [30] immersed an autoclave in a sonic bath to improve the carbonation of calcium hydroxide using supercritical carbon dioxide (13 MPa). The conversion to CaCO_3 after 60 min increased from 50 wt% without agitation, to 65 wt% with mechanical stirring, and 89 wt% with sonication.

2.3. Stainless steel slag

A class of waste materials that has good potential for implementation as a feed material for mineral carbonation is steel slags.

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