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Carbonation of alkaline paper mill waste to reduce CO_2 greenhouse gas emissions into the atmosphere

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ABSTRACT

The global warming of Earth's near-surface, air and oceans in recent decades is a direct consequence of anthropogenic emission of greenhouse gases into the atmosphere such as CO_2, CH_4, N_2O and CFCs. The CO_2 emissions contribute approximately 60% to this climate change. This study investigates experimentally the aqueous carbonation mechanisms of an alkaline paper mill waste containing about 55 wt% portlandite ($Ca(OH)_2$) as a possible mineralogical CO_2 sequestration process. The overall carbonation reaction includes the following steps: (1) Ca release from portlandite dissolution, (2) CO_2 dissolution in water and (3) $CaCO_3$ precipitation. This CO_2 sequestration mechanism was supported by geochemical modelling of final solutions using PHREEQC software, and observations by scanning electron microscope and X-ray diffraction of final reaction products. According to the experimental protocol, the system proposed would favour the total capture of approx. 218 kg of CO_2 into stable calcite/ton of paper waste, independently of initial CO_2 pressure. The final product from the carbonation process is a calcite (ca. 100 wt%)-water dispersion. Indeed, the total captured CO_2 mineralized as calcite could be stored in degraded soils or even used for diverse industrial applications. This result demonstrates the possibility of using the alkaline liquid–solid waste for CO_2 mitigation and reduction of greenhouse effect gases into the atmosphere.

1. Introduction

Coal caused the first industrial revolution that transformed the agrarian societies. Electricity allowed the formation of great urban centres. The advance of the industrialized societies has taken place in exchange for the unconditional burning of fossil fuels. This has caused an increase of the CO_2 concentration in the atmosphere from 280 ppm in the pre-industrial revolution to 379 ppm in 2005, rising faster in the last 10 a (average 1995–2005: 1.9 ppm a^{-1}) (IPCC, 2007a).

The temperature of Earth's near-surface, air and oceans is basically controlled by the capacity of the atmosphere to reflect, adsorb and emit the solar energy. However, the continuous emissions of CO_2 into the atmosphere (26.4 ± 1.1 Gt CO_2 a^{-1} for 2000–2005) have altered this natural equilibrium and have led to an increase of the greenhouse effect and the consequent climatic change. The global surface average temperature will increase 2–4.5 °C when the atmospheric CO_2 concentration doubles the pre-industrial revolution concentration (IPCC, 2007a).

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These alterations are leading to stress on drinking water availability, species extinction, melting of ice sheets and coastal flooding (IPCC, 2007b).

The energy production system is currently profitable, thus any modification is nonviable since it could produce huge imbalances in the global economy. An alternative to reduce the CO_2 emission is the retention of CO_2 in natural reservoirs. Three possibilities for sequestration of CO_2 are currently being studied: aqueous carbon sequestration, geological carbon sequestration and mineralogical carbon sequestration.

Aqueous carbon sequestration involves CO_2 dissolution in water to produce a H_2CO_3 solution, which later is neutralized and equilibrated with limestone as shown by the following reaction (Rau et al., 2007):

$$CO_2(g) + H_2O + CaCO_3(s) \rightarrow Ca^{2+}(aq) + 2HCO_3^-(aq) \qquad (1)$$

The dissolved $Ca(HCO_3)_2$ produced is then released and diluted in the deep ocean where these ions, already present in seawater, would cause only minimal and localized environmental impact (Golomb, 1997). Moreover, this process is geochemically comparable to the natural mechanism of CO_2 mitigation by continental and marine carbonate weathering, but over a time scale of many millennia (Murray and Wilson, 1997).

Geological carbon sequestration consists of capturing gaseous CO_2 from emission sources and injecting it in terrestrial reservoirs, such as saline aquifers, depleted oil and gas fields or deep coal seams (Bachu, 2000, 2002; Bachu and Adams, 2003; Friedmann, 2007). The main scientific concerns involving the applicability of geological carbon sequestration are the high pressure and temperature variations, caused by the large CO_2 accumulation, on the reservoirs. These thermodynamic variations could exert forces that diminish reservoir confinement due to the formation of cracks and faults either in the reservoir itself or in the cap rocks. Moreover, the CO_2 dissolution in the pore water and the subsequent formation of H_2CO_3 can result in the rapid dissolution of several minerals (mainly carbonate, oxide and hydroxide minerals) affecting the long-term confinement properties of the reservoirs (Kharaka et al., 2006).

In terrestrial reservoirs, the CO_2 pressure can decrease in the long term as a consequence of a mineralogical carbon sequestration or mineral trapping. The stored CO_2 may transform to stable carbonate minerals by reactions with aqueous ions (mainly Ca, Mg and Fe) resulting from silicate weathering (Gunter et al., 2000; Kaszuba et al., 2003, 2005; Giammar et al., 2005; Bénézeth et al., 2007). Although this mechanism favours permanent CO_2 sequestration, it is expected to be slow in geological formation (hundreds of years) due to the slow kinetics of silicate mineral dissolution and carbonate mineral precipitation. However, mineralogical carbon trapping could contribute significantly to CO_2 sequestration in the proximity of the emission source, without the need for storing the gas in a geological reservoir. Some authors have proposed the use of mineralogical carbon sequestration in controlled reactors as a viable approach to reduce CO_2 emissions into the atmosphere using either: (1) industrial by-products such as coal combustion fly-ash (Montes-Hernandez et al., 2008), coal combustion fly-ash plus brine solution from gas production (Soong et al., 2006) or municipal solid waste bottom-ash (Rendek et al., 2006); or (2) primary minerals such as serpentine/olivine (Maroto-Valer et al., 2005) or wollastonite (Huijgen et al., 2006). These materials act as Ca and Mg sources favouring CO_2 retention by carbonate precipitation.

Montes-Hernandez et al. (2007a) proposed an experimental method to synthesize fine particles of calcite by means of aqueous carbonation of pure portlandite at high pressure of CO_2 (initial $P_{CO_2} = 55$bar) and moderate and high temperature (30 and 90 °C). This aqueous carbonation process suggests dissolution of CO_2 into water and consequent calcite precipitation. This method also has important ecological implications for mineral carbon sequestration. However, the use of pure portlandite and other primary minerals may result in high economic and environmental costs as these are typically resources and not residues.

In cellulose pulp production for paper manufacture, the dominant process involves cooking woodchips in high concentrations of NaOH and Na_2S for 2–4 h at 170 °C. This process, known as kraft pulping, favours lignin dissolution and separation of the cellulose fibers that are recovered by means of sieving. The residual liquids or black liquor containing most of the dissolved lignin are transformed to white liquor and re-used in the cooking stage. This transformation is carried out by both combustion in a boiler and alkalizing with lime and results in the production of several types of portlandite-rich solid wastes with an alkaline nature known generically as alkaline paper mill wastes.

In some pulp and paper industries, the alkaline by-products are sold for cement manufacture and as alkaline amendment for agricultural soils. Nevertheless, their recycling is limited by the presence of Cl^- and metals, and in many instances they must be stored near the industrial facilities. A few investigations focused on the reusability of these wastes have been reported in the literature; the existing ones being based on their application for the neutralization of acid mine drainage (Bellaloui et al., 1999). The main aim of this paper is to show the efficiency of the utilization of these wastes as a Ca source for aqueous carbonation, calcite precipitation and mineralogical CO_2 sequestration. From a sustainable development point of view, the treatment proposed is especially attractive because a low-cost residue is used to reduce the emissions of greenhouse gasses into the atmosphere.

2. Materials and methods

2.1. Alkaline paper mill waste

The alkaline paper waste used in the present study was collected from a cellulose pulp factory (ENCE) located in Huelva, south-western Spain. This by-product, so-called Ca mud, is the waste of the calcination or conversion of $CaCO_3$ to lime for alkalizing the black liquor. Calcium mud was selected since it has a higher Ca content than other alkaline paper wastes.

The particle size of paper mill waste ranges from 1 to 100 μm with a median size of 15 μm, as determined by laser diffraction. This waste is made up of portlandite

($Ca(OH)_2$; 55 wt%), calcite ($CaCO_3$; 33 wt%) and hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$; 12 wt%). The portlandite particles have a laminar-pseudohexagonal habit, as observed by scanning electron microscopy equipped with an energy dispersive system (SEM-EDS, JEOL JSM-5410 instrument) (Fig. 1). The determination of the chemical composition of dry (105 °C) waste by X-ray fluorescence (XRF, BRUKER PIONEER instrument) shows a high content of Ca (83.2 wt% CaO), C (10.3 wt% CO_2), P (2.4 wt% P_2O_5), S (2 wt% SO_3), Na (0.88 wt% Na_2O), Mg (0.35 wt% MgO), Si (0.34 wt% SiO_2), Al (0.17 wt% Al_2O_3) and K (0.13 wt% K_2O), and minor amounts of Cl (590 ppm), Fe (96 ppm), Sr (96 ppm), Cu (25 ppm) and Ni (13 ppm). The water content determined by drying at 105 °C until constant weight was about 21 wt%. The presence of high concentrations of portlandite in paper mill waste accounts for the high alkalinity and potential for CO_2 sequestration as discussed below.

2.2. CO_2 sequestration experiments

The CO_2 sequestration experiments were conducted in a 2 L (total volume) closed Ti-lined pressure reactor (Parr Instrument Co., USA, Model 4843) equipped with a heating jacket (Fig. 2). In each experiment, the autoclave was charged with approximately 1 L of Millipore MQ water (18.2 MΩ) and 20 g of paper mill waste. The waste particles were immediately dispersed by mechanical agitation (450 rpm) and the dispersion heated to 30 or 60 °C. When the temperature was reached, 10, 20, 30 or 40 bar of CO_2 (provided by Linde Gas S.A.) was injected into the reactor by opening a valve and adjusting the pressure to the desired one, and the reaction was commenced. This initial pressure of CO_2 was equal to the total initial pressure in the system. A summary of the experiments carried out and the initial experimental conditions is shown in Table 1. A long-term experiment (48 h) at 30 bar of initial pressure of CO_2 allowed both optimizing the experimental duration of the remaining experiments at 2 h and study the kinetic evolution of the carbonation process.

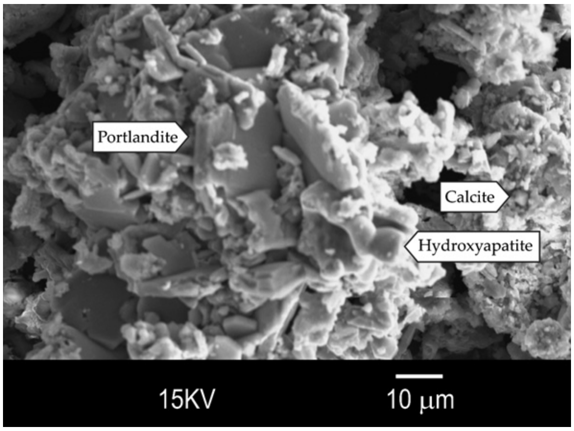

Fig. 1. SEM image of paper mill waste before experimentation showing the initial crystals of portlandite, calcite and hydroxyapatite.

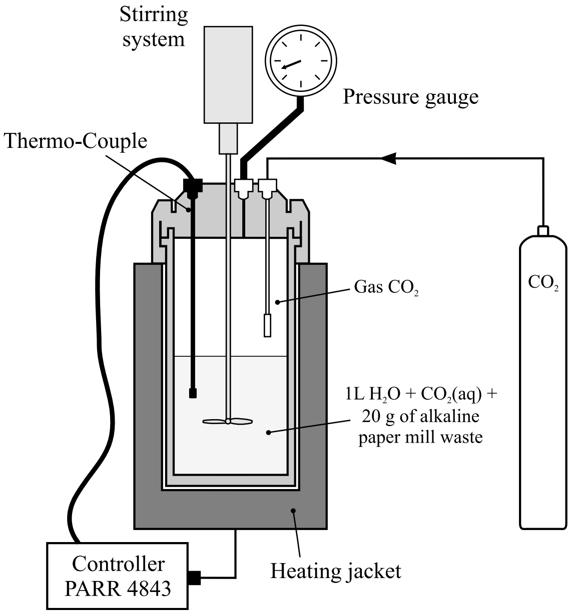

Fig. 2. Schematic experimental system for sequestration of CO_2 by aqueous carbonation of paper mill waste in a continuously stirred reactor.

The global pressure drop in the system, $P_{\mathrm{global\_pressure\text{-}drop}}$, is a consequence of both the dissolution–dissociation of CO_2 in the solution and aqueous carbonation process of $Ca(OH)_2$. In order to calculate the pressure drop produced only by the carbonation process ($P_{\mathrm{carbonation\_pressure\text{-}drop}}$), two independent but complementary experiments were proposed for each experiment: (1) to measure the pressure drop related to the dissolution-dissociation of CO_2 into pure water ($P_{\mathrm{water\_pressure\text{-}drop}}$), and (2) to measure the pressure drop related to the dissolution-dissociation of CO_2 in a Ca-rich solution ($P_{\mathrm{Ca\text{-}rich\_pressure\text{-}drop}}$). In this second experiment, a concentration of 1 g L^{-1} Ca was chosen, that represented the average concentration after paper waste dispersion in water. These two experiments demonstrated that the Ca-concentration (0–1 g L^{-1}) has no measurable effect on the dissolution–dissociation of CO_2 since the monitored pressure drop in pure water ($P_{\mathrm{water\_pressure\text{-}drop}}$) was equivalent to the monitored pressure drop in the presence of Ca ($P_{\mathrm{Ca\text{-}rich\_pressure\text{-}drop}}$). Consequently, the pressure drop produced by the carbonation process of $Ca(OH)_2$ was calculated by a simple pressure balance:

$$P_{\mathrm{carbonation\_pressure-drop}} = P_{\mathrm{global\_pressure-drop}} - P_{\mathrm{water\_pressure-drop}} \tag{2}$$

Under isothermal conditions, $P_{\mathrm{global\_pressure-drop}}$ and $P_{\mathrm{water\_pressure-drop}}$ are proportional to the initial CO_2 pressure.

At the end of the experiment, the reactor was removed from the heating system and was immersed in cold water. The reaction cell was depressurized during the cooling water period at 25 °C (about 15 min). Subsequently, the reactor was disassembled and the supernatant was separated from the solid product by centrifugation at 12,000 rpm for 30 min. Finally, the solid product was dried directly in the centrifugation flasks for 48 h at 65 °C. The supernatant solutions were filtered through a 0.2-µm Teflon filter. Adsorption on the filter and filter holder

Table 1

Experimental conditions, results of the CO_2 sequestration process, and saturation indices of the final solutions with respect to portlandite, hydroxyapatite and calcite calculated using the PHREEQC code (Parkhurst and Appelo, 2005)

Experiment	Reactor content	Duration (h)	Temp. (°C)	CO_2 pressure (bar)			Carbonation pressure (bar)	$SI_{\_portlandite}$	$SI_{\_hydroxyapatite}$	$SI_{\_calcite}$
				Initial	Final	Drop				
Experiment 1	Blanks*	2	30	40	30.5	9.5	–	–	–	–
	1 L pure water + 20 g of paper waste	2	30	40	28	12	2.5	−12.77	8.69	1.51
Experiment 2	Blanks*	2	30	30	22.5	7.5	–	–	–	–
	1 L pure water + 20 g of paper waste	2	30	30	20	10	2.5	−12.52	9.47	1.62
Experiment 3	Blanks*	2	30	20	15	5	–	–	–	–
	1 L pure water + 20 g of paper waste	2	30	20	12.5	7.5	2.5	−12.18	10.54	1.79
Experiment 4	Blanks*	2	30	10	7.5	2.5	–	–	–	–
	1 L pure water + 20 g of paper waste	2	30	10	5.3	4.7	2.2	−11.58	12.31	2.08
Experiment 5	Blanks*	48	30	30	21.5	8.5	–	–	–	–
	1 L pure water + 20 g of paper waste	48	30	30	19	11	2.5	−12.52	9.47	1.62
Experiment 6	Blanks*	2	60	30	24.5	5.5	–	–	–	–
	1 L pure water + 20 g of paper waste	2	60	30	21.5	8.5	3	−10.63	9.58	1.87

* Blanks include two experiments of dissolution–dissociation of CO_2: (1) into pure water and (2) into a solution containing 1 g L^{-1} of Ca. Both experiments showed identical results.

was considered negligible. The filtered solutions were immediately acidified for measurement of [Ca], [Fe], [Sr], [Cu] and [Ni] by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES, Perkin Elmer Optima 3300DV). The analytical uncertainty for all analysis was <5%.

2.3. *Characterization of solid phase*

The mineralogical characterization of the starting material and solid products was carried out by X-ray diffraction (XRD, powder method) using a D501 SIEMENS diffractometer. Semi-quantitative mineralogical determination was estimated with DIFFRACplus software. Working conditions were Co Kα monochromatic radiation (λ = 1.7902 Å), 37.5 mA and 40 kV. The experimental measurement parameters were 12 s counting time per 0.02° 2θ step in the 5–80° 2*θ* range. The detection was performed by a Kevex Si(Li) detector. Morphological analyses of solid products were characterized by means of SEM-EDS. The metal content of final products was also determined by digestion with HCl followed by ICP-AES analysis.

Solution saturation indices with respect to solid phases [$SI = \log(IAP/K_S)$, where SI is the saturation index, IAP is the ion activity product and K_S is the solid solubility product] and aqueous speciation of the leachates were calculated by simulating the reaction with the equilibrium geochemical speciation/mass transfer model PHREEQC (Parkhurst and Appelo, 2005) and the database of the speciation model MINTEQ.v4. Zero, negative or positive SI values indicate that the solutions are saturated, undersaturated and supersaturated, respectively, with respect to a solid phase. Simulation was performed considering Millipore MQ water in contact with 20 g of alkaline paper mill waste (0.11729 mol of portlandite, 0.05209 mol of calcite and 0.00189 mol of hydroxyapatite) for different initial conditions of temperature (30 or 60 °C) and CO_2 pressure (10, 20, 30 or 40 bar). The amount in mol of each mineral contained in the paper waste (n_{min}) was easily calculated according to

$$n_{min} = \frac{m_{paper\_waste}}{M_{min}} \times \left(\frac{\%_{min}}{100}\right) \times \left(1 - \frac{\%_{water\_content}}{100}\right) \qquad (3)$$

where m_{paper_waste} is the mass of paper mill waste used in the experiments (20 g), M_{min} is the molar mass of mineral, $\%_{min}$ is the percentage of mineral in the waste and $\%_{water\_content}$ is the percentage water content in the waste (21 wt%).

3. Results and discussion

3.1. *Reaction mechanisms of CO_2 sequestration*

In an aqueous system, the water–CO_2–paper waste interaction would suppose the carbonation of portlandite ($Ca(OH)_2$; 55 wt%) according to well-known reactions (4-8) described in numerous works (e.g., Juvekar and Sharma, 1973; Shih et al., 1999; Beruto and Botter, 2000). On one hand, the $Ca(OH)_2$ is dissociated and increases the pH up to values around 12 (Eq. (4)):

$$Ca(OH)_2(s) \leftrightarrow Ca^{2+}(aq) + 2OH^-(aq) \qquad (4)$$

On the other hand, the gaseous CO_2 is dissolved in the solution and reacts with the water to form H_2CO_3 (Eq. (5)). Once equilibrium is established between the gaseous CO_2 and H_2CO_3, the H_2CO_3 further dissociates into HCO_3^- and CO_3^{2-} ions (Eqs. (6) and (7)). At alkaline pH, the CO_3^{2-} ion is the dominant species occurring in solution.

$$CO_2(g) + H_2O \leftrightarrow CO_2(aq) + H_2O \leftrightarrow H_2CO_3^* \quad (5)$$

$$H_2CO_3^* + OH^-(aq) \rightarrow HCO_3^-(aq) + H_2O \quad (6)$$

$$HCO_3^-(aq) + OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O \quad (7)$$

The presence of CO_3^{2-} anions together with high Ca concentrations from the portlandite dissolution favours supersaturation, and hence, the precipitation of $CaCO_3$ (Eq. (8)):

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \leftrightarrow CaCO_3 \quad (8)$$

The overall reaction for the process can be written as

$$Ca(OH)_2(s) + CO_2(aq) \rightarrow CaCO_3(s) + H_2O \quad (9)$$

The thermodynamic calculations and the mineralogical characterization of solid products after experiments suggest that this simple reaction mechanism explains the CO_2 sequestration by paper mill waste. After the reaction, PHREEQC code indicates that the solutions are undersaturated with respect to portlandite and supersaturated in $CaCO_3$ (Table 1). Saturation indices of calcite are in the range 1.51–2.08. Comparison of X-ray diffraction spectra of the starting material and the solid product demonstrates that the portlandite contained in the starting material is totally carbonated and transformed to calcite (Fig. 3). Moreover, the resulting solutions are supersaturated in hydroxyapatite, which indicates that this mineral is not dissolved during the experiment, as also shown in XRD spectra (Fig. 3). Therefore, both pre-existing calcite and hydroxyapatite in the starting material seem not to be involved in the CO_2 sequestration process. The newly-formed calcite is characterized by micrometric agglomerates of rhombohedral-crystals (Fig. 4).

During the aqueous carbonation process, toxic elements initially contained in the alkaline waste such as Fe, Sr, Cu and Ni are released into solution. Metals could be captured by calcite precipitation as long as their concentrations are higher than 10^{-5} M, as proposed by Ettler et al. (2006). In these conditions metal uptake by calcite formation is likely caused by co-precipitation, i.e. as a true solid solution and not simply by physical trapping. In fact, metal co-precipitation with calcite is a successful mechanism for reducing metal mobility in natural aqueous systems (e.g., Montes-Hernandez et al., 2007b). After dissolution of alkaline waste in the experiments, Fe and Sr concentrations in solution are higher than the limit established by Ettler et al. (2006), and for this reason, the concentration of these metals analyzed in the final calcite imply a high transfer factor of around 100 and 75% for Fe and Sr, respectively. However, Ni and Cu concentrations in solution are much lower and consequently the transfer factor to the final calcite is only around 25 and 10%, respectively. The remaining Ni and Cu are expected to be associated with organic compounds existing typically in the cellulose wastes (ca. 2 wt% of total organic C; Nurmesniemi et al., 2008). The association of metals with solid phases explains why the Fe, Ni and Cu concentrations in solution were below the detection limit ($< 6\ \mu g\ L^{-1}$). Strontium was the only trace element detected by ICP-AES in the solution though in very low concentrations ($[Sr] \approx 0.25\ mg\ L^{-1}$).

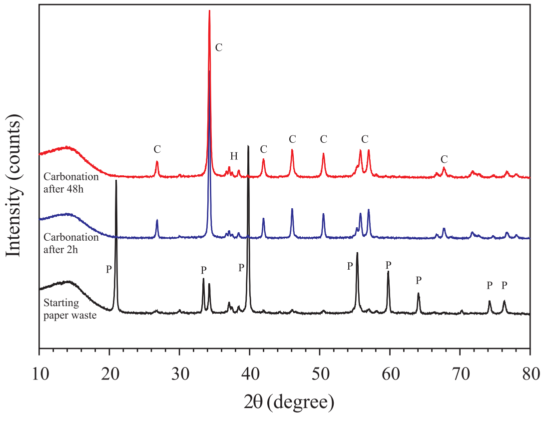

Fig. 3. XRD patterns of starting paper mill waste and solid products after carbonation over 2 and 48 h. C: Calcite, P: Portlandite, H: Hydroxyapatite. These spectra demonstrate the total consumption of portlandite and the production of calcite.

In summary, the final product from the carbonation process is a solid containing ca. 100 wt% of calcite, as found in the experiments of Montes-Hernandez et al. (2007a), but using a low-cost portlandite-rich waste instead of pure portlandite. Moreover, the final calcite-water dispersion could be used as a reagent for further aqueous carbon sequestration (see Introduction, Eq. (1)). Hence, the final result of these experiments would allow continuing sequestering CO_2 and the total amount of captured CO_2 could be poured directly into the sea. The addition of HCO_3-rich effluents to the oceans would be even environmentally beneficial for marine biota (Rau et al., 2007). Nevertheless, this application could potentially cause metal release and provoke some negative impact on the marine environment, mainly for Ni and Cu because Fe and Sr are trace components of seawater, and in the case of Fe an essential nutrient for some ecosystems. Albeit, the amount of Ni and Cu contained in 1 tonne of alkaline paper waste, and that could be released into the sea after the carbonation process, is lower by a factor of approx. 2×10^9 of the global gross flux of dissolved Ni and Cu transported by rivers into the oceans (Gaillardet et al., 2003). This would mean that to cause harmful effects on the environment, it is necessary to use a much larger amount of waste alkaline than those produced annually worldwide.

The application of the final product from the carbonation process for oceanic carbon sequestration inevitably requires establishing a balance between the economic benefits and the potential environmental impacts. Another possible environmental application for this final product would be its storage in soils. Although organic acids commonly present in soils could favour the release of minor metals, this application would be a very advantageous and viable possibility in soil already contaminated by metals and with a scarcity of nutrients and organic matter. This is especially attractive for ENCE-Huelva factory since

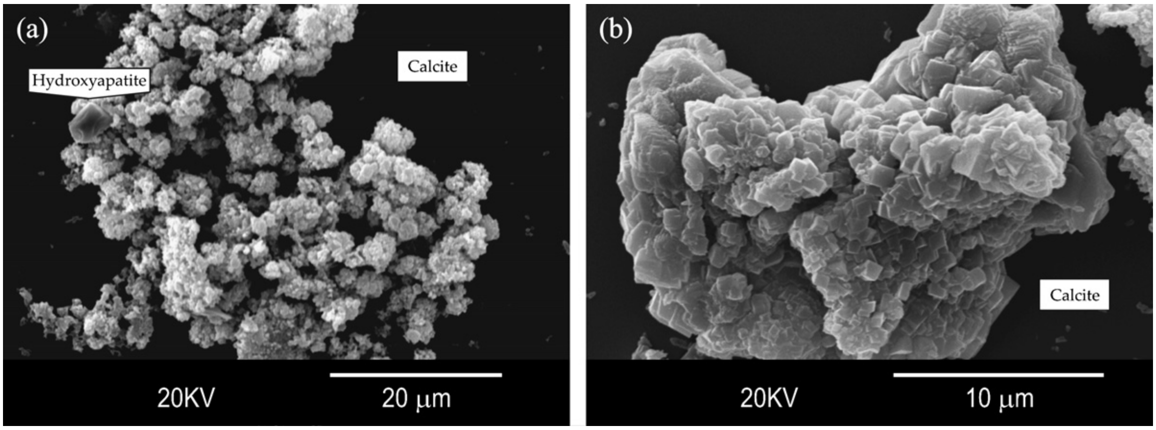

Fig. 4. (a–b) SEM images of calcite particles precipitated during CO_2 sequestration experiments.

it is located about 60 km from the Iberian Pyrite Belt (IPB), one of the largest massive sulphide deposits in the world (Sáez et al., 1999). The intense mining activity in the IPB has produced a huge volume of metal-rich mining wastes and the degradation of soils, which maintain abnormally high concentrations of contaminant metals (Rufo et al., 2007). Alkalinity production by calcite dissolution could even result in a decrease of metal mobility and in an improvement of the quality of soil properties (see for example, Fernández-Caliani et al., 2008). This process would also favour the retention of metals associated initially with alkaline paper mill waste, and not contribute therefore to increasing the pollution with additional elements of soils already affected by mining activity.

3.2. Amount of sequestered CO_2

A simplified method was developed to estimate the quantity of CO_2 sequestered by carbonate precipitation. This method was partially described in Section 2.2. Herein, the pressure drop produced by the carbonation process of $Ca(OH)_2$ (Eq. (9)) in the system was calculated by a simple pressure balance (Eq. (2)). Knowing the pressure drop values in each experiment (Table 1), the amount of CO_2 consumed by calcite precipitation ($n_{\text{carbonation\_CO\_2,real}}$ in mol) could be calculated using the ideal gas law

$$n_{\text{carbonation\_CO}_2\text{,real}} = \frac{P_{\text{carbonation\_pressure–drop}} V}{RT} \tag{10}$$

where V is the reactor volume occupied with gas (1 L), T is the reaction temperature (≈303 °K) and R is the gas constant (0.08314472 L bar K^{-1} mol^{-1}).

In experiments at 30 °C and 2 h of experimental duration, the pressure drop by portlandite carbonation was around 2.5 bar, independent of initial CO_2 pressure (Fig. 5a). Although the results of the long-term experiment (48 h, 30 bar and 30 °C) show that equilibrium is obtained after about 5 h of solid–fluid interaction, the maximum pressure drop by carbonation is already reached at 2 h of experiment (Fig. 5b), and thus the experimental duration of the remaining experiments was correctly optimized. According to Eq. (10), the real amount consumed by carbonation was 0.09923 mol of CO_2.

Based on the stoichiometry of Reaction (9), the theoretical amount of CO_2 ($n_{\text{carbonation\_CO}_2\text{,theoretical}}$) that should be sequestered by the carbonation process (i.e., if all Ca is carbonated) is equal to the quantity of portlandite contained in the paper mill waste (0.11729 mol). This supposes a carbonation efficiency (CE) of 85% at 30 °C according to

$$CE = \frac{n_{\text{carbonation\_CO}_2\text{,real}}}{n_{\text{carbonation\_CO}_2\text{,theoretical}}} \times 100 \tag{11}$$

In the experiment at high temperature (60 °C, 30 bar), the pressure drop by carbonation is slightly superior (3 bar), albeit the sequestered amount of CO_2 and the carbonation efficiency are very similar since this process depends inversely on the reaction temperature (Eq. (10)).

Theoretically, the extrapolation of this experiment to a real industrial scale would suppose a maximum CO_2 sequestration capacity of 258.54 kg of CO_2/ton of paper mill waste containing 55 wt% of portlandite. However, with the experimental protocol, 218.37 kg of CO_2/ton of paper mill waste could be successfully sequestered into stable calcite. Obviously, this is very attractive for the mineral trapping of CO_2.

3.3. Kinetic modelling of sequestered CO_2

The monitoring of the pressure drop for any controlled system under ideal gas conditions allows the kinetic modelling of sequestered CO_2 after gas injection in a solid-liquid system (paper mill waste-water dispersion for this study). This can be done using a simple correlation function, $n_{\text{total\_CO}_2} = f(t)$, where $n_{\text{total\_CO}_2}$ is the total mol quantity of sequestered CO_2 in the paper waste-water dispersion and t is the time after gas injection.

Several kinetic models including first-order, pseudo-first-order, second-order, pseudo-second-order, parabolic diffusion and power function kinetic expressions are reported in the literature for fitting the kinetic experimental or calculated data of solid–fluid interaction processes (e.g. Lagergren, 1898; Ho and Mckay, 1999). For this study, the kinetic modelling concerns the total sequestered quantity of CO_2 in a paper mill waste-water dispersion, i.e. the CO_2 dissolution–dissociation in water, possibly the CO_2 adsorption on the paper waste and, sequestered CO_2 by

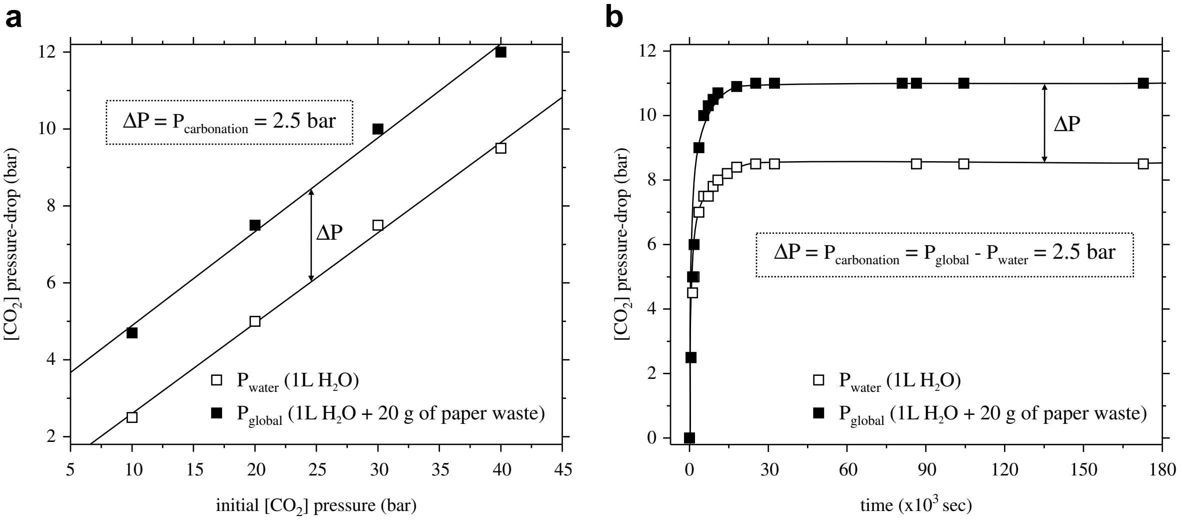

Fig. 5. (a) Linear correlation between the pressure drop and the initial pressure of CO_2 for experiments at 30 °C, an initial pressure of CO_2 equal to 10, 20, 30 and 40 bar and 2 h of carbonation. (b) Kinetic behaviour of the CO_2 pressure drop in the long-term experiment (48 h) at 30 °C and 30 bar of initial pressure of CO_2. In both, constant pressure drop of 2.5 bar is independent of the initial pressure of CO_2, showing that the thermodynamic state of CO_2 (gaseous or supercritical) does not modify the reaction kinetics.

the carbonation process. For this case, the best fit (attested by a correlation factor close to 1) of the experimental-calculated data was achieved when using a pseudo-second-order kinetic model according to the following expression:

$$\frac{dn_{\text{total\_CO}_2,t}}{dt} = k_s(n_{\text{total\_CO}_2,\max} - n_{\text{total\_CO}_2,t})^2 \qquad (12)$$

where k_s is the rate constant of sequestered CO_2 [$\text{mol}^{-1}\ \text{s}^{-1}$] for a given initial pressure of CO_2 in the system, $n_{\text{total\_CO}_2,\max}$ is the maximum sequestered quantity of CO_2 at equilibrium [mol], $n_{\text{total\_CO}_2,t}$ is the sequestered quantity of CO_2 at any time, t, [mol].

The integrated form of Eq. (12) for the boundary conditions $t = 0$ to $t = t$ and $n_{\text{total\_CO}_2,t} = 0$ to $n_{\text{total\_CO}_2,t} = n_{\text{total\_CO}_2,t}$ is represented by a hyperbolic equation (Eq. (13)):

$$n_{\text{total\_CO}_2,t} = \frac{n_{\text{total\_CO}_2,\max} \times t}{\left(\frac{1}{k_s \times n_{\text{total\_CO}_2,\max}}\right) + t} \qquad (13)$$

In order to simplify the fitting of experimentally-calculated data, the constant $t_{1/2} = 1/\ k_s \times n_{\text{total\_CO}_2,\max}$ has been defined. Physically, $t_{1/2}$ represents the time after which half of the maximum sequestered quantity of CO_2 was reached and is called "half-sequestered CO_2 time". It can be used to calculate the initial rate of sequestered CO_2, $v_{0,s}$, [mol s^{-1}] (Eq. (14)):

$$v_{0,s} = \frac{n_{\text{total\_CO}_2,\max}}{t_{1/2}} = k_s(n_{\text{total\_CO}_2,\max})^2 \qquad (14)$$

The fitting of the experimental-calculated kinetic curve at 30 bar and 30 °C ($n_{\text{total\_CO}_2,t}$ vs. t) using Eq. (13) is shown in Fig. 6. The parameters $t_{1/2}$ and $n_{\text{total\_CO}_2,\max}$ were estimated by applying non-linear regression using the least squares method. The initial rate of sequestered CO_2 was calculated using the Eq. (14) ($v_{0,s} = 3.3 \times 10^{-4}$ mol s^{-1}) at 30 °C. This value indicates that the mass transfer of compressed CO_2 in contact with solid-water dispersion is higher than CO_2 transfer at atmospheric conditions or at low pressure (Haubrock et al., 2007; Akanksha et al., 2008).

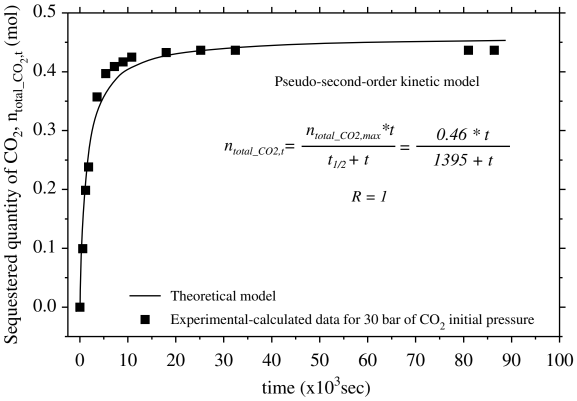

Fig. 6. Kinetic modelling of sequestered quantity of CO_2 in the long-term experiment (48 h) at 30 °C and 30 bar of initial pressure of CO_2.

3.4. Possible financial benefits

The Kyoto Protocol is a protocol from the international Framework Convention on Climate Change with the objective of reducing Greenhouse gases that cause climate change, mainly CO_2, by at least 5% from the 1990 levels by the period 2008–2012. The European Union attaches national quotas of tradable emission rights. Likewise, governments allocate a specific number of emission rights to each high-energy consumption company. If a company emits more CO_2 than the assigned level, they must buy emission rights at €25 for each tonne of CO_2 or, otherwise, shall be punished with a high penalty amounting to €100 for each tonne of CO_2 emitted in excess. Currently, Spain is the member country with the least possibility of fulfilling this agreement.

ENCE-Spain group has 3 cellulose pulp factories: Huelva, Pontevedra and Navia. Each factory has a production capacity ranging from 300,000 to 400,000 tonnes/a of ECF (Elemental Chlorine Free) pulp, generating a total of approximately 65,000 tonnes of alkaline paper mill waste. Extrapolating the sequestration capacity obtained in this study for the waste from ENCE-Huelva, the total CO_2 that could be sequestered in calcite would be of 15,000 tonnes. Although ENCE complies with CO_2 emissions at present, this company could use their own alkaline waste in order to sequester some of the CO_2 emitted and certainly sell emission rights worth €375,000/a. In this way, other companies that do not comply with their emission rights would avoid paying penalties amounting to €1,500,000/a. Moreover, the CO_2 sequestration in cellulose pulp factories could help to capture other sulphurous gases, and hence, to reduce the characteristic smell of the emissions from these factories (Shih et al., 1999).

Finally, the generation of a solid product containing ca. 100% calcite also revalues the original waste since this mineral could be suitable for use in rubber, plastic, printing ink, paper making, oil paint, toothpaste, cosmetics and food industries (Chan et al., 2002; Kugge and Daicic, 2004).

4. Remarks and conclusions

In search of the most effective technique to reduce point CO_2 emissions into the atmosphere, the aqueous carbonation of alkaline paper mill waste (approx. 55 wt% in portlandite) could fulfil all necessary expectations for the following reasons:

1. The CO_2 sequestration is mainly produced by portlandite dissociation, CO_2 dissolution and calcite precipitation, as shown by means of XRD and SEM-EDS techniques, and thermodynamic calculations with PHREEQC. It is estimated that, the system proposed in this study would favour the mineralogical sequestration of approx. 218.37 kg of CO_2 into stable calcite/ton of paper waste. The amount sequestered by carbonation is independent of both temperature (30 or 60 °C) and initial pressure of CO_2 injected in the system (10, 20. 30 or 40 bar).
2. The independence of temperature and pressure in the sequestration efficiency, probably because the reaction between portlandite and CO_2 is extremely fast, could reduce the costs for the process on an industrial scale since: (1) additional energy is not required for excessive increase of both parameters and (2) the system does not need special materials for reactor design.
3. The capacity of mineral CO_2 sequestration of alkaline paper mill waste is much higher than those of other materials reported in the literature. As a comparison, municipal solid waste bottom-ash could sequester 23.08 kg of CO_2 per ton (Rendek et al., 2006) and coal combustion fly-ash 26.19 kg of CO_2 per ton (Montes-Hernandez et al., 2008), that is, both wastes have a sequestration capacity ca. 10 times lower than paper wastes. Wollastonite has a very similar sequestration capacity, i.e. 329 kg of CO_2 per ton (Huijgen et al., 2006); however, this primary mineral is not a residue.
4. The result of the carbonation process is a free-metal solution in contact with a solid containing practically 100 wt% of calcite. This final product could be used as a reagent for further aqueous carbon sequestration. The result of this additional CO_2 sequestration may be stored in the ocean, though with some negative impacts on the environment, or used as an alkaline amendment in soils contaminated by metals.
5. The utilization of other wastes to sequester CO_2 would result in the production of calcite in a matrix of silicate minerals that would continue to be a waste product with little application. In addition, these final products could be neither used for further aqueous carbon sequestration nor stored in soils or in the ocean.
6. Carbonation is an exothermic process for portlandite (Montes-Hernandez et al., 2007a), which potentially reduces the overall energy consumption and costs of carbon sequestration.

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