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## Carbonation of alkaline paper mill waste to reduce CO<sub>2</sub> greenhouse gas emissions into the atmosphere

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1 **Carbonation of alkaline paper mill waste to reduce CO<sub>2</sub> greenhouse gas**  
2 **emissions into the atmosphere**

3

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16 **Abstract**

17

18 The global warming of Earth's near-surface, air and oceans in recent decades is a direct  
19 consequence of anthropogenic emission of greenhouse gases into the atmosphere such as CO<sub>2</sub>,  
20 CH<sub>4</sub>, N<sub>2</sub>O and CFCs. The CO<sub>2</sub> emissions contribute approximately 60% to this climate change.  
21 This study investigates experimentally the aqueous carbonation mechanisms of an alkaline paper  
22 mill waste containing about 55 wt% of portlandite (Ca(OH)<sub>2</sub>) as a possible mineralogical carbon  
23 dioxide sequestration process. The overall carbonation reaction includes the following steps: (1)  
24 Ca release from the portlandite dissolution, (2) CO<sub>2</sub> dissolution in water and (3) calcium  
25 carbonate precipitation. This CO<sub>2</sub> sequestration mechanism was supported by geochemical  
26 modelling of final solutions using PHREEQC software, and observations of scanning electron  
27 microscope and X-ray diffraction of final reaction products. According to our experimental  
28 protocol, the system proposed would favour the total capture of approx. 218 kg of CO<sub>2</sub> into stable  
29 calcite per every ton of paper waste, independently of initial CO<sub>2</sub> pressure. The final product  
30 from carbonation process is a calcite (ca. 100 wt%)-water dispersion. Indeed, the total captured  
31 CO<sub>2</sub> mineralized as calcite could easily be stored in soils or in the ocean without any significant  
32 environmental negative impact. This result demonstrates the possibility to use the alkaline liquid-  
33 solid waste for CO<sub>2</sub> mitigation and reduction of greenhouse effect gases into the atmosphere.

34

35 **Keywords:** *Portlandite; Paper waste; Aqueous carbonation; Mineral trapping of CO<sub>2</sub>; Calcite*

36

37 **1. Introduction**

38

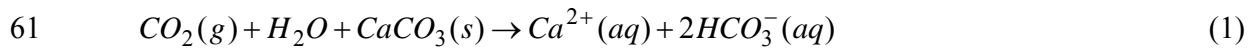
39 Coal caused the first industrial revolution that transformed the agrarian societies. Electricity  
40 allowed the formation of great urban centres. The advance of the industrialized societies has  
41 taken place in exchange for the unconditional burning of fossil fuels. This has caused an increase  
42 of the CO<sub>2</sub> concentration in the atmosphere from 280 ppm in the pre-industrial revolution to 379  
43 ppm in 2005, rising faster in the last 10 years (average 1995-2005: 1.9 ppm yr<sup>-1</sup>) (IPCC, 2007a).

44 The temperature of Earth's near-surface, air and oceans is basically controlled by the capacity  
45 of the atmosphere to reflect, adsorb and emit the solar energy. However, the continuous  
46 emissions of CO<sub>2</sub> into the atmosphere ( $26.4 \pm 1.1$  Gt CO<sub>2</sub> yr<sup>-1</sup> for 2000-2005) have altered this  
47 natural equilibrium and have led to the increase of the greenhouse effect and the consequent  
48 climatic change. The global surface average temperature will increase 2-4.5 °C when the  
49 atmospheric CO<sub>2</sub> concentration doubles the pre-industrial revolution concentration (IPCC,  
50 2007a). These alterations are leading to stress on drinking water availability, species extinction,  
51 melting of ice sheets and coastal flooding (IPCC, 2007b).

52 The energy production system is currently profitable, thus any modification is unviable since  
53 it could produce huge imbalances in the global economy. An alternative to reduce the CO<sub>2</sub>  
54 emission is the retention of carbon dioxide in natural reservoirs. Three possibilities for  
55 sequestration of carbon dioxide are currently being studied: aqueous carbon sequestration,  
56 geological carbon sequestration and mineralogical carbon sequestration.

57 Aqueous carbon sequestration involves the CO<sub>2</sub> dissolution into water to produce a carbonic  
58 acid solution, which later is neutralized and equilibrated with limestone as shown by the  
59 following reaction (Rau et al., 2007):

60



62

63 The dissolved calcium bicarbonate produced is then released and diluted in the ocean where  
64 these ions are already present abundantly in seawater. Moreover, this process is geochemically  
65 comparable to the natural mechanism of CO<sub>2</sub> mitigation by continental and marine carbonate  
66 weathering, but over many millennia time scales (Murray and Wilson, 1997).

67 Geological carbon sequestration consists of capturing gaseous CO<sub>2</sub> from emission sources  
68 and injecting it in terrestrial reservoirs, such as saline aquifers, depleted oil and gas fields or deep  
69 coal seams (Bachu, 2000, 2002; Bachu and Adams, 2003; Friedmann, 2007). The main scientific  
70 concerns involving the geological carbon sequestration applicability are the high pressure and  
71 temperature variations caused by the large CO<sub>2</sub> accumulation on the reservoirs. These  
72 thermodynamic variations could exert forces that diminish the reservoir confinement due to the  
73 formation of cracks and faults either in reservoir itself, or in the cap rocks. Moreover, the CO<sub>2</sub>  
74 dissolution into the pore water and the consecutive carbonic acid formation can result in the rapid  
75 dissolution of several minerals (mainly carbonate, oxides and hydroxide minerals) affecting the  
76 long-term confinement properties of the reservoirs (Kharaka et al., 2006).

77 In terrestrial reservoirs, the CO<sub>2</sub> pressure can decrease in the long term as a consequence of a  
78 mineralogical carbon sequestration or mineral trapping. The stored CO<sub>2</sub> may transform to stable  
79 carbonate minerals by reactions with aqueous ions (mainly calcium, magnesium and iron)  
80 resulting from silicate weathering (Gunter et al., 2000; Kaszuba et al., 2003, 2005; Giammar et  
81 al., 2005; Bénézech et al., 2007). Although this mechanism favours the permanent CO<sub>2</sub>  
82 sequestration, it is expected to be slow in geological formation (hundreds of years) due to the  
83 slow kinetics of silicate mineral dissolution and carbonate mineral precipitation. However, the

84 mineralogical carbon sequestration could contribute significantly to CO<sub>2</sub> sequestration in the  
85 proximity of the emission source, without the need of storing the gas into a geological reservoir.  
86 Some authors proposed the use of mineralogical carbon sequestration in controlled reactors as a  
87 viable approach to reduce CO<sub>2</sub> emissions into the atmosphere using either: (1) industrial by-  
88 products such as coal combustion fly-ash (Montes-Hernandez et al. 2007a), coal combustion fly-  
89 ash plus brine solution from gas production (Soong et al., 2006) or municipal solid waste bottom-  
90 ash (Rendek et al., 2006); or (2) primary minerals such as serpentine/olivine (Maroto-Valer et al.,  
91 2005) or wollastonite (Huijgen et al., 2006). These materials act as calcium and magnesium  
92 source favouring the CO<sub>2</sub> retention by carbonate precipitation.

93 Montes-Hernandez et al. (2007b) proposed an experimental method to synthesize fine  
94 particles of calcite by means of aqueous carbonation of pure portlandite at high pressure of CO<sub>2</sub>  
95 (initial P<sub>CO<sub>2</sub></sub>=55 bar) and moderate and high temperature (30 and 90 °C). This aqueous  
96 carbonation process implies dissolution of CO<sub>2</sub> into water and the consequent calcite  
97 precipitation. This method also has important ecological implications for mineral carbon  
98 sequestration. However, the use of pure portlandite and other primary minerals may suppose a  
99 high economic and environmental cost as these are typically resources and not residues.

100 In the cellulose pulp production for paper manufacture, the dominant process involves  
101 cooking woodchips in high concentrations of sodium hydroxide and sodium sulphide for 2-4 h at  
102 170 °C. This process, known as kraft pulping, favours the lignin dissolution and the separation of  
103 the cellulose fibers that are recovered by means of sieving. The residual liquids or black liquor  
104 containing the most of the dissolved lignin are transformed to white liquor and reused in the  
105 cooking stage. This transformation is carried out by both combustion in a boiler and causticizing  
106 with lime and implies the production of several types of portlandite-rich solid wastes with  
107 alkaline nature known generically as alkaline paper mill wastes.

108 In some pulp and paper industries, the alkaline by-products are usually sold for the cement  
109 manufacture and as alkaline amendment for agricultural soils. Nevertheless, their recycling is  
110 limited by the presence of chloride and metals, and in numerous occasions must be stored near  
111 the industrial facilities. A few investigations focused on the reusability of these wastes have been  
112 reported in the literature, and the existing ones are based on their application for the  
113 neutralization of acid mine drainages (Bellaloui et al., 1999). The main aim of this paper is to  
114 show the efficiency of the utilization of these wastes as a calcium source for aqueous  
115 carbonation, calcite precipitation and mineralogical CO<sub>2</sub> sequestration. From the sustainable  
116 development point of view, the treatment proposed is especially attractive because a low-cost  
117 residue is used to reduce the emissions of greenhouse gasses into the atmosphere.

118

119

## 120 **2. Materials and methods**

121

### 122 *2.1. Alkaline paper mill waste*

123

124 The alkaline paper waste used in the present study was collected from a cellulose pulp factory  
125 (ENCE) located in Huelva, south-western Spain. This by-product, so-called calcium mud, is the  
126 waste of the calcination or conversion of calcium carbonate to lime for the causticizing of the  
127 black liquor. Calcium mud was selected since it presents a higher Ca content than the remaining  
128 alkaline paper wastes.

129 The particle size of paper mill waste ranges from 1 to 100 μm with a median size of 15 μm,  
130 as determined by laser diffraction. This waste is made up of portlandite (Ca(OH)<sub>2</sub>; 55 wt%),  
131 calcite (CaCO<sub>3</sub>; 33 wt%) and hydroxyapatite (Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>; 12 wt%). The portlandite

132 particles present a laminar-pseudo-hexagonal habit, as observed by scanning electron microscopy  
133 equipped with an energy dispersive system (SEM-EDS, JEOL JSM-5410 instrument) (Fig. 1).  
134 The chemical composition analyzed with X-ray fluorescence (XRF, BRUKER PIONEER  
135 instrument) shows high content of Ca (83.2 wt% CaO), C (10.3 wt% CO<sub>2</sub>), P (2.4 wt% P<sub>2</sub>O<sub>5</sub>), S  
136 (2 wt% SO<sub>3</sub>), Na (0.88 wt% Na<sub>2</sub>O), Mg (0.35 wt% MgO), Si (0.34 wt% SiO<sub>2</sub>), Al (0.17 wt%  
137 Al<sub>2</sub>O<sub>3</sub>) and K (0.13 wt% K<sub>2</sub>O), and minor amounts of Cl (590 ppm), Fe (137 ppm), Ni (130  
138 ppm), Sr (114 ppm) and Cu (108 ppm). The water content determined by drying at 105 °C until  
139 constant weight was about 21 wt%. The presence of high concentrations of portlandite in paper  
140 mill waste accounts for the high alkalinity and potential for carbon dioxide sequestration as  
141 discussed below.

142

## 143 *2.2. CO<sub>2</sub> sequestration experiments*

144

145 The CO<sub>2</sub> sequestration experiments were conducted in a 2 L (total volume) closed titanium-  
146 lined pressure reactor (Parr Instrument Co., USA, Model 4843) equipped with a heating jacket  
147 (Fig. 2). In each experiment, the autoclave was charged with approximately 1L of Millipore MQ  
148 water (18.2 MΩ) and 20 g of paper mill waste. The waste particles were immediately dispersed  
149 with mechanical agitation (450 rpm) and the dispersion heated to 30 or 60 °C. When the  
150 temperature was reached, 10, 20, 30 or 40 bar of CO<sub>2</sub> (provided by Linde Gas S.A.) was injected  
151 into the reactor by opening a valve and adjusting the pressure to the desired one, and the reaction  
152 was commenced. This initial pressure of CO<sub>2</sub> was equal to the total initial pressure in the system.  
153 A summary of the experiments carried out and the initial experimental conditions is shown in  
154 Table 1. A long-term experiment (48 hours) at 30 bar of initial pressure of CO<sub>2</sub> allowed us to



155 both optimize the experimental duration of the remaining experiments at 2 hours and study the  
156 kinetic evolution of the carbonation process.

157 The global pressure drop in the system,  $P_{global\_pressure-drop}$ , is a consequence of both the  
158 dissolution-dissociation of CO<sub>2</sub> in the solution and aqueous carbonation process of Ca(OH)<sub>2</sub>. In  
159 order to calculate the pressure drop only produced by the carbonation process  
160 ( $P_{carbonation\_pressure-drop}$ ), two independent but complementary experiments were proposed for  
161 each experiment: (1) to measure the pressure drop related to the dissolution-dissociation of CO<sub>2</sub>  
162 into pure water ( $P_{water\_pressure-drop}$ ), and (2) to measure the pressure drop related to the  
163 dissolution-dissociation of CO<sub>2</sub> in a Ca-rich solution ( $P_{Ca-rich\_pressure-drop}$ ). In this second  
164 experiment, a concentration of 1 g L<sup>-1</sup> of calcium was chosen, that represented the average  
165 concentration after paper waste dispersion in water. These two experiments demonstrated that the  
166 Ca-concentration (0-1g L<sup>-1</sup>) has no measurable effect on the dissolution-dissociation of CO<sub>2</sub> since  
167 the monitored pressure drop in pure water ( $P_{water\_pressure-drop}$ ) was equivalent to the monitored  
168 pressure drop in presence of Ca ( $P_{Ca-rich\_pressure-drop}$ ). Consequently, the pressure drop produced  
169 by the carbonation process of Ca(OH)<sub>2</sub> was calculated by a simple pressure balance:

170

$$171 \quad P_{carbonation\_pressure-drop} = P_{global\_pressure-drop} - P_{water\_pressure-drop} \quad (2)$$

172

173 Under isothermal conditions,  $P_{global\_pressure-drop}$  and  $P_{water\_pressure-drop}$  are proportional to the  
174 initial CO<sub>2</sub> pressure.

175 At the end of the experiment, the reactor was removed from the heating system and was  
176 immersed in cold water. The reaction cell was depressurized during the cooling water period at

177 25 °C (about 15 minutes). Subsequently, the reactor was disassembled and the supernatant was  
178 separated from the solid product by centrifugation at 12,000 rpm for 30 minutes. Finally, the  
179 solid product was dried directly in the centrifugation flasks for 48 h at 65 °C. The supernatant  
180 solutions were filtered through a 0.2- $\mu\text{m}$  Teflon filter. Adsorption on the filter and filter holder  
181 was considered negligible. The filtered solutions were immediately acidified for measurement of  
182 [Ca], [Ni], [Zn], [Cu] and [Sr] by Inductively Coupled Plasma Atomic Emission Spectrometry  
183 (ICP-AES).

184

### 185 *2.3. Characterization of solid phase*

186

187 The mineralogical characterization of the starting material and solid products was carried out  
188 by X-ray diffraction (XRD, powder method) using a D501 SIEMENS diffractometer. Working  
189 conditions were  $\text{CoK}\alpha$  monochromatic radiation ( $\lambda=1.7902 \text{ \AA}$ ), 37.5 mA and 40 kV. The  
190 experimental measurement parameters were 12 s counting time per  $0.02^\circ 2\theta$  step in the  $5\text{-}80^\circ 2\theta$   
191 range. The detection is performed by a Kevex Si(Li) detector. Morphological analyses of solid  
192 products were also characterized by means of SEM-EDS.

193 Solution saturation indexes with respect to solid phases ( $\text{SI}=\log(\text{IAP}/\text{K}_s)$ , where SI is the  
194 saturation index, IAP is the ion activity product and  $\text{K}_s$  is the solid solubility product) and  
195 aqueous speciation of the leachates were calculated using the equilibrium geochemical  
196 speciation/mass transfer model PHREEQC (Parkhurst and Appelo, 2005) and the database of the  
197 speciation model MINTEQ. Zero, negative or positive SI values indicate that the solutions are  
198 saturated, undersaturated and supersaturated, respectively, with respect to a solid phase.

199

200

### 201 **3. Results and discussion**

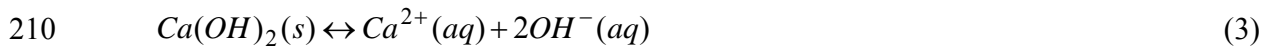
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#### 203 *3.1. Reaction mechanisms of CO<sub>2</sub> sequestration*

204

205 In an aqueous system, the water-CO<sub>2</sub>-paper waste interaction would suppose the carbonation  
206 of portlandite (Ca(OH)<sub>2</sub>; 55 wt%) according to well-known reactions (3-7) described in numerous  
207 works (e.g., Juvekar and Sharma, 1973; Shih et al., 1999; Beruto and Botter, 2000). On one hand,  
208 the calcium hydroxide is dissociated and increases the pH up to values around 12 (Eq. 3):

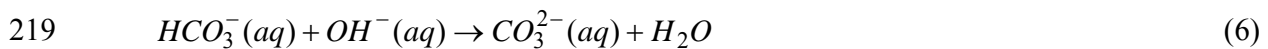
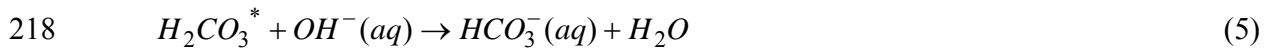
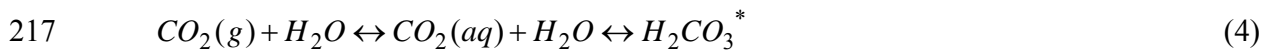
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211

212 On the other hand, the gaseous CO<sub>2</sub> is dissolved into the solution and reacts with the water to  
213 form carbonic acid (Eq. 4). Once equilibrium is established between the gaseous CO<sub>2</sub> and H<sub>2</sub>CO<sub>3</sub>,  
214 the carbonic acid further dissociates into bicarbonate and carbonate ions (Eqs. 5 and 6). At  
215 alkaline pH, the carbonate ion (CO<sub>3</sub><sup>2-</sup>) is the dominant species occurring in solution.

216



220

221 The presence of CO<sub>3</sub><sup>2-</sup> anions together with high Ca concentrations from the portlandite  
222 dissolution favours the supersaturation, and hence, the precipitation of calcium carbonate (Eq. 7):

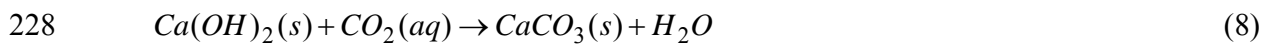
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225

226 The overall reaction for the process can be written as:

227



229

230 The thermodynamic calculations and the mineralogical characterization of solid products  
231 after experiments suggest that this simple reaction mechanism explains the CO<sub>2</sub> sequestration by  
232 paper mill waste. After the reaction, PHREEQC code indicates that the solutions are  
233 supersaturated with respect to calcium carbonate. Saturation indexes of calcite are in the range  
234 1.13-1.71 (Table 1). Comparison of X-ray diffraction spectra of the starting material and the solid  
235 product demonstrates that the portlandite contained in the starting material is totally carbonated  
236 and transformed to calcite (Fig. 3). The precipitated calcite is characterized by micrometric  
237 agglomerates of rhombohedral-crystals (Fig. 4). Both pre-existing calcite and hydroxyapatite in  
238 the starting material do not intervene in the CO<sub>2</sub> sequestration process.

239 One possible disadvantage of using paper mill waste is that this waste contains initially some  
240 toxic elements such as Ni, Zn, Cu and Sr that may be released in solution. However, the  
241 carbonation process also favoured the co-precipitation and/or incorporation of the dissolved  
242 impurities into the calcite crystal lattice. In fact, the Ni, Zn and Cu concentrations were below  
243 detection limit (< 6 µg L<sup>-1</sup>). Strontium was the only trace element detected by ICP-AES ([Sr] ≈  
244 0.25 mg L<sup>-1</sup>) in the solution. Nevertheless, the Sr concentrations are lower than the ones that

245 should have a pre-potable water for human consumption according to the established  
246 requirements by World Health Organisation (4 mg L<sup>-1</sup>).

247 In summary, the final product from carbonation process is a solid containing ca. 100 wt% of  
248 calcite, as occurs with the experiments from Montes-Hernandez et al. (2007b), but using a low-  
249 cost portlandite-rich waste instead of pure portlandite. Moreover, taking into account that the  
250 paper mill waste does not favour the liberation of toxic metallic ions at the CO<sub>2</sub> sequestration  
251 experiments, the final calcite-water dispersion could be used as reagent for a further aqueous  
252 carbon sequestration (see Introduction, Eq. 1). Hence, the final result of these experiments would  
253 allow us to continue sequestering CO<sub>2</sub> and the total amount of captured CO<sub>2</sub> could be poured  
254 either directly into the sea (not contribute with trace elements), being even beneficial for marine  
255 biota (Rau et al., 2007) or into soils.

256

### 257 3.2. Amount of sequestered CO<sub>2</sub>

258

259 A simplified method was developed to estimate the quantity of CO<sub>2</sub> sequestered by carbonate  
260 precipitation. This method was partially described in the section 2.2. Herein, the pressure drop  
261 produced by the carbonation process of Ca(OH)<sub>2</sub> (Eq. 8) in the system was calculated by a simple  
262 pressure balance (Eq. 2). Knowing the pressure drop values in each experiment (Table 1), the  
263 amount of CO<sub>2</sub> consumed by calcite precipitation ( $n_{carbonation\_CO_2,real}$  in mol) could be calculated  
264 using the ideal gas law:

265

$$266 \quad n_{carbonation\_CO_2,real} = \frac{P_{carbonation\_pressure-drop}V}{RT} \quad (9)$$

267

268 where  $V$  is the reactor volume occupied with gas (1 L),  $T$  is the reaction temperature ( $\approx 303$  °K)  
269 and  $R$  is the gas constant ( $0.08314472$  L bar K<sup>-1</sup> mol<sup>-1</sup>).

270 In experiments at 30 °C and 2 h of experimental duration, the pressure drop by portlandite  
271 carbonation was around 2.5 bar, independently of initial CO<sub>2</sub> pressure (Fig. 5a). Although the  
272 results of the long-term experiment (48 h, 30 bar and 30 °C) show that the equilibrium is obtained  
273 after about 5 hours of solid-fluid interaction, the maximum pressure drop by carbonation is  
274 already reached at 2 hours of experiment (Fig. 5b), and thus the experimental duration of the  
275 remaining experiments was correctly optimized. According to Eq. 9, the real amount consumed  
276 by carbonation was of 0.09923 mol of CO<sub>2</sub>.

277 The theoretical amount of CO<sub>2</sub> ( $n_{carbonation\_CO_2,theoretical}$ ) that should be sequestered by  
278 carbonation process (i.e., if all calcium is carbonated) could be calculated based on both the  
279 stoichiometry of reaction (8) and the quantity of portlandite contained into the paper mill waste  
280 (55 wt%):

281

$$282 \quad n_{carbonation\_CO_2,theoretical} = \frac{w_{Ca(OH)_2}}{M_{Ca(OH)_2}} \quad (10)$$

283

284 where  $M_{Ca(OH)_2}$  is the molar mass of Ca(OH)<sub>2</sub> (74.093 g mol<sup>-1</sup>) and  $w_{Ca(OH)_2}$  is the starting  
285 mass of Ca(OH)<sub>2</sub> in the reactor (8.69 g) which was calculated as follows:

286

$$287 \quad w_{Ca(OH)_2} = m_{paper\_waste} \times \left( \frac{\% \text{ portlandite}}{100} \right) \times \left( 1 - \frac{\% \text{ water\_content}}{100} \right) \quad (11)$$

288

289 where  $m_{paper\_waste}$  is the mass of paper mill waste used in the experiments (20 g),  $\%_{portlandite}$  is  
290 the percentage of portlandite in the waste (55 wt%) and  $\%_{water\_content}$  is the water content  
291 percentage in the waste (21 wt%). The theoretical amount of CO<sub>2</sub> that should be sequestered is  
292 0.11729 mol. This supposes a carbonation efficiency ( $CE$ ) of 85% at 30 °C according to:

293

$$294 \quad CE = \frac{n_{carbonation\_CO_2,real}}{n_{carbonation\_CO_2,theoretical}} \times 100 \quad (12)$$

295

296 In the experiment at high temperature (60 °C, 30 bar), the pressure drop by carbonation is  
297 slightly superior (3 bar), albeit the sequestered amount of CO<sub>2</sub> and the carbonation efficiency are  
298 very similar since this process depends inversely on the reaction temperature (Eq. 9).

299 Theoretically, the extrapolation of this experiment to real industrial scale would suppose a  
300 maximum CO<sub>2</sub> sequestration capacity of 258.54 kg of CO<sub>2</sub> per every ton of paper mill waste  
301 containing 55 wt% of portlandite. However, with our experimental protocol, 218.37 kg of CO<sub>2</sub>  
302 per every ton of paper mill waste could be successfully sequestered into stable calcite. Obviously,  
303 this is an attractive result concerning the mineral trapping of CO<sub>2</sub>.

304

### 305 *3.3. Kinetic modelling of sequestered CO<sub>2</sub>*

306

307 The monitoring of the pressure drop for any controlled system under ideal gas conditions  
308 allows the kinetic modelling of sequestered CO<sub>2</sub> after gas injection in a solid-liquid system (paper  
309 mill waste-water dispersion for this study). This can be done using a simple correlation function,

310  $n_{total\_CO_2} = f(t)$ , where  $n_{total\_CO_2}$  is the total mol quantity of sequestered CO<sub>2</sub> in the paper  
311 waste-water dispersion and  $t$  is the time after gas injection.

312 Several kinetic models including first-order, pseudo-first-order, second-order, pseudo-second-  
313 order, parabolic diffusion and power function kinetic expressions are reported in the literature for  
314 fitting the kinetic experimental or calculated data of solid-fluid interaction processes (e.g.  
315 Lagergren, 1898; Ho and Mckay, 1999). For this study, the kinetic modelling concerns the total  
316 sequestered quantity of CO<sub>2</sub> in a paper mill waste-water dispersion, i.e. the CO<sub>2</sub> dissolution-  
317 dissociation in water, possibly the CO<sub>2</sub> adsorption on the paper waste and, sequestered CO<sub>2</sub> by  
318 carbonation process. For this case, the best fit (attested by a correlation factor close to 1) of the  
319 experimental-calculated data was achieved when using a pseudo-second-order kinetic model  
320 according to the following expression:

321

$$322 \quad \frac{dn_{total\_CO_2,t}}{dt} = k_s (n_{total\_CO_2,max} - n_{total\_CO_2,t})^2 \quad (13)$$

323

324 where  $k_s$  is the rate constant of sequestered CO<sub>2</sub> [mol<sup>-1</sup> s<sup>-1</sup>] for a given initial pressure of CO<sub>2</sub> in  
325 the system,  $n_{total\_CO_2,max}$  is the maximum sequestered quantity of carbon dioxide at equilibrium  
326 [mol],  $n_{total\_CO_2,t}$  is the sequestered quantity of carbon dioxide at any time,  $t$ , [mol].

327 The integrated form of Eq. 13 for the boundary conditions  $t = 0$  to  $t = t$  and  $n_{total\_CO_2,t} = 0$   
328 to  $n_{total\_CO_2,t} = n_{total\_CO_2,t}$  is represented by a hyperbolic equation (Eq. 14):

329



330 
$$n_{total\_CO_2,t} = \frac{n_{total\_CO_2,max} \times t}{\left( \frac{1}{k_s \times n_{total\_CO_2,max}} \right) + t} \quad (14)$$

331  
 332 In order to simplify the fitting of experimental-calculated data, we have defined the constant  
 333  $t_{1/2} = 1/k_s \times n_{total\_CO_2,max}$ . Physically,  $t_{1/2}$  represents the time after which half of the maximum  
 334 sequestered quantity of carbon dioxide was reached and is called “half-sequestered CO<sub>2</sub> time”. It  
 335 can be used to calculate the initial rate of sequestered CO<sub>2</sub>,  $v_{0,s}$ , [mol s<sup>-1</sup>] (Eq. 15):

336  
 337 
$$v_{0,s} = \frac{n_{total\_CO_2,max}}{t_{1/2}} = k_s (n_{total\_CO_2,max})^2 \quad (15)$$

338  
 339 The fitting of the experimental-calculated kinetic curve at 30 bar and 30 °C ( $n_{total\_CO_2,t}$  vs.  
 340  $t$ ) using Eq. 14 is shown in Figure 6. The parameters  $t_{1/2}$  and  $n_{total\_CO_2,max}$  were estimated by  
 341 applying non-linear regression using the least squares method. The initial rate of sequestered CO<sub>2</sub>  
 342 was calculated using the Eq. 15 ( $v_{0,s} = 3.3 \times 10^{-4}$  mol s<sup>-1</sup>) at 30 °C. This value indicates that the  
 343 mass transfer of compressed CO<sub>2</sub> in contact with solid-water dispersion is higher than CO<sub>2</sub>  
 344 transfer at atmospheric conditions or at low pressure (Akanksha et al., 2007; Haubrock et al.,  
 345 2007).

346

347

348 **4. Remarks and conclusions**

349

350 In search of the most effective technique to reduce the point CO<sub>2</sub> emissions into the  
351 atmosphere, the aqueous carbonation of alkaline paper mill waste (approx. 55 wt% in portlandite)  
352 could fulfil all necessary expectations for the following reasons:

353

354 1. The CO<sub>2</sub> sequestration is mainly produced by the portlandite dissociation, CO<sub>2</sub> dissolution  
355 and calcite precipitation, as shown by means of XRD and SEM-EDS techniques, and  
356 thermodynamic calculations with PHREEQC. According to our estimations, the system  
357 proposed in this study would favour the mineralogical sequestration of approx. 218.37 kg  
358 of CO<sub>2</sub> into stable calcite per every ton of paper waste. The amount sequestered by  
359 carbonation is independent of both temperature (30 or 60 °C) and initial pressure of CO<sub>2</sub>  
360 injected in the system (10, 20, 30 or 40 bar).

361 2. The independence of temperature and pressure in the sequestration efficiency, probably  
362 owing to that the reaction between portlandite and CO<sub>2</sub> is extremely fast, could reduce the  
363 costs for the process in a industrial scale since: (1) additional energy is not required for the  
364 excessive increasing of both parameters and (2) the system does not need special materials  
365 for reactors design.

366 3. The capacity of mineral CO<sub>2</sub> sequestration of alkaline paper mill waste is much higher than  
367 those in other materials reported in the literature. As a comparison, the municipal solid  
368 waste bottom-ash could sequester 23.08 kg of CO<sub>2</sub> per ton (Rendek et al., 2006) and coal  
369 combustion fly-ash 26.19 kg of CO<sub>2</sub> per ton (Montes-Hernandez et al. 2007a), that is, both  
370 wastes present a sequestration capacity ca. 10 times lower than paper wastes. Wollastonite  
371 presents a sequestration capacity very similar, i.e. 329 kg of CO<sub>2</sub> per ton (Huijgen et al.,  
372 2006); however, this primary mineral is not a residue.

- 373 4. The result from carbonation process is a free-metal solution in contact with a solid  
374 containing practically 100 wt% of calcite. This final product could be used as reagent for a  
375 further aqueous carbon sequestration. The result of this additional CO<sub>2</sub> sequestration may  
376 be stored in the ocean where it would add minimally to the large, benign pool of these ions  
377 already present in seawater.
- 378 5. The generation of a solid product containing ca. 100% calcite also revalues the original  
379 waste since this mineral is amply used in rubber, plastic, printing ink, paper making dope,  
380 oil point, toothpaste, cosmetics and food industries (Chan et al., 2002; Kugge and Daicic et  
381 al., 2004).
- 382 6. The utilization of other wastes to sequester CO<sub>2</sub> would result in the production of calcite in  
383 a matrix of silicate minerals that would continue constituting a waste with low application.  
384 In addition, these final products could be neither used for a further aqueous carbon  
385 sequestration nor stored in soils or in the ocean.
- 386 7. The carbonation is an exothermic process for portlandite (Montes-Hernandez et al., 2007b),  
387 which potentially reduces the overall energy consumption and costs of carbon  
388 sequestration.
- 389

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396

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476



477 **Tables**

478

479 Table 1. Experimental conditions and results of CO<sub>2</sub> sequestration experiments using paper mill  
480 waste. Saturation state of calcite was calculated simulating with PHREEQC the reaction between  
481 Millipore MQ water (pH 5.6) and portlandite (8.69 g) for different initial conditions of  
482 temperature and CO<sub>2</sub> pressure.

483

484

485 **Figure captions**

486

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

489

490 Figure 2. Schematic experimental system for sequestration of CO<sub>2</sub> by aqueous carbonation of  
491 paper mill waste in a continuously stirred reactor.

492

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

496

497 Figure 4. (a-b) SEM images of calcite particles precipitated during CO<sub>2</sub> sequestration  
498 experiments.

499

500 Figure 5. (a) Linear correlation between the pressure drop and the initial pressure of CO<sub>2</sub> for  
501 experiments at 30 °C, an initial pressure of CO<sub>2</sub> equal to 10, 20, 30 and 40 bar and 2 h of  
502 carbonation. (b) Kinetic behaviour of the CO<sub>2</sub> pressure drop in the long-term experiment (48 h) at  
503 30 °C and 30 bar of initial pressure of CO<sub>2</sub>. In both, constant pressure drop of 2.5 bar is  
504 independent on the initial pressure of CO<sub>2</sub>, showing that the thermodynamic state of CO<sub>2</sub>  
505 (gaseous or supercritical) does not modify the kinetics of reaction.

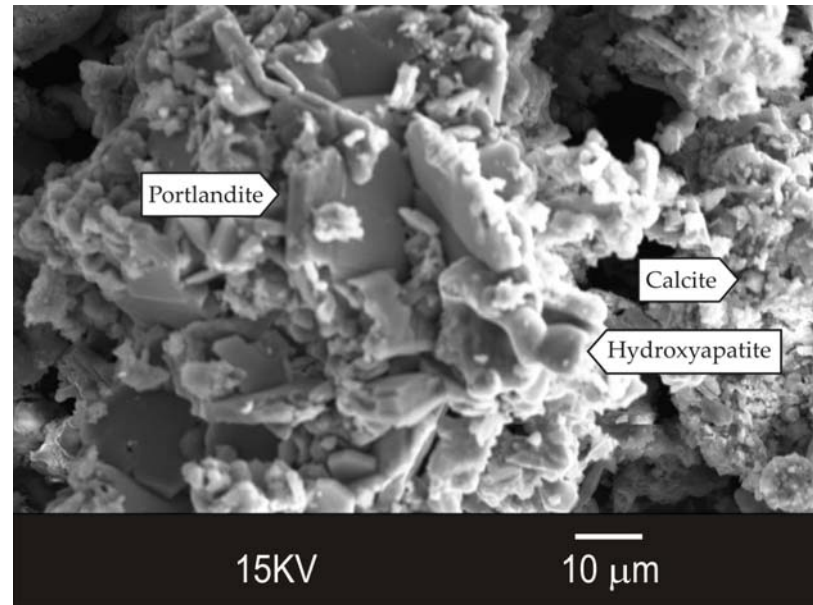
506

507 Figure 6. Kinetic modelling of sequestered quantity of CO<sub>2</sub> in the long-term experiment (48 h) at  
508 30 °C and 30 bar of initial pressure of CO<sub>2</sub>.

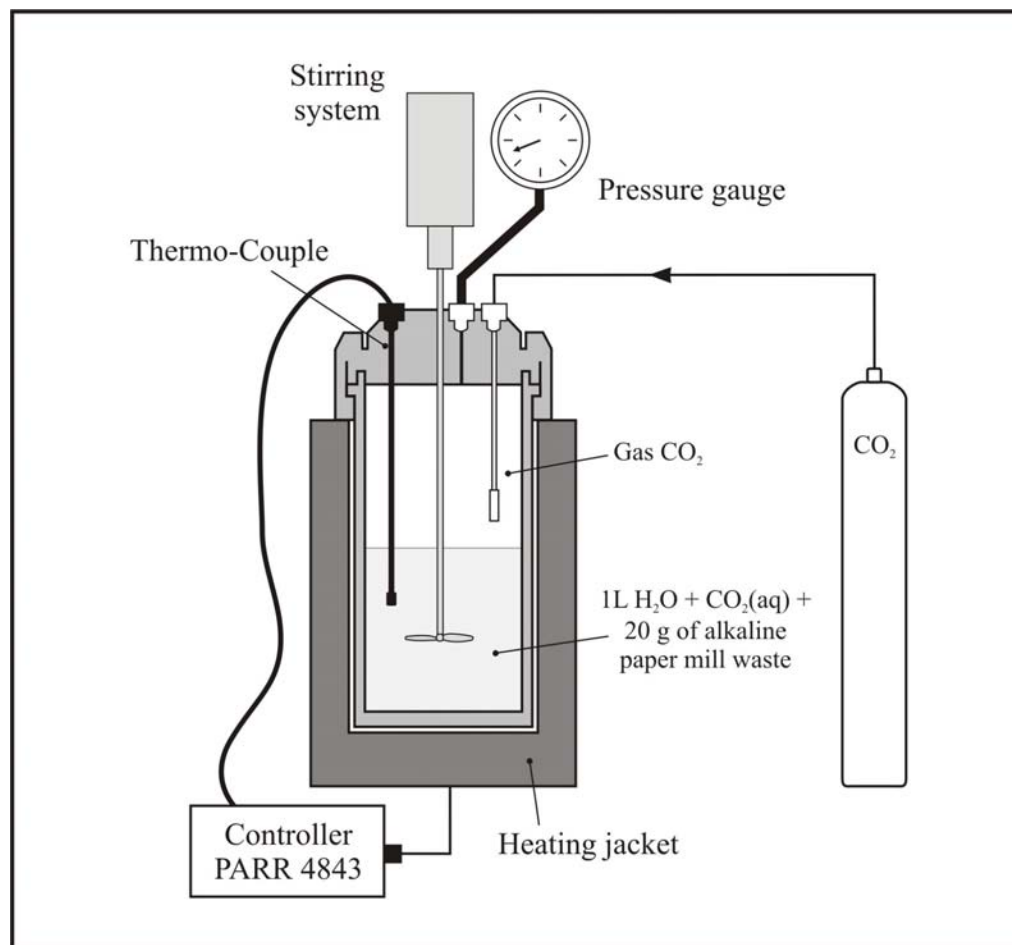
Experiment	Reactor content	Duration (h)	Temp. (°C)	Initial CO <sub>2</sub> pressure (bar)	Final CO <sub>2</sub> pressure (bar)	CO <sub>2</sub> pressure-drop (bar)	Carbonation pressure (bar)	SI <sub>calcite</sub>
Experiment 1	Blanks*	2	30	40	30.5	9.5	-	-
	1L pure water + 20 g of paper waste	2	30	40	28	12	2.5	1.13
Experiment 2	Blanks*	2	30	30	22.5	7.5	-	-
	1L pure water + 20 g of paper waste	2	30	30	20	10	2.5	1.25
Experiment 3	Blanks*	2	30	20	15	5	-	-
	1L pure water + 20 g of paper waste	2	30	20	12.5	7.5	2.5	1.42
Experiment 4	Blanks*	2	30	10	7.5	2.5	-	-
	1L pure water + 20 g of paper waste	2	30	10	5.3	4.7	2.2	1.71
Experiment 5	Blanks*	48	30	30	21.5	8.5	-	-
	1L pure water + 20 g of paper waste	48	30	30	19	11	2.5	1.25
Experiment 6	Blanks*	2	60	30	24.5	5.5	-	-
	1L pure water + 20 g of paper waste	2	60	30	21.5	8.5	3	1.52

\*Blanks include two experiments of dissolution-dissociation of CO<sub>2</sub>: (1) into pure water and (2) into a solution containing 1 g L<sup>-1</sup> of Ca. Both experiments showed identical results.

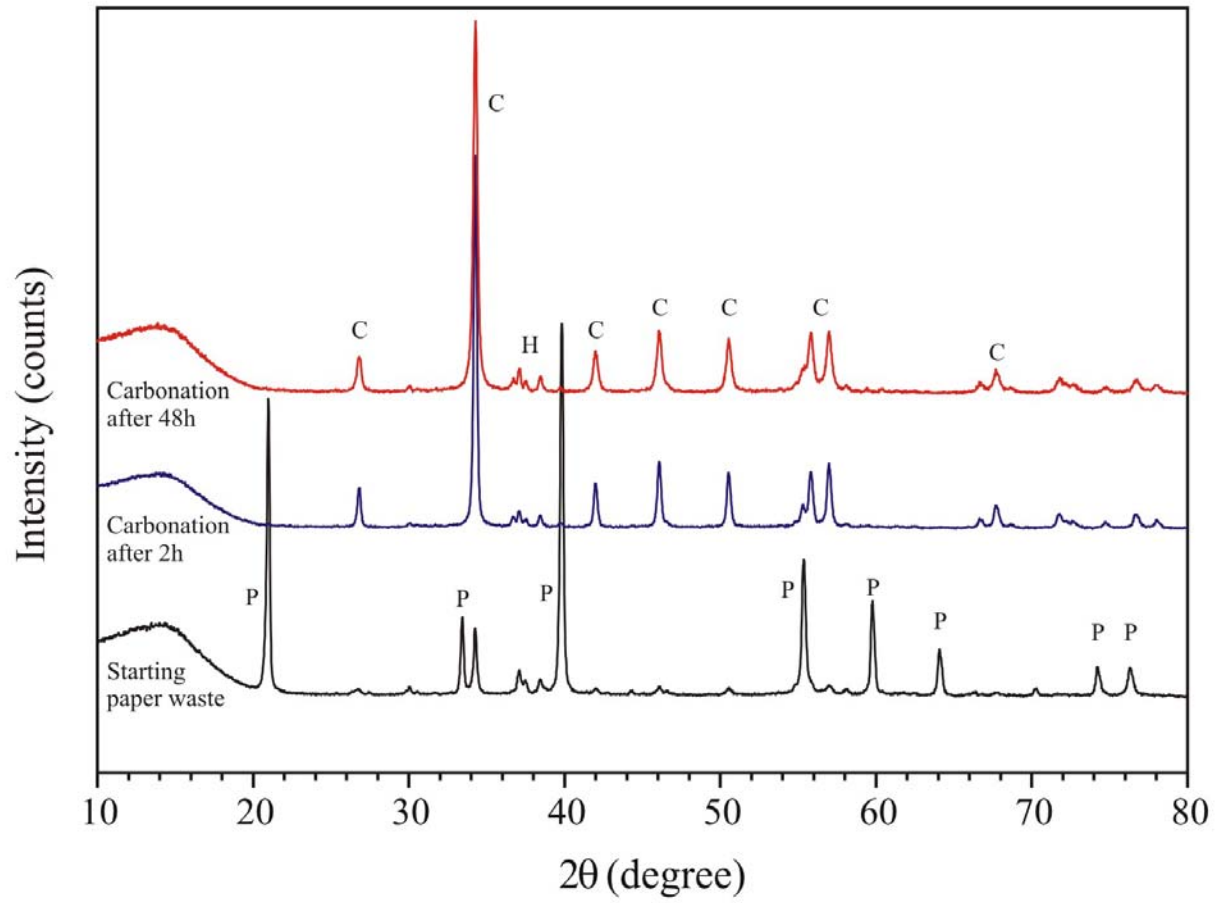
**Table 1**



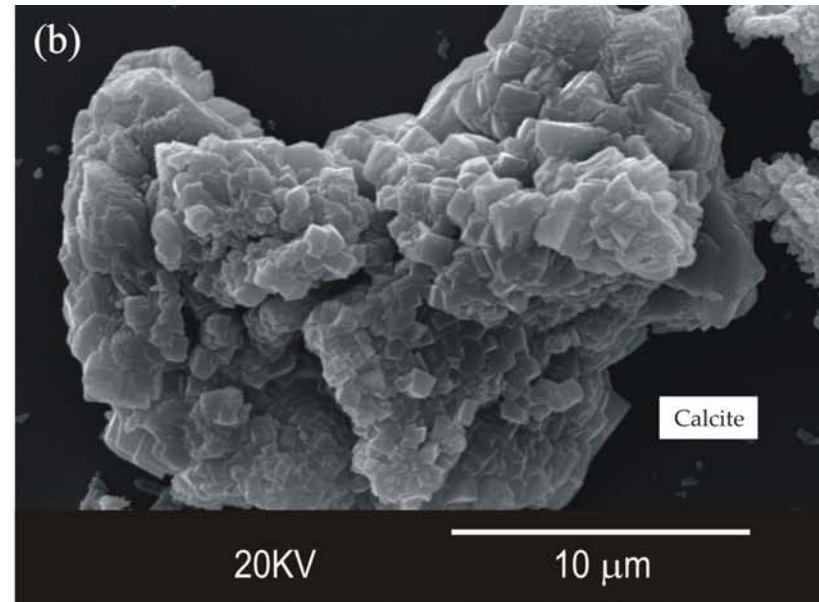
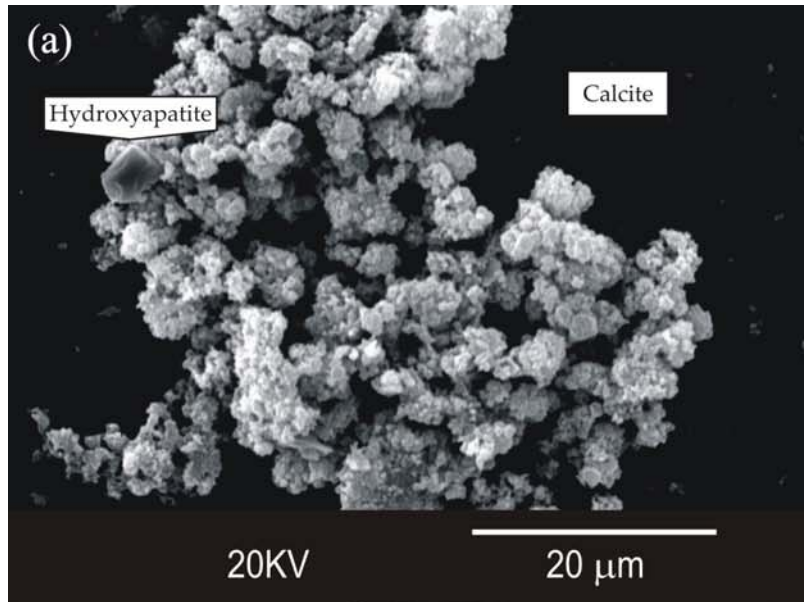
**Figure 1**



**Figure 2**



**Figure 3**



**Figure 4**

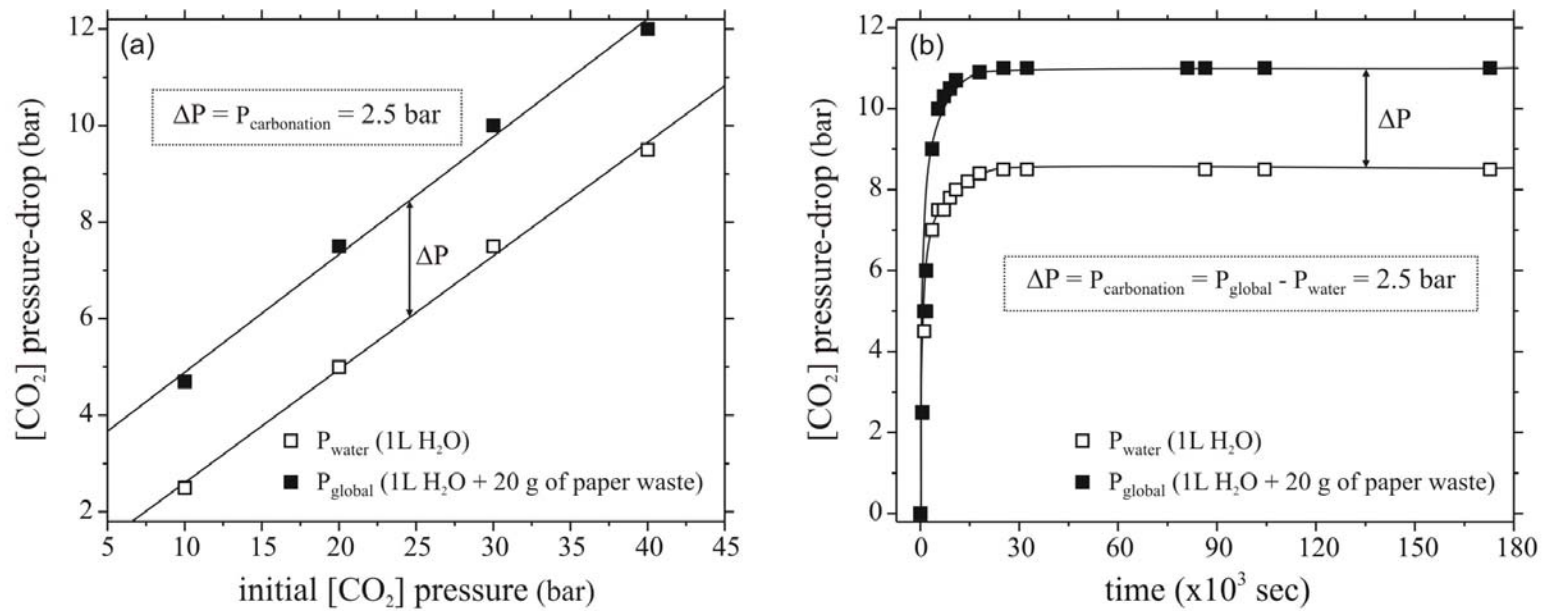
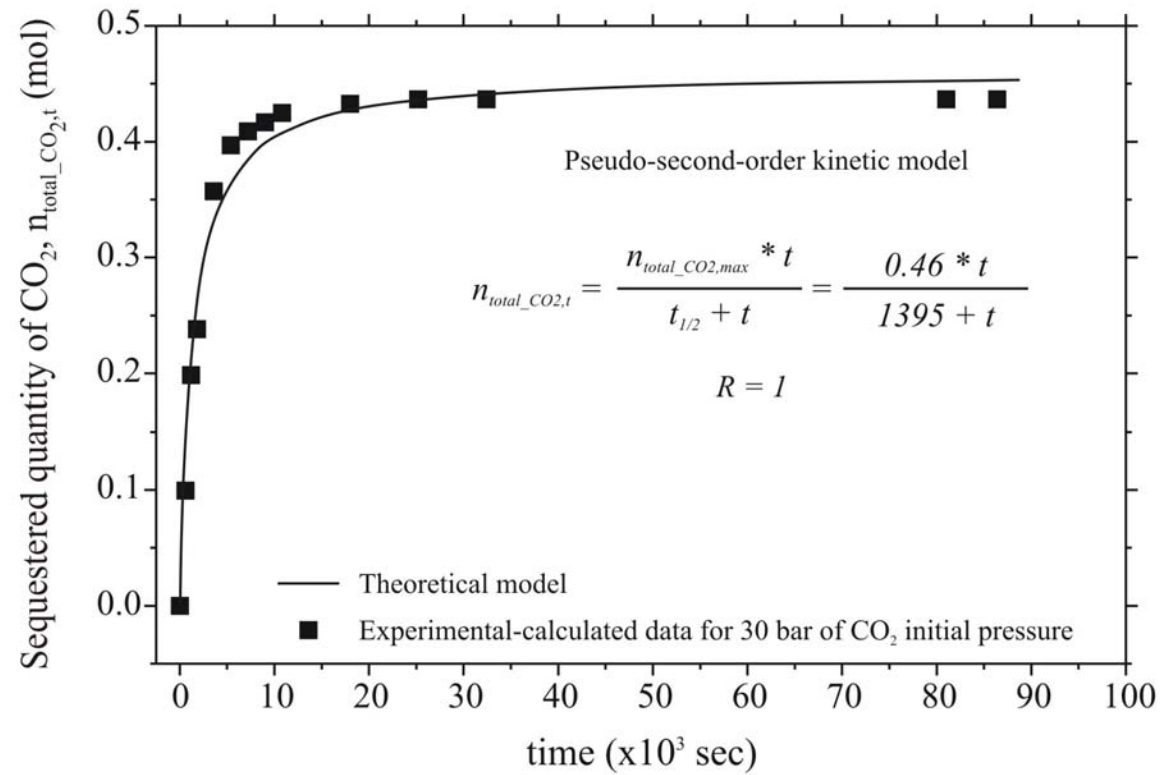


Figure 5





**Figure 6**