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Comparison of different reaction routes for carbonation of APC residues

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Abstract

This paper analyses and compares the results of accelerated carbonation experiments for CO₂ storage carried out on the air pollution control (APC) residues of a waste incineration plant, via both the dry and the wet route. The two routes achieved a similar maximum calcium conversion to carbonates (around 65%) corresponding to a potential CO₂ storage capacity of 250 g/kg residues. For the dry route, maximum conversion was achieved in a few minutes at 400°C under a 10% CO₂ atmosphere, whereas for the wet route it was obtained in about 10 minutes under a 100% CO₂ atmosphere, with a liquid to solid ratio of 0.2, at 30°C and 3 bar, or without water addition at 50°C. These results suggest that carbonation of APC residues, and possibly of other combustion residues, through either the dry or wet route, may be effectively applied for CO₂ storage, at least in the niche market of waste incineration.

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Keywords: APC residues; carbonation; kinetics; leaching.

1. Introduction

Increasing concerns over climate change and its correlation with anthropogenic greenhouse gas emissions are forcing the international community to adopt actions aimed in particular at reducing CO₂ discharge into the atmosphere. At least until energy production will continue to rely on fossil fuel combustion, CO₂ capture and storage (CCS) technologies are indicated as one of the most viable and effective measures [1]. One of the CCS techniques currently being investigated is an ex situ processes by which CO₂ is stored as thermodynamically stable carbonates by carbonation of Ca and Mg silicate minerals [2-8]. Large availability of magnesium silicates, such as olivine and serpentine, has been discovered worldwide [9]; however mineral carbonation requires high operation temperatures (180°C) and pressures (15 MPa) [10]. Alternatively, alkaline residues from industrial processes can be

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employed as alkalinity sources. The most promising residues in terms of CO₂ storage capacity, due to significant contents of Ca (hydro)oxides, are residues from thermal processes, e.g.: pulverized coal fly ash, steel slag, bottom ash and APC residues from municipal solid waste incineration, as well as deinking ash and cement waste from construction and demolition activities [11]. These materials are chemically more unstable than geologically derived minerals, and hence require a lower degree of pre-treatment and less energy intensive operating conditions [4,5]. Furthermore, although their availability is quite limited when compared to silicate minerals, they are produced at CO₂ point-source emission locations, such as coal fired power plants or waste to energy facilities.

A number of studies have recently focused on accelerated carbonation of municipal solid waste (MSW) incineration residues [12]. In the majority of these works, accelerated carbonation tests were performed on humidified samples, applying moderate pressures of CO₂ (1 to 10 bar) and temperatures (20 to 50 °C) [4,5,13-16]. Via this process route, known as the aqueous or wet route, the reaction occurs in a three phase system. Alternatively, carbonation was also performed via the gas-solid route, traditionally applied for the carbonation of raw materials, such as calcium oxides [17] and in which the reactions are rapid and completion can be achieved in minutes at a temperature above 350°C and ambient CO₂ pressure [18].

APC residues exhibit a considerably larger CO₂ uptake capacity compared to other MSW combustion residues, mainly due to their high content in reactive Ca species. In addition, these residues are generally classified as hazardous waste due to significant leaching of heavy metals and soluble salts [19]. Carbonation has been shown to generally improve the chemical stability and leaching behaviour of MSW residues, reducing Pb, Zn and Cu mobility, whereas exerting a possible mobilization effect on oxyanionic metals including Cr and Sb [14,15,20-22].

This paper presents the results of an extended study on the accelerated carbonation of APC residues, both in terms of the CO₂ storage capacity of the material and of the effects of the process on ash properties. Two reaction routes were investigated and compared; the dry route, performed as a gas-solid reaction between CO₂ and APC residues, operated at 1 bar, with a CO₂ concentration ranging from 10 to 50% and temperature values between 350 and 500°C; and the wet route, operated at low temperature (30-50°C), with a 100% CO₂ flow at a pressure ranging between 1 and 10 bar, and liquid to solid ratios (L/S) from 0 to 0.6. For each route the effect of operational parameters on process kinetics was investigated in order to identify the most promising conditions for a full scale application.

2. Materials

The APC residues analyzed in this study were sampled from the baghouse section of a hospital waste incinerator located near Rome. Characterization of the APC ash included the determination of water content and loss on ignition (LOI), element and major anion content, carbonate content, mineralogy, acid/base neutralization capacity (ANC/BNC) as well as leaching behaviour, following the EN 12457-2 leaching test. The methodology used is described in detail elsewhere [13,23].

The water content, LOI and main chemical composition of the APC ash are reported in Table 1. Ca and chloride were by far the major constituents, accounting for more than 50% of the total ash mass, consistent with the large Ca(OH)₂ excess used for acid gas abatement. Significant amounts of heavy metals were observed, namely Zn, Cu and Pb, with values comparable to results of a previous study on the same residues [18].

Table 1: Physical properties and chemical composition of the APC ash on a dry weight basis.

Physical Property	Value (% w/w)	Element	Concentration (mg/kg)	Element	Concentration (mg/kg)
Water content	1.78	Al	2140	Mg	8440
LOI	21.37	Ca*	350000	Mn	30.0
		Cd	2.1	Na	38440
Anion	Concentration (g/kg)	Cr	38.0	Ni	20.0
Cl ⁻	179.7	Cu	712.0	Pb	588.0
SO ₄ ⁻²	33.6	Fe	934.0	Si	10080
		K	5620	Zn	4456

* indirect calculation based on Ca speciation

The main crystalline phases detected by XRD analysis in the APC residues at ambient temperature, shown in Figures 2a and 4, were $\text{Ca}(\text{OH})_2$, CaClOH , CaCO_3 , CaSO_4 , NaCl and KCl , in accordance with prior investigations on this type of material [24]. The amount of Ca available for carbonation was estimated to be 38% as $\text{Ca}(\text{OH})_2$ and 29% as CaClOH . Mg species were not considered since they could not be detected by XRD analysis and the Mg content of the ash (0.8%) was much lower than the Ca content. Calcium speciation calculations and assumptions are reported elsewhere [13,23].

3. Dry-route carbonation experiments

Carbonation experiments were carried out in a Thermogravimetric system (TGA, Netzsch STA 409 CD) coupled with Gas Chromatography (GC, 2-channel Varian Micro GC, equipped with a Molsieve-5A and a Poraplot-U columns) for measurement of the evolving CO_2 . An average amount of 44 mg of APC residues was placed on a holder in a uniform layer of 3 mm and carbonated at operating temperatures ranging between 300 and 500°C feeding a CO_2 -argon gas mixture (10-50% vol. CO_2).

A typical TG profile of a carbonation experiment is shown in Figure 1, where the different steps of the experiments were the following; step 1: APC sample pre-heating to the operating temperature under argon flow; step 2: sample kept at the operating temperature under argon flow; step 3: change of the flow composition to a CO_2 -argon mixture, temperature kept constant until completion of carbonation.

As shown in Figure 1, carbonation kinetics was characterized by three stages: an induction period, a fast kinetically controlled reaction stage, and, finally, a diffusion-controlled stage. Initially, a weight decrease of the APC residue was typically observed at the end of step 1 and also through step 2. It was ascribed either to moisture loss or to the transformation of the existing phases, with water loss. As a consequence, the reacting phases available at the beginning of the carbonation experiments were different from those present in the original material, depending on the operating temperature. X-ray diffraction, SEM and TGA of the untreated material have been used as analytical techniques to identify the reactive phases at the applied operating temperatures and to describe the reaction pathways.

XRD analysis of samples of APC residues at 25 °C (Figure 2.a), as previously mentioned, indicated the presence of two forms of calcium amenable for carbonation: CaOHCl and $\text{Ca}(\text{OH})_2$. After pre-heating to at least 350°C, the peaks corresponding to both hydroxides disappeared, suggesting their transformation to calcium oxide (Figure 2.b). However, $\text{Ca}(\text{OH})_2$ and CaOHCl could still be present in the material, but as amorphous phases that cannot be observed with X-ray analysis. SEM and TGA measurements confirmed this observation, allowing to evaluate the amount of each calcium species available at the different reaction temperatures at the beginning of the carbonation step (step 3 in Figure 1). Considering the following gas-solid carbonation reactions (equations 1 to 3), at each operating temperature it was then possible to evaluate the conversion of the carbonation reaction (η , %) as the ratio between the measured weight increase and the maximum weight increase expected from the complete carbonation of the reacting phases, i.e. $\text{Ca}(\text{OH})_2$, CaOHCl , and CaO [25].

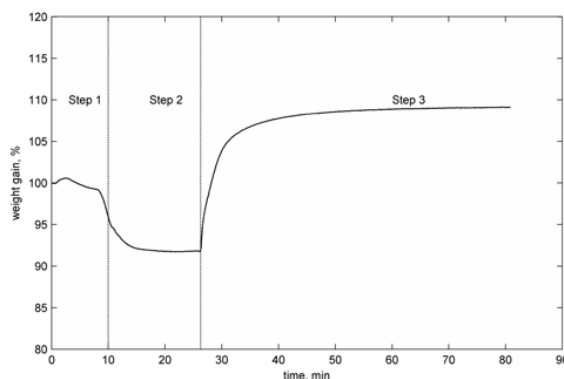
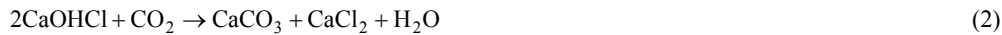


Figure 1: Typical thermogravimetric profile of a carbonation experiment.

The conversion measured at the end of step 3, representing the maximum conversion of the carbonation reaction for each run, ranged between 60% and 80% depending on the operating temperature and CO₂ concentration.



The variation of η over time is reported in Figures 3. The influence of temperature on the rate of the carbonation reaction was negligible, whereas the kinetics was slightly affected by CO₂ concentration. Although the fastest kinetics were observed at 400°C and 50%vol. CO₂ (Figure 3.c), reasonably fast reaction rates were observed also at 10%vol. CO₂ concentration (Figure 3.a), the typical composition of combustion flue gas.

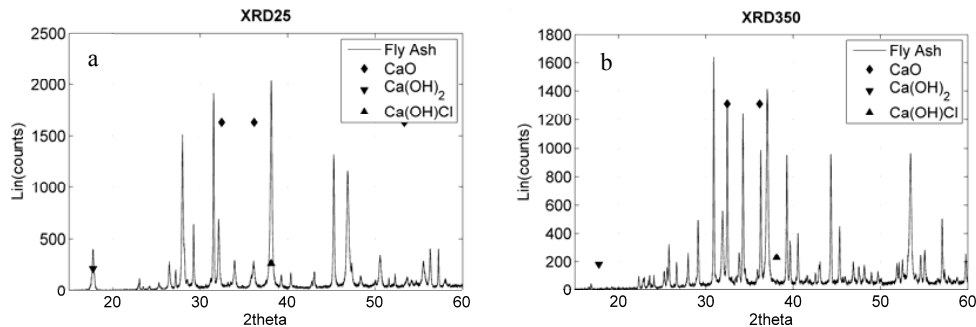


Figure 2: XRD patterns of APC samples: (a) as-received; (b) pre-heated in He atmosphere at 350°C [25].

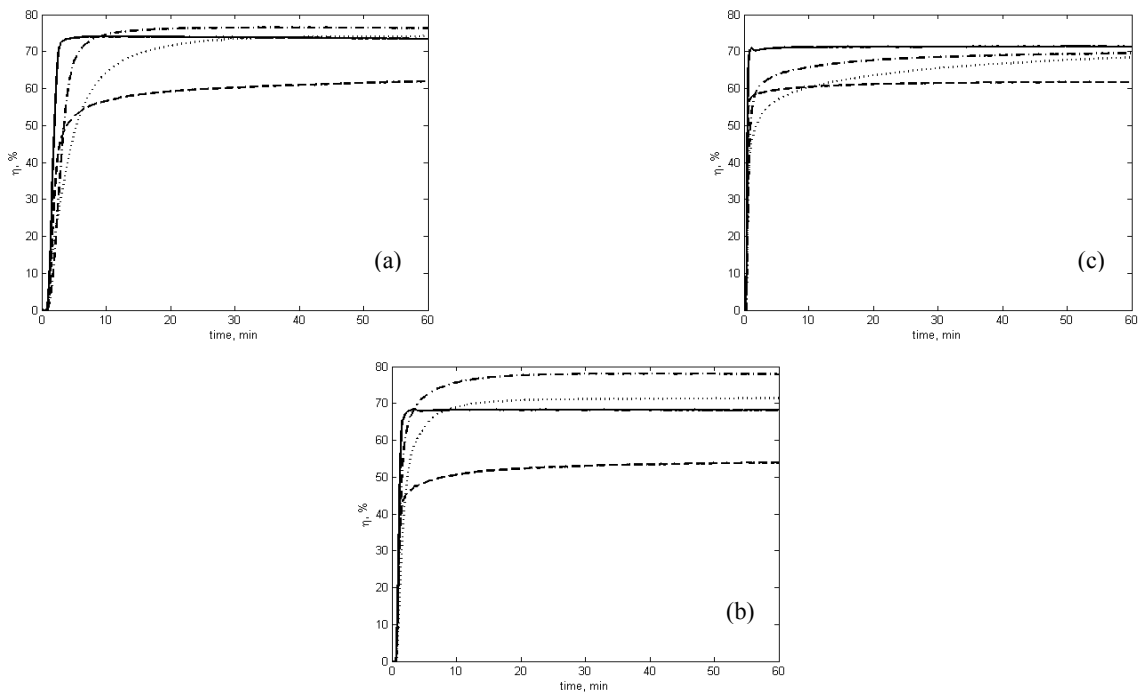


Figure 3: Carbonation kinetics measured at different operating temperatures: dashed line at 350 °C; continuous line at 400°C; dotted line at 450°C; dashed-dotted line at 500 °C. (a) 10% vol., (b) 22% vol., (c) 50% vol. CO₂ concentration [25].

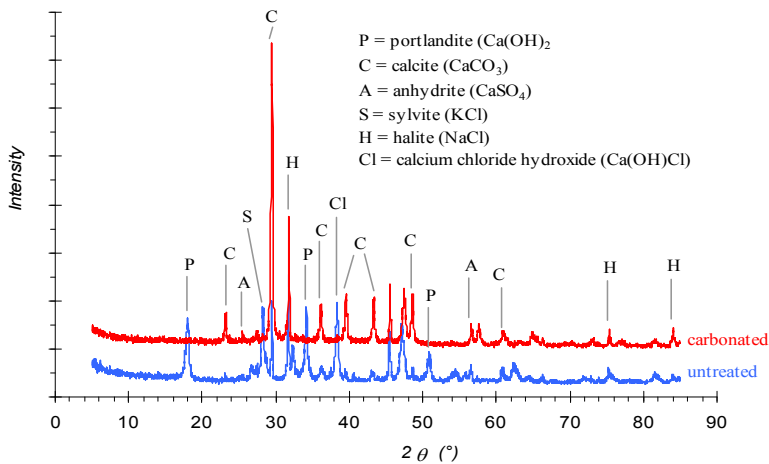


Figure 4: XRD patterns of untreated and carbonated (24 h, 30°C, 3 bar, L/S 0.02) APC ash.

4. Wet-route carbonation experiments

Wet carbonation experiments were performed in a 150 ml stainless steel reactor placed in a thermostatic bath to allow for temperature control at 30, 40 and 50°C. Ash samples were oven dried at 105°C, then mixed with distilled water at L/S ratios of 0.02, 0.1, 0.2, 0.4 and 0.6 l/kg and placed in aluminium foil containers. Three samples of 1 g of dry ash were treated in each experiment with a continuous 100% CO₂ flow. Gas pressure was set at 1, 3, 5, 7 or 10 bar using a pressure gauge.

Temperature was monitored with a thermocouple, while gas humidity was maintained at 75% using a saturated NaCl solution in the reactor. For each experiment a control sample was prepared with the same procedure and stored in closed containers in contact with air at atmospheric pressure in the thermostatic bath for the whole length of the experiment. The reactor was flushed with CO₂ at the beginning of each run to ensure air expulsion. The experiments were conducted for reaction times from 10 min to 48 h to study the CO₂ uptake kinetics under different operating conditions [13,23].

Carbonated samples showed a markedly different mineralogy, morphology and acid neutralization capacity compared to the untreated ash. XRD analysis, Figure 4, showed a significant presence of Ca(OH)₂ and Ca(OH)Cl in the untreated material, but not in the carbonated samples which instead were characterized by a strong predominance of CaCO₃. The acid/base neutralization capacity (ANC/BNC) of the APC ash is shown in Figure 5. The curve for the untreated material exhibited a high buffering capacity at a pH value of around 12, typical of calcium hydroxide species, while for the carbonated ash, upon addition of 1 meq/g HNO₃, the pH dropped to approximately 5.5, at which a plateau, typical of carbonate and bicarbonate species, was observed. The total amount of acid neutralized at this pH was of about 12 meq/g, corresponding to a CaCO₃ content of 60 wt.%, in good agreement with the values measured by calcimetry analysis for fully carbonated samples. Conversely, NaOH additions resulted in very similar shapes of titration curves for untreated and carbonated ash.

The extent of carbonation was assessed by measuring the weight gain upon carbonation and the increase in the carbonate content of the samples, measured by calcimetry analysis, accounting for the weight increase upon carbonation, as follows (equation 4):

$$\text{CO}_{2\text{uptake}} [\%] = \frac{\text{CO}_{2(\text{final})} [\%] - \text{CO}_{2(\text{initial})} [\%]}{100 - \text{CO}_{2(\text{final})} [\%]} \times 100 \quad (4)$$

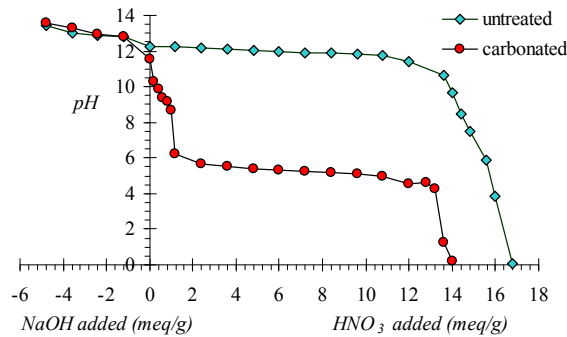


Figure 5: ANC/BNC curves for untreated and carbonated (1.5 h, 30°C, 3 bar, L/S 0.2) APC ash.

Maximum uptakes of 25% were achieved. The resulting Ca conversion (η), calculated using equation (5), with $\text{Ca}_{\text{reactive}}$ being the sum of the initial contents of CaOHCl and $\text{Ca}(\text{OH})_2$, gave a yield of 67%, comparable to results obtained by Baciocchi et al. [18] and Prigiobbe et al. [25] applying the direct gas-solid route.

$$\eta[\%] = \frac{\text{CO}_{2\text{uptake}}[\%]}{\text{Ca}_{\text{reactive}}[\%]} \times \frac{40}{44} \times 100 \quad (5)$$

Reaction kinetics was greatly influenced by the operating conditions, particularly by the L/S ratio and temperature. As shown in Figure 6 (a), the L/S ratio had a strong impact on CO_2 uptake, particularly at low (< 8 h) treatment durations; beyond these times the NaCl solution was sufficient to humidify even initially dry ash. After 4 h, for example, dry samples showed half the reactivity compared to samples with L/S 0.02 and about one third that of samples with L/S 0.1 and 0.2. This result confirms that water is necessary for hydration and solvation of CO_2 and Ca^{+2} to a degree that depends on the characteristics of the residue, in agreement with Fernández-Bertos et al. [14], who reported an optimal L/S ratio of 0.2-0.3 for a reaction time of 2.5 h. Higher L/S ratios were found to decrease the CO_2 uptake of the ash, probably due to a decrease in CO_2 diffusion through the intergranular water film. As shown in Figure 6 (b), a temperature increase from 30 to 50°C greatly affected the kinetics for an L/S ratio of 0.02, enhancing the reactivity in 1 h from 33 to 98%. Conversely, temperature at an L/S ratio of 0.2 did not affect the reaction kinetics (data not shown), indicating that this parameter has a similar effect as L/S ratio enhancing Ca dissolution and is hence significant only for relatively dry ash. Pressure did not appear to greatly influence carbonation kinetics, particularly for low reaction times; this is probably related to the fact that with a 100% CO_2 gas flow, the controlling reaction step was related to Ca dissolution rather than to CO_2 diffusion.

5. Effects on the leaching behaviour of APC residues

The effects of carbonation on heavy metal leaching from the APC residues were similar for both route [13,18]. In this paper the results of the tests performed on samples carbonated via the wet carbonation route, reported in detail elsewhere [13], are discussed. The results of the EN 12457-2 leaching test on untreated and carbonated ash, along with the Italian regulatory limits for landfill disposal showed that the critical species for the untreated ash were: Pb, Zn, Cu, Cr, Sb and soluble salts (Cl^- and SO_4^{2-}). Carbonation strongly reduced leaching to below the limits prescribed for non hazardous waste landfills (for Pb) and inert waste landfills (for Cu and Zn). Oxyanion-forming elements showed a different behaviour, with Cr being only slightly affected by the treatment, and Sb leaching increasing upon carbonation to values corresponding to disposal in hazardous waste landfills. The soluble salts content was also affected by carbonation even though chloride concentrations in the eluate, in particular, still largely exceeded the limits for hazardous waste landfills. Leaching of other major elements, such as Ca and Na for example,

was only slightly affected by carbonation. These results are in good agreement with previous studies on APC carbonation [18,21,23].

To better understand the changes in the leaching behaviour of the ash, the amounts of heavy metals released by untreated and treated ash as a function of pH was also investigated [13,23]. From these analysis it was possible to conclude that Pb leaching was reduced by more than two orders of magnitude in a pH range between 6 and 12. Similar trends were also observed by Baciocchi et al. [18] and Astrup et al. [20], who indicated cerrusite (PbCO_3) as the Pb solubility-controlling species For Zn and Cu; significant changes in leaching were observed in the pH ranges:11-13.5 and 8-13.5 respectively; for Cu, precipitation of copper carbonates [20] or a pH reduction to the range of minimum solubility [13,18,23] were indicated as possible reasons for the observed reduction. The leaching curves for the oxyanion-forming species showed quite a different behaviour [13,23]. In particular, Sb leaching showed a slight reduction for carbonated samples at pH 8-11; but at higher pH values, while Sb concentrations dropped in the eluates of untreated samples, carbonated samples showed quite stable values; a relatively similar behaviour was found by Van Gerven et al. [16] for carbonated MSWI bottom ash. Johnson et al. [26] indicated the Ca mineral $\text{Ca}(\text{Sb}(\text{OH})_6)_2$ as the controlling species for Sb (V) dissolution in soils with a high alkalinity. This mechanism could explain the increase observed in Sb elution from carbonated samples of APC ash, in which the initial Ca hydroxides content was strongly reduced after reaction with CO_2 .

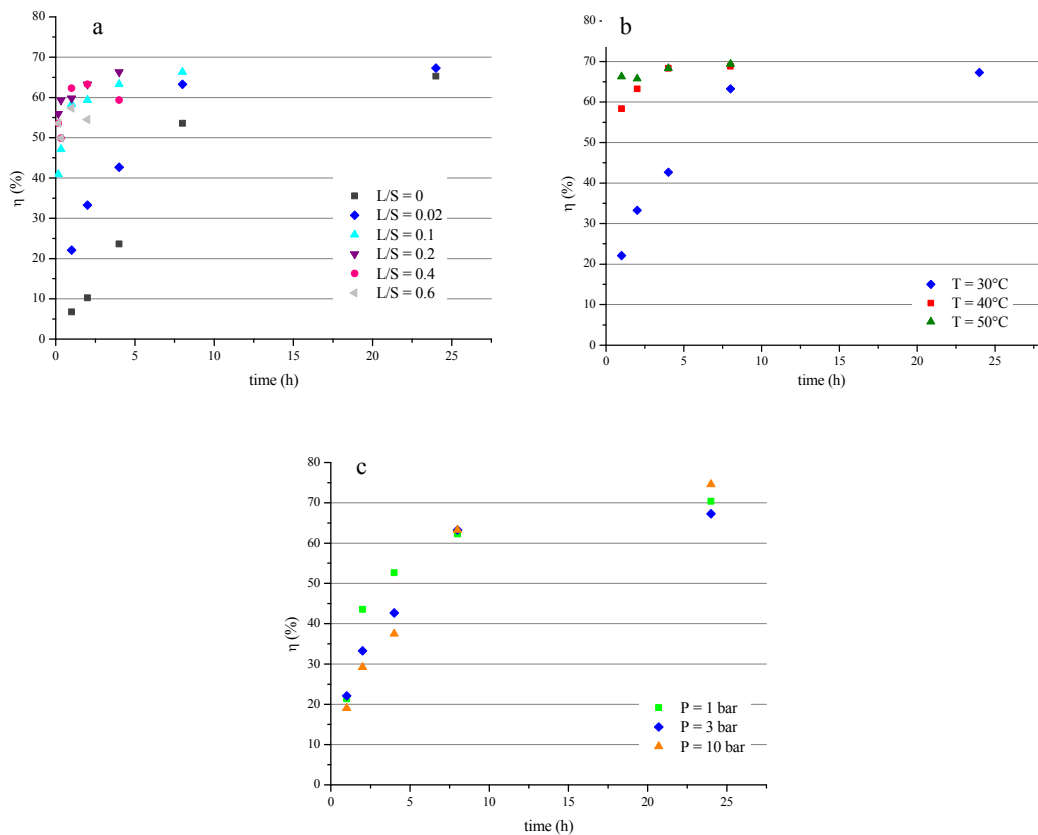


Figure 6: CO₂ uptake kinetics as a function of: (a) L/S ratio (30°C, 3 bar), (b) temperature (3 bar, L/S 0.02), (c) pressure (30°C, L/S 0.02).

6. Conclusions

The investigated process routes showed similar maximum CO₂ uptakes of around 250 g/kg, hence proving that CO₂ uptake depends primarily on the amount of reactive species in the residues and not on the chosen process route. Reaction kinetics instead, depended strongly on the process, proving much faster for the gas-solid route. The other interesting aspect of dry carbonation was that fast kinetics could be achieved also with 10% CO₂ gas flows, indicating that CO₂ capture and storage processes could be carried out in a single step by directly contacting the flue gases with these residues. Dry route carbonation though required temperatures above 400°C for kinetics optimization and hence should be carried out in sections of the incineration plant where flue gas is at an appropriate temperature, or where part of the steam used for energy production could be used to re-heat the gas. Optimal conditions to speed up the kinetics of wet carbonation were: a liquid to solid ratio of 0.2 at 30°C or a temperature of 50°C with un-humidified ashes. The kinetics of this process though, proved to be fast only for 100% CO₂ gas flows, implying that a CO₂ capture unit would be required before the actual carbonation reactor. Accelerated carbonation showed also to be a promising technology for reducing heavy metal leaching prior to landfill disposal. Significant improvement was found for Pb, Zn and Cu leaching, while slight mobilization of Sb was observed.

The APC residues produced from the existing incineration plants would cover only 0.02–0.05% of the total CO₂ European storage capacity required to comply with the Kyoto protocol objectives. Nevertheless, both carbonation routes could be applied to other residues, such as Cement Kiln Dust, Paper mill residues and Stainless Steel Desulphurization slags, characterized by a high content of free calcium oxides and hydroxides, thus increasing the impact of this process option.

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