

# Monitoring of carbon dioxide uptake in accelerated carbonation processes applied to air pollution control residues

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## Abstract:

The application of Accelerated Carbonation Technology (ACT) has potential for the sequestration of carbon in waste and geological materials. ACT also has potential to be supported by carbon credit mechanisms based upon the amount of carbon sequestered from industrial emissions. For this to happen, the routine monitoring of CO<sub>2</sub> sequestered into the solid phase is required for the planning and operation of any accelerated carbonation plant. The present paper reports the preliminary results from an assessment of existing methods for measuring CO<sub>2</sub> imbibed into a solid by an accelerated carbonation processes. Laboratory-scale experiments were carried out to evaluate the accuracy of methodologies for measuring mineralised carbon including: loss on ignition, acid digestion and total carbon analysis. The CO<sub>2</sub> reactivity of several wastes from municipal incineration known as Air Pollution Control residues (APCr) were also included in the study. A detailed characterisation of the materials being carbonated, using X-ray diffraction (XRD), X-ray fluorescence (XRF), thermogravimetric analysis (TGA) and ion chromatography was carried out. The results of this study showed that monitoring CO<sub>2</sub> during accelerated carbonation is made difficult by the complex mineralogy of materials such as APCrs. As such, the presence of calcium bearing species and polymorphs of calcium carbonate formed varied between the materials investigated. The use of an acid digestion technique was not subject to interference from the chemistry or mineralogy of an ash. Among the investigated methods, acid digestion gives the most promising results as it provided robust data on the amount of carbon imbibed during processing.

## Keywords:

Accelerated carbonation technology (ACT), Air pollution control residues (APCr), CO<sub>2</sub> uptake.

## 1. Introduction

Carbonation is a natural phenomenon occurring when gaseous carbon dioxide (CO<sub>2</sub>) reacts with substrate materials, resulting in the production of carbonate salts. Carbonation can be accelerated using management techniques such as accelerated carbonation technology (ACT) working under a gaseous, carbon dioxide (CO<sub>2</sub>)-rich environment [1]. Chemical stability and leaching behaviour of materials such as alkaline combustion residues is improved and carbonated materials can be diverted from landfill into beneficial use as engineering media [1-4].

The accelerated carbonation of alkaline combustion residues is an attractive Carbon Capture and Storage (CCS) option. These residues such as Air Pollution Control residues (APCr), are capable of

combining with significant amounts of CO<sub>2</sub>, and are often generated by processes also producing large amount of CO<sub>2</sub> [1,5-7]. APCr are produced from dry and semi-dry scrubber systems fitted to municipal incinerator flue stacks, which involve the injection of an alkaline powder or slurry to remove acid gases, particulates and condensation/reaction products. Fabric filters in baghouses are used after the scrubber systems to remove fine particulates (baghouse filter dust). APCr also include the solid phase generated by wet scrubber systems (scrubber sludge) [4]. These particulates residues can contain large amounts of reactive calcium species coming from the alkaline sorbents commonly used [8,9].

The amount of CO<sub>2</sub> sequestered during industrial-scale carbonation has potential to be traded as a commodity. Companies, governments, or other entities buy carbon offsets in order to comply with caps on the total amount of carbon dioxide they are allowed to emit. This market exists in order to achieve compliance with obligations of Annex 1 Parties under the Kyoto Protocol, and of liable entities under the European Emissions Trading Scheme (EU-ETS). Carbon Capture and Storage is being introduced in the EU-ETS in 2013, initially for geological storage [10, 11]. It is anticipated that a carbon market will eventually provide a financial incentive for the minimization of CO<sub>2</sub> emissions from a wider range of industrial processes. In addition to geological storage of carbon, processes that encourage the beneficial re-use of captured carbon (e.g. in solid materials) by technologies such as ACT, will be supported.

The monitoring of the amount of carbon sequestered by carbonation processes, also known as CO<sub>2</sub> uptake, is a key aspect of process planning and operation. Different methods to measure the CO<sub>2</sub> uptake by accelerated carbonation are reported in literature. In several works the CO<sub>2</sub> uptake was assessed by calcimetry [12, 13], by thermo-gravimetric analysis [1, 14, 15, 16], or by gravimetric methods [14, 16, 18].

In order to ensure that the emission reductions claimed during the life time of an accelerated carbonation plant are verifiable and permanent, reliable methods for the monitoring of CO<sub>2</sub> uptake are currently needed that are both accurate and economical. This investigation evaluates the suitability of three methods: loss on ignition, acid digestion and total carbon analysis. A validation of these analytical methods has been carried out and presented in to ensure that future measurements in routine analysis will be close enough to the unknown true value for the CO<sub>2</sub> uptake.

## **2. Material and methods**

### **2.1. Accelerated Carbonation of APCr**

An accelerated carbonation treatment was applied to seven APCr samples (APCr 1-7) supplied by different incinerators in the UK. The APCrs were mixed with water (30% to 40% w/w) and treated with 100% CO<sub>2</sub> in static reaction vessels held at atmospheric pressure for 72 hours.

In order to investigate the effect of the accelerated carbonation on mineralogy, the APCrs were analysed by X-ray diffraction (XRD). A Siemens D500 diffractometer with a CuK $\alpha$  radiation source at 40 kV and 30 mA was used for analysis. The APCr samples were prepared as powder tablets and scanned between 5° and 65° 2 $\theta$ , with a step size of 0.02° each lasting 1.2 seconds. Peak identification and interpretation of the X-ray diffractograms was achieved using DIFFRACplus EVA software (Bruker AXS).

Thermo-gravimetric analysis (TGA) and differential thermo analyses (DTA) was performed on both untreated and carbonated APCrs using a Stanton-Redcroft STA-780 Series analyser. The temperature was raised between 20 °C and 1000 °C at a constant heating rate of 10 °C/min.

### **2.2. Synthetic standards**

To test the accuracy of the three methods, ten synthetic standards (STD1-10) representative of the mineralogical composition of APCr were formulated. Analytical grade reagents; calcium carbonate (CaCO<sub>3</sub>), portlandite (Ca(OH)<sub>2</sub>), lime (CaO), anhydrite (CaSO<sub>4</sub>), gypsum (CaSO<sub>4</sub>.2H<sub>2</sub>O), bassanite (CaSO<sub>4</sub>.0.5H<sub>2</sub>O), halite (NaCl), sylvite (KCl) and quartz (SiO<sub>2</sub>) were combined according to Table

1. The produced synthetic standards were stored in a desiccated environment to avoid possible alteration due to atmospheric humidity.

STD1 to STD4 were formulated with a high percentage of reactive calcium phases (portlandite and lime) and a low content of calcium carbonate, simulating the composition of an untreated APCr. Other standards (STD7, STD9 and STD10) were formulated without reactive calcium species and with higher percentage of calcium carbonate, simulating the composition of a carbonated APCr. The influence of the other phases including gypsum and anhydrite were also investigated.

*Table 1. Percentage mineralogical composition of synthetic standards*

Standard ID	CaCO <sub>3</sub> (Calcite)	Ca(OH) <sub>2</sub> (Portlandite)	CaO (Lime)	CaSO <sub>4</sub> (Anhydrite)	CaSO <sub>4</sub> .2H <sub>2</sub> O Gypsum	CaSO <sub>4</sub> .0.5H <sub>2</sub> O Bassanite	NaCl Halite	KCl Sylvite	SiO <sub>2</sub> Quartz
STD1	0.2	-	20.8	6.5	14.1	14.9	22.3	6.1	15.1
STD2	14.1	21.9	10.4	18.8	-	-	20.0	9.9	5.0
STD3	20.7	37.2	-	-	10.0	-	15.9	5.6	10.6
STD4	20.6	24.4	-	6.5	-	6.2	31.8	10.5	-
STD5	24.7	5.0	-	-	-	9.5	14.6	17.1	29.3
STD6	40.0	6.9	9.9	5.4	3.9	17.1	4.9	9.2	2.7
STD7	36.1	-	-	4.5	-	14.8	26.9	17.8	-
STD8	50.9	4.3	5.1	4.0	15.9	19.8	-	-	-
STD9	51.3	-	-	8.2	5.3	10.1	14.9	10.2	-
STD10	55.6	-	-	19.9	-	-	14.6	-	9.9

The synthetic standards were tested using the three methods to assess their carbon dioxide content [CO<sub>2</sub> (%)]. All tests were conducted in triplicate for each material. The carbon dioxide uptake [CO<sub>2,uptake</sub> (%)] can be calculated as difference between carbon dioxide content of treated sample [CO<sub>2,treated</sub> (%)] minus the carbon dioxide content of untreated sample [CO<sub>2,untreated</sub> (%)] according to eq. (1).

$$CO_{2,uptake} (\%) = CO_{2,treated} (\%) - CO_{2,untreated} (\%) \quad (1)$$

A validation process was carried out. Carbon dioxide content [CO<sub>2</sub>(%)] in synthetic standards was measured and compared with the expected values. The accuracy and precision of the methods was evaluated. Equation (2) was used to assess the relative error of mean (RE<sub>m</sub>) [19]:

$$RE_m = \frac{|Z - T|}{T} \quad (2)$$

where Z is the analytical result and T is the calculated true value. Precision was assessed by sample standard error of the mean (SE<sub>m</sub>) (3), where σ is the standard deviation according to (4), n is the number of measurements and x<sub>i</sub> are the observed value for the sample and x<sub>m</sub> is the mean value of these measurements:

$$SE_m = \frac{\sigma}{\sqrt{n}} \quad (3)$$

$$\sigma = \sqrt{\frac{\sum_{i=1}^N (x_i - x_m)^2}{n-1}} \quad (4)$$

## 2.3. Carbonation measuring methods

Three different experimental methods were used to assess the CO<sub>2</sub> content of the synthetic standards. These are summarised in figure 1.

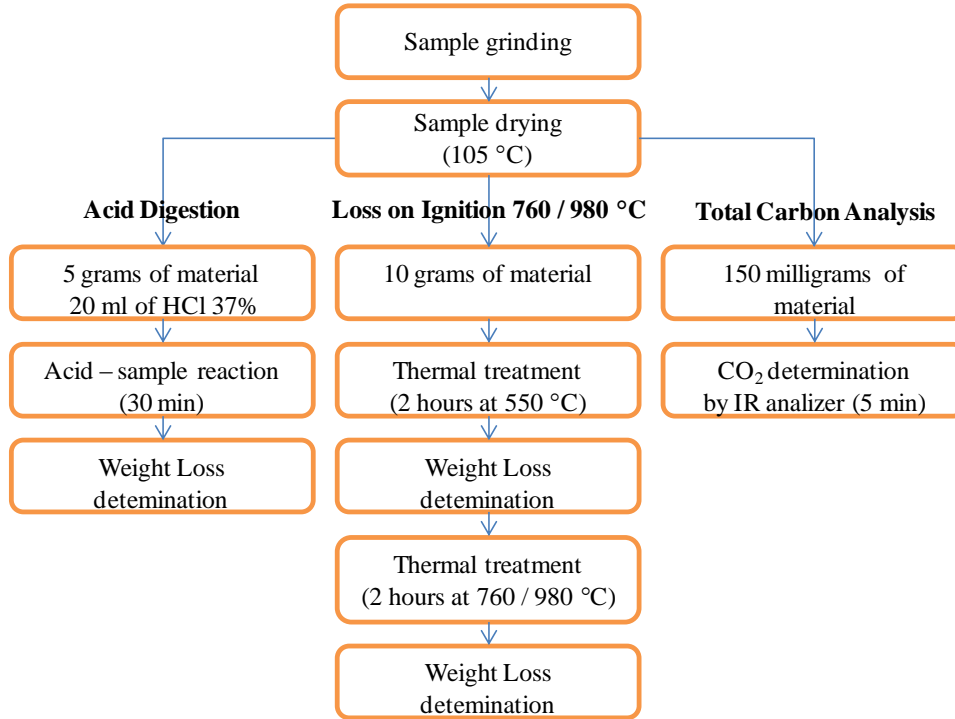


Fig. 1. Experimental methods

### 2.3.1. Loss on ignition (LOI)

About 10 grams of <125µm oven dried material were accurately weighed (2 d.p.) into a ceramic crucible. The crucible was placed in a temperature-controlled furnace at 550 °C for two hours. After cooling in a desiccator the mass was re-determined. LOI was determined by two further ignition cycles at 760 °C and 980 °C, being the two main decomposition ranges identified by thermogravimetric analysis. LOI was determined according to equations 6 and 7:

$$LOI(\%)_{760} = \frac{W_{550} - W_{760}}{W_{Sample}} \times 100 \quad (5)$$

$$LOI(\%)_{980} = \frac{W_{550} - W_{980}}{W_{Sample}} \times 100 \quad (6)$$

Where  $W_{550}$  is the mass of the sample after heating to 550°C,  $W_{760}$  is the mass of the sample after heating to 760°C,  $W_{980}$  is the mass of the sample after heating to 980°C, and  $W_{sample}$  is the mass of the sample after heating to 105°C.

### 2.3.2. Acid digestion (AD)



APCr1	•	•	•	•	•	•
APCr2	•	•	•	•	•	•
APCr3	•	•	•	•	•	•
APCr4	•	•	•	•	•	•
APCr5	•	•	•	•	•	•
APCr6	•	•	•	•	•	•
APCr7	•	•	•	•	•	•

DTA analysis of the untreated APCrs show three clear events occurring between 400 – 440 °C, 465 – 550 °C, and 550 – 760 °C. This is illustrated in the DTA curves for APCr7 (see figure 2). According to Bodenan and Deniard [8] the peak in the 400 – 440 °C interval corresponds to  $\text{Ca(OH)}_2$  decomposition and the peak in the 465– 550 °C interval is related to that of calcium hydroxide-chloride ( $\text{CaOHCl}$ ). The 550–760 °C interval corresponds to  $\text{CaCO}_3$  decomposition.

In the accelerated carbonated APCrs, the  $\text{Ca(OH)}_2$  and  $\text{CaOHCl}$  signatures are absent, and there is an increase in the  $\text{CaCO}_3$  peak. DTA was used to assess the calcium phases present in the remaining six untreated and accelerated carbonated APCrs (see tables 4 and 5).

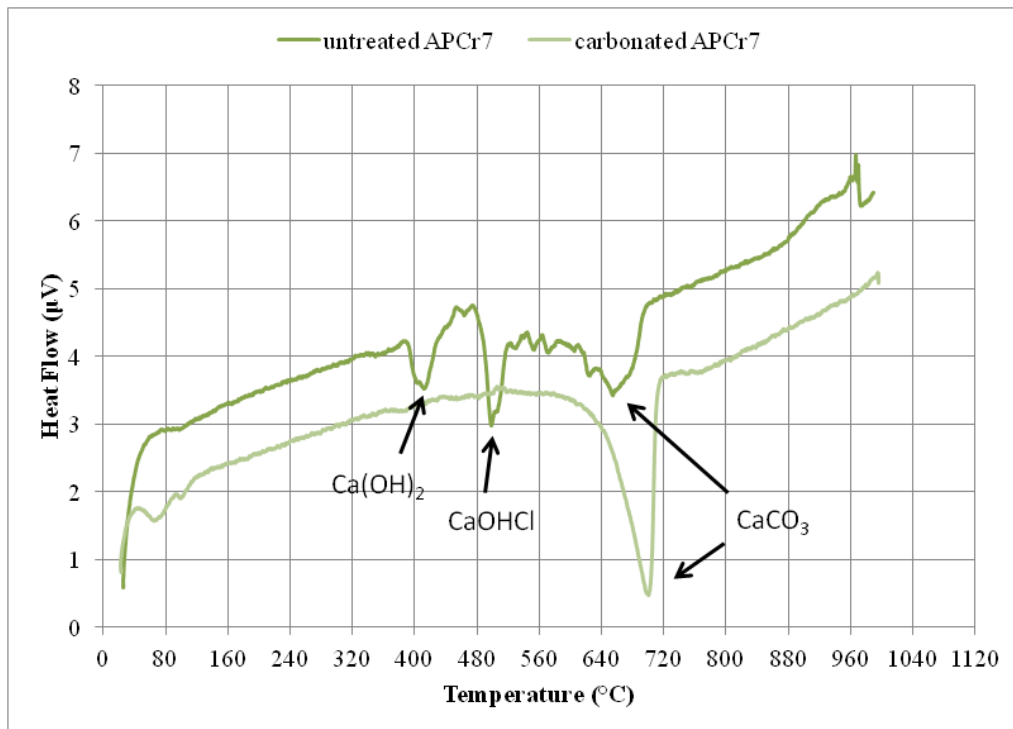


Fig. 2. DTA of untreated and accelerated carbonated APCr7

Table 4. Calcium phases of the untreated APCrs by DTA analysis

	$\text{Ca(OH)}_2$ (Portlandite)	$\text{CaOHCl}$ (calcium hydroxide-chloride)	$\text{CaCO}_3$
APCr1		•	•
APCr2		•	•
APCr3		•	•
APCr4	•		•
APCr5	•	•	
APCr6	•	•	
APCr7	•	•	

Table 5. Calcium phases of the accelerated carbonated APCrS by DTA analysis

	Ca(OH) <sub>2</sub> (Portlandite)	CaClOH (calcium hydroxide-chloride)	CaCO <sub>3</sub>
APCr1			•
APCr2			•
APCr3			•
APCr4			•
APCr5			•
APCr6			•
APCr7			•

TGA analyses of APCrS show slightly differing behaviours between untreated and treated materials up to 500 °C. These differences are due to the portlandite and calcium hydroxide chloride that were found to be present only in untreated APCrS. They are responsible for two small decomposition steps at 400 °C and 500 °C respectively, due to bound water loss. In accelerated carbonated APCrS these steps are not present, although a gradual decomposition process starts at temperatures lower than 300 °C. Most significant is a sudden change in mass in the region 550–760 °C. This mass change is significantly greater in the accelerated carbonated APCrS. A second major event begins at 800 °C (see figure 3).

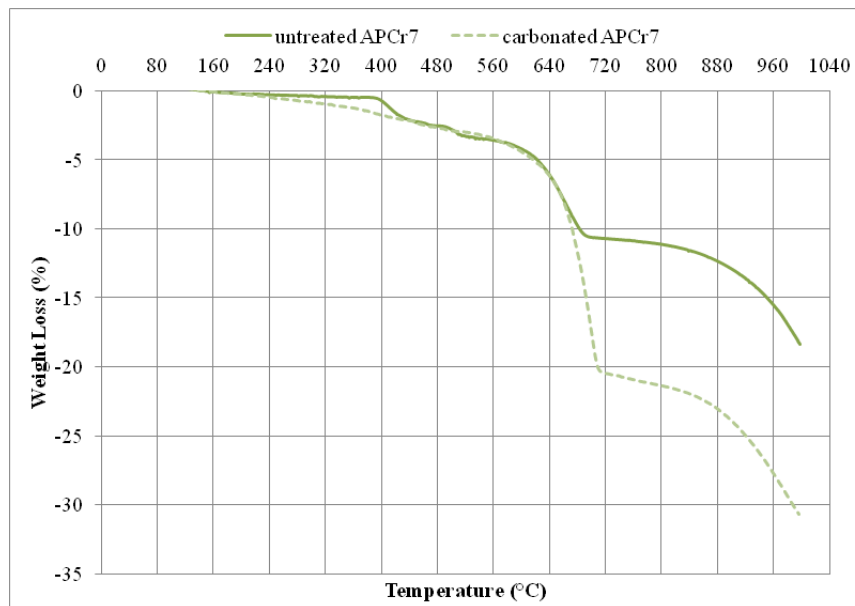


Fig. 3. TGA of untreated and accelerated carbonated APCr7

### 3.2. Carbonation Measuring Methods

The CO<sub>2</sub> content of the synthetic standards was measured by AD, TCA, LOI 550-760 °C and LOI 550-980 °C and compared with known compositions. SE<sub>m</sub> and RE<sub>m</sub> for all the developed methods and for all the tested standards are summarised in Table 4 and Table 5.

Table 4. Relative Error (%) of the mean (RE<sub>m</sub>) of carbon content determination for synthetic standards.

	STD1	STD2	STD3	STD4	STD5	STD6	STD7	STD8	STD9	STD10
AD	2991	32,1	7,6	6,8	5,6	1,2	3,4	5,3	4,7	13,5
TCA	515	37,75	39,70	35,2	15,0	21,8	6,8	19,7	16,5	7,1
LOI 550-760 °C	1420	125,3	107,4	94,6	70,8	68,5	43,6	51,7	25,9	62,4
LOI 550-980 °C	10919	132,3	82,9	83,8	89,2	31,8	360,7	3,1	35,8	6,1

Table 5. Standard Error (%) of the mean ( $SE_m$ ) of carbon content determination for synthetic standards.

	$SE_m$										N
	STD1	STD2	STD3	STD4	STD5	STD6	STD7	STD8	STD9	STD10	
AD	0,4	0,2	0,9	1,2	0,8	0,9	1,1	0,1	0,9	0,2	3
TCA	0,2	0,2	0,5	0,7	0,5	0,5	0,6	0,1	0,5	0,1	3
LOI 550-760 °C	0,2	0,4	0,8	0,7	1,3	2,6	2,7	2,7	0,6	4,2	4
LOI 550-980 °C	0,3	0,8	0,1	1,3	2,4	0,9	0,4	0,2	0,8	0,9	3

### 3.2.1 Loss on ignition (LOI) results

The results of the LOI analyses are shown in figure 4. LOI methods were found to have a poor degree of accuracy (see table 4) and a weak linear relationship between observed and calculated  $CO_2$  content (see figure 4). Overlaps with thermal events associated with other phases, or the presence of  $CO_2$  bound as different polymorphs with the effect of broadening the decomposition temperature range, can be considered as possible mechanisms of affecting the measurement.

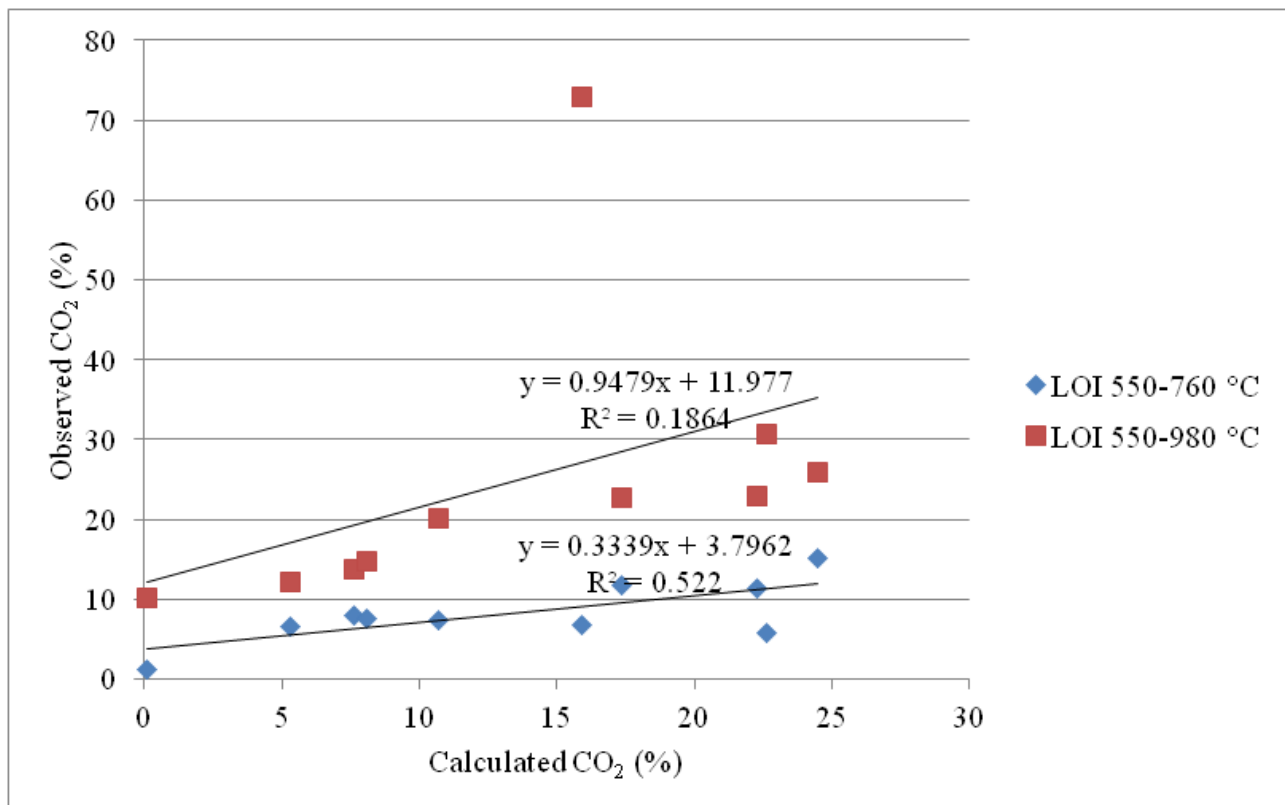


Fig. 4.  $CO_2$ (%) in synthetic standards measured by LOI (550-760) and LOI (550-980).

The significant endothermic event occurring in the range 550 – 760 °C is due to calcium carbonate decomposition.



Treated APCrs have different thermal behaviours compared to untreated APCrs. The first decomposition step starts slower and at a lower temperature (Fig. 6), affecting the accuracy of the tested LOI methods. This decomposition step could be due to decomposition of amorphous or finely divided vaterite. This polymorph of calcium carbonate is the main mineralogical product of the accelerated carbonation process. One study [20] conducted by TGA-TDA coupled with an on-line gas chromatography confirms  $\text{CO}_2$  leaving the carbonated APCr samples at temperatures lower than  $500\text{ }^\circ\text{C}$ .

TGA analysis of STD7 identified further events in the  $760 - 980\text{ }^\circ\text{C}$  range (see figure 3). Analysis of Analar grade NaCl and KCl shows that decomposition of these minerals takes place within this range (see figure 5). Consequently, the presence of NaCl and KCl together with  $\text{CaCO}_3$  can result in the overestimation of  $\text{CO}_2(\%)$  by LOI  $550-980\text{ }^\circ\text{C}$ .  $\text{CaSO}_4$  and his hydrated forms ( $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$  and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), does not affect the LOI measurements.  $\text{CaSO}_4 \cdot \text{H}_2\text{O}$  profile shows weight loss below  $500\text{ }^\circ\text{C}$ , related to the bound-water loss (see figure 5).

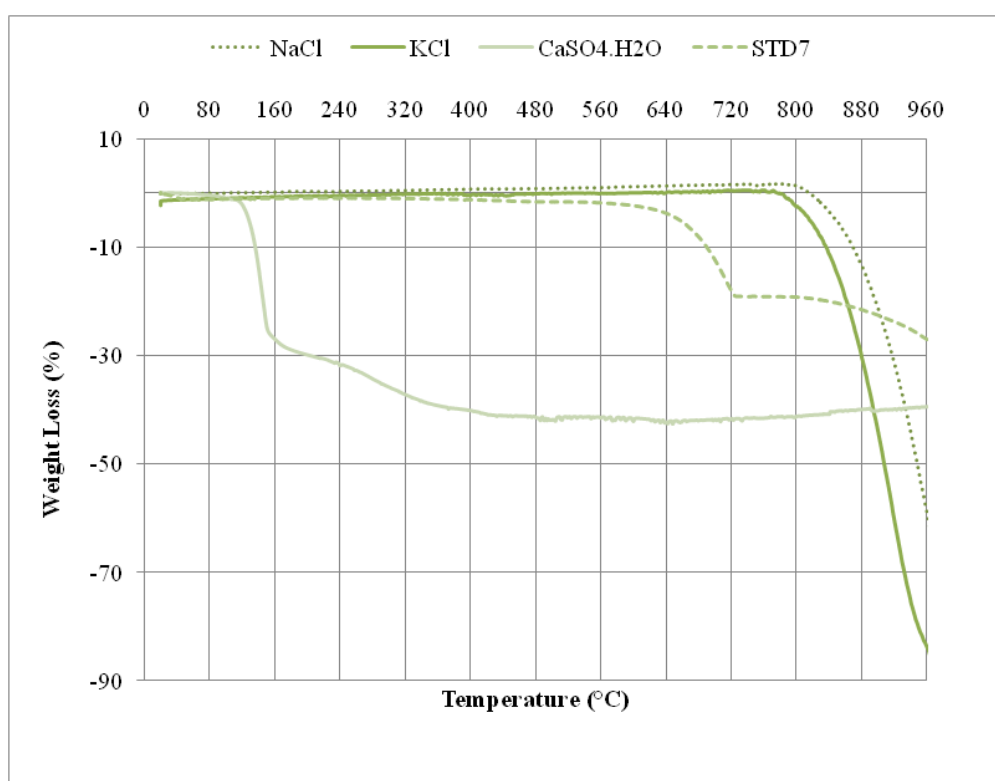
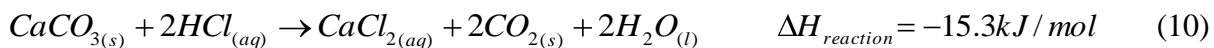


Fig. 5. Thermo-gravimetric profiles of STD7 compared to 100% NaCl and 100% KCl.

### 3.2.2 Acid digestion (AD) results

The results of the AD analyses are shown in figure 6. AD results show a very good linear relationship between observed and calculated  $\text{CO}_2$  content ( $R^2$  value 0.9824), low values of  $\text{SE}_m$  (Table 5), and low values of  $\text{RE}_m$  (Table 4) except for STD1 and STD2 characterized by a low  $\text{CO}_2$  content (less than 5%).

During the digestion process, a ‘rebound’ in the weight of the sample is observed (see figure 7), which may be ascribed to evaporation of the dilute acid, followed by condensation. Hydrochloric acid can produce three different exothermic reactions with the APCr or synthetic standards (8, 9, 10). Particularly when using concentrated acid, a heating of the samples occurs due to the exothermic neutralization reactions.



In order to minimize any loss by evaporation, the acid must be diluted to 30% w/w to minimise heating of the system.

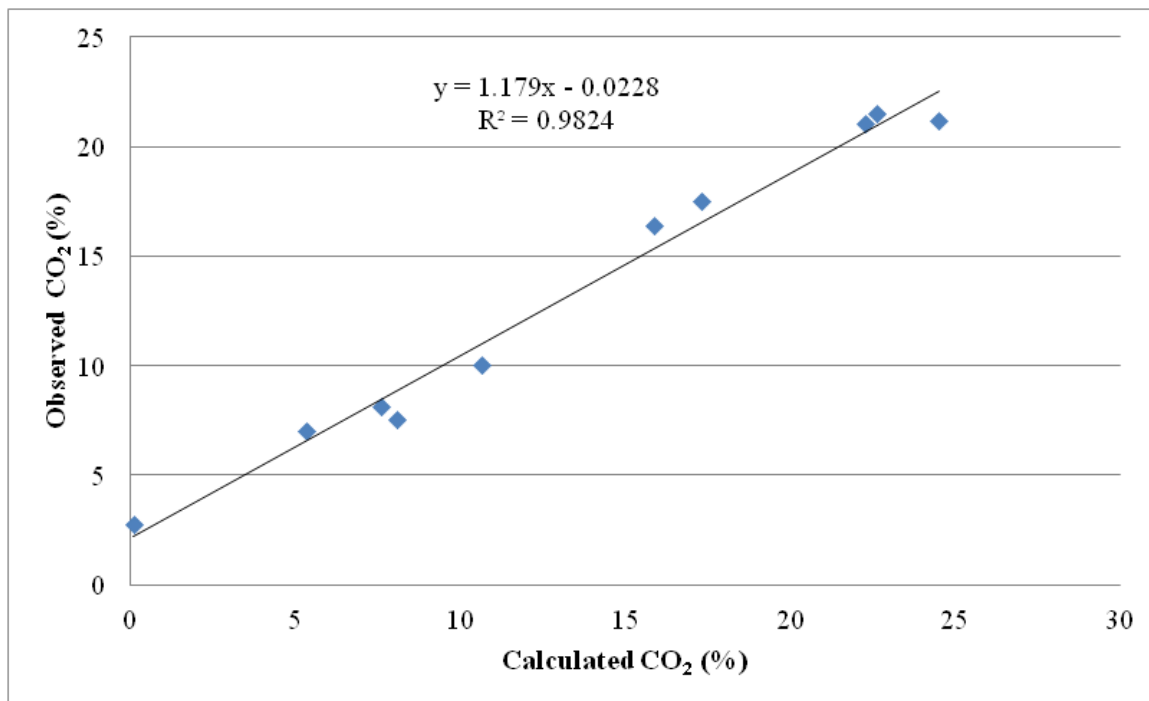


Fig. 6. CO<sub>2</sub>(%) in synthetic standards measured by AD.

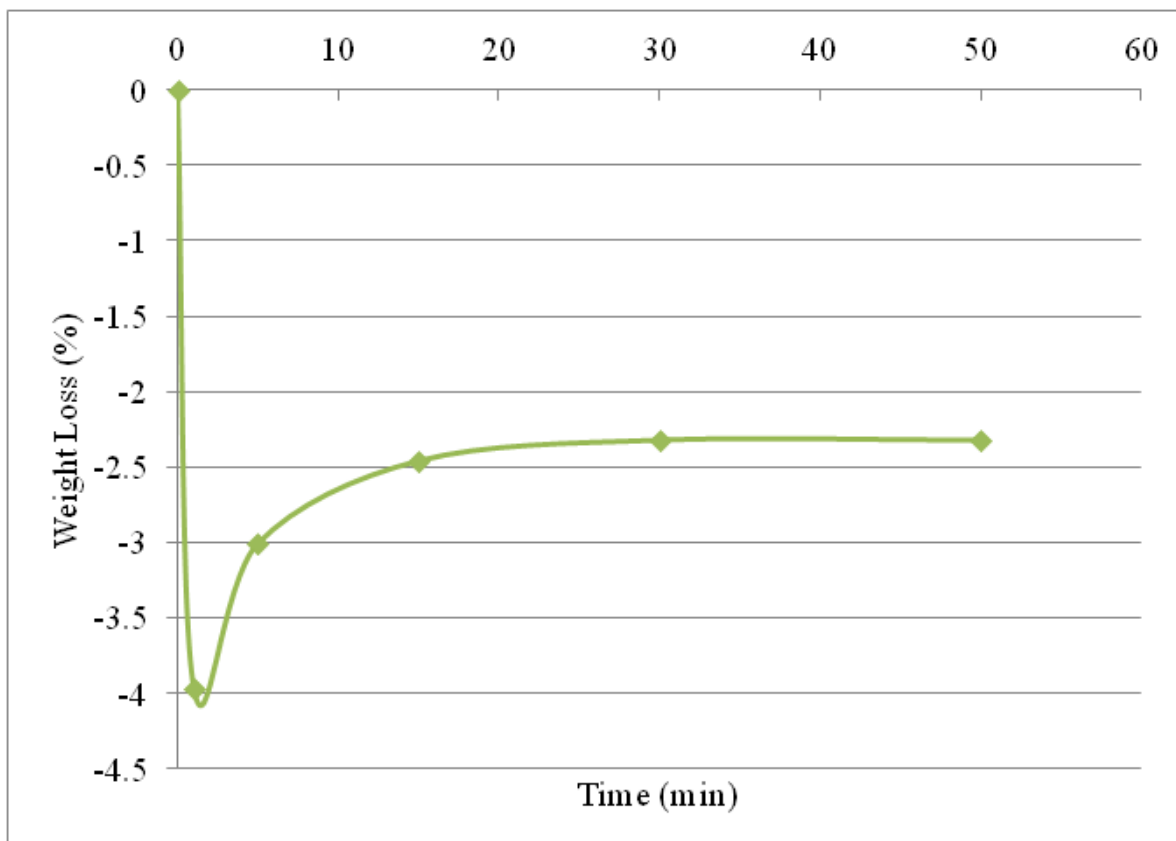


Fig. 7. Rebound effect in AD measurements.

### 3.2.3 Total Carbon Analysis (TCA) results

The results of the TCA analyses are shown in figure 10. The correlation coefficient shows a good relationship between the observed and calculated values. However, the accuracy of the TCA results were found to be lower than those for AD (see table 4).

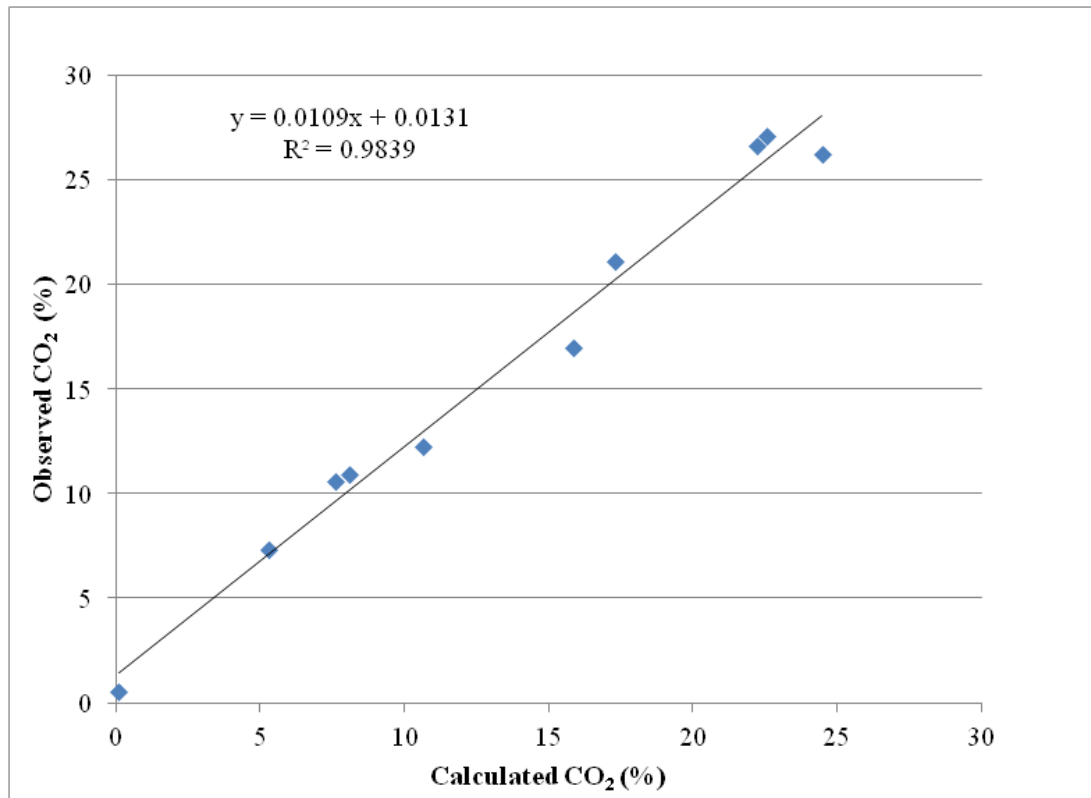


Fig. 8. CO<sub>2</sub> (%) in synthetic standards measured by TCA.

## 4. Conclusions

The accurate measurement of bound carbon dioxide in reactive materials, including wastes, is important for the purposes of assessing Carbon Capture and Storage. Municipal incineration APC residues are mineralogically complex materials. XRD and TGA-DTA have identified the presence of calcium-bearing minerals e.g. lime, portlandite, calcium hydroxide-chloride and calcium carbonate. Since different reaction mechanisms and carbonation pathways can be involved, the accurate measurement of imbibed carbon dioxide becomes challenging.

APCRs subjected to accelerated carbonation show a decrease in the minimum temperature and a broadening of the range at which calcium carbonate decomposes. TGA-DTA analyses have shown that calcium carbonate decomposition starts at temperatures lower than 500°C for treated APCr, at which point overlap with thermal events associated with calcium hydroxide and calcium hydroxide chloride occurs. Consequently, this has a significant effect upon the measured values obtained with thermo-gravimetric methods using fixed temperature ranges.

Among the tested methods, acid digestion has been shown to have good precision and a linear correlation between measured and calculated CO<sub>2</sub> contents. Total carbon analysis measurements show a good linear correlation with calculated results, but overall accuracy is lower while loss on ignition was found to be unreliable due to different thermal behaviour between APC residues before and after carbonation.

Obtained CO<sub>2</sub> uptake values, corrected for the mass balance (input/output) of the carbonation process, can be integrated during the operational life of the plant through a continuous monitoring process. This gives the opportunity of monitoring the total amount of CO<sub>2</sub> sequestered and the related amount of potential carbon credits.

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