Carbon Dioxide Sequestration in Wastes: The SAPICO2 Project

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Abstract
The SAPICO2 project is an INTERREG IVA cross channel collaboration established to develop new technologies utilising accelerated carbonation for the creation of eco-construction materials from solid wastes. Over three phases, the project has identified carbon dioxide reactivity of solid wastes, produced prototype-construction materials (from these wastes), and manufactured bulk samples of carbonated products. The project aims to introduce carbonated building products into continental Europe, by demonstrating the potential of this emerging technology to meet the EU sustainability agenda. By collaborating with the major bodies responsible for environmental matters, it is hoped that new policy and mechanisms can be developed that facilitate the full commercial valorisation of waste using gaseous CO_2.

Introduction

The SAPICO2 (Sustainable Aggregate Product with Imbibed CO_2) project is a collaboration between the University of Greenwich (UK), the University of Picardie Jules Verne (France), and Carbon8 Systems (a spinout company from the University of Greenwich).[1] SAPICO2 is a European Regional Development Fund project, supported by the INTERREG's Manche (Channel) programme.[2] The 2-year project began in August 2013, and will soon be coming to a successful conclusion.

The SAPICO2 project aims to develop new technology for combining gaseous CO_2 with solid waste to manufacture carbonate-cemented eco-construction materials (including aggregates) and introduce this to the French Channel region.

The first phase of the project involved identifying available waste streams in France and in the UK for their suitability with accelerated carbonation treatment. By gathering samples of these wastes, a laboratory assessment of their chemical and physical properties, along with CO_2 reactivity, was made. In the second phase, those materials reactive with were developed into prototype aggregates for preliminary testing. The prototype aggregates meeting the agreed specification were developed further through a series of pilot scale trials to produce bulk quantities for rigorous end-use testing.

In the UK, consultations with the Environment Agency (EA), along with the Building Research Establishment, the Quarry Products Association, British Cement Association and the UK Quality Ash Association have taken place. In France, UPJV have had dialogues with the French Environment and Energy Management Agency (ADEME), through their Waste and Soils Management Office and the Picardie Regional and Departmental Councils, as well as with private waste management/processing organisations.

The project was recently showcased at the Large-Volume CO_2 Utilization International Conference in Lyon, France.[3] The world's first carbon negative 'welcome' bench was also unveiled to the public during the conference, and is now being used by the students of the University of Lyon.

Now in the third and final phase of the project, bulk samples have been manufactured using paper ash and municipal waste incinerator residues from the UK, and using biomass ashes and quarry fines from France. Plans are in place to conduct a proof-of-concept demonstration to manufacture 1-2 tonnes of biomass ash aggregate for end-use trials in conjunction with a construction block manufacturer in France. This will be a key step in obtaining validation of the aggregate as a product, by demonstrating that the end-of-waste criteria has been fulfilled.

The pressure to decrease the amount of waste sent to landfill through recycling has forced the waste classification system to be altered. Recently, the UK Environment Agency signalled changes to the de-classification of certain wastes into by-products, if they meet the following criteria:

i) there is an established use for the material;

ii) no further processing is required for this use; and

iii) the material is used as an integral part of the continuing production process.

Currently, a comparable 'end-of-waste' process does not exist in France. However, it is hoped that this project (and others like it) will motivate ADEME towards a change of approach and that a route to facilitate waste de-classification is possible in France.

Methodology

Materials

The European Waste Catalogue has been used to classify wastes in this project. The two relevant chapters are 10 "Inorganic wastes from thermal processes" and 19 "Wastes from treatment facilities, off-site waste water treatment plants and the water industry".[4]

More than 100 waste samples were obtained across the UK and France, and were grouped into 13 categories (Table 1).

Characterisation and Carbon Reactivity

The procedure for evaluating the carbon reactivity of the wastes is outlined below.

Sample Preparation. The materials were homogenised by riffling the sample down to a usable size (200g for fine powders, 500g for coarser materials). The materials were then dried to constant weight at 105°C, and reduced to less than 2mm using a jaw crusher, and ground to less than 125μm using a disc mill (where necessary).

Sample Characterisation. Each sample was analysed by X-Ray Fluorescence (XRF) (Bruker D8) to determine bulk chemistry, X-Ray Diffraction (XRD) (Bruker S4) to identify mineral phase composition, and total carbon (TC) content by thermal analysis (Hach Lange TOC-550TN).

Carbonation Technique. Complete carbonation of the materials was achieved by repeated cycles of exposure to CO_2, oven drying, crushing, re-wetting, and further exposure to CO_2. The ground waste was mixed with 10% by weight of water, and placed in a CO_2 chamber pressurised at 2 bar. Initial carbonation cycle lengths were one hour. However, as sample reactivity decreased with repeated carbonation (as verified by TC analysis), the cycle lengths were increased progressively up to 7 days. Total carbonation was verified through analysis of the wastes by XRD.

Table 1. Residues examined

No.	Waste Group	Source	No. of Samples
1	Biomass Ash - Bottom Ash (BBA)	Heavy material remaining in the grate after combustion	7
2	Biomass Ash - Fly Ash (BFA)	Lighter material carried from the combustion zone in the flue gasses before removal	6
3	Cement Kiln Dust (CKD)	Cement kiln dusts (CKDs), including bypass dusts (CBDs) consist of alkali-rich particulate matter removed from cement kiln exhaust gasses	5
4	Coal Combustion – Furnace Bottom Ash (FBA)	Grate residue from coal combustion	4
5	Coal Combustion – Pulverised Fuel Ash (PFA)	Flue gas particulate matter from coal combustion	7
6	Metallurgical (MTL)	Residues from metal production/processing	5
7	Municipal Solid Waste Incineration (MSWI) – APC	Fine grained hazardous dust produced by flue gas treatment systems	21
8	Municipal Solid Waste Incineration (MSWI) - Bottom Ash (BA)	Coarse grained residue remaining in the incineration zone after combustion	12
9	Municipal Solid Waste Incineration (MSWI) - Fly Ash (FA)	Airborne particulate matter carried in the combustion gas and collected in the emissions filtration system	10
10	Municipal Solid Waste Incineration (MSWI) - Boiler Ash (BLA)	Other residues arising from municipal incineration	3
11	Paper Sludge Incineration Ash (PSIA)	Incineration residue from paper making wastewater sludge	3
12	Sewage Sludge Ash (SSA)	Ash from incineration of wastewater treatment sludge	5
13	Steel Slags (SS)	Metallic waste from steel manufacture	13

Aggregate Development

Aggregate development was carried out in two phases. Firstly, aggregates were manufactured according to a standard set of formulations. These were subjected to basic testing (strength, leaching). The results were used to identify the aggregates conforming to the designed specification. Secondly, selected compliant aggregates were manufactured in larger quantities, and subjected to more rigorous testing.

Manufacture. Products were manufactured using a combined carbonation-induced forming technique described previously.[5]

Product Testing. The tests applied are summarised in Table 2.

Table 2. Tests applied

Test	Standard
Apparent Density[6]	EN 1097-6
Bulk Density[7]	EN 1097-3
Water Absorption[6]	EN 1097-6
Crushing Resistance[8]	EN 13055-1
Concrete test specimen manufacture[9]	EN 12390-2
Concrete Flexural Strength[10]	EN 12390-5
Concrete Compressive Strength[11]	EN 12390-3
Concrete Thermal Properties[12]	ASTM C177-13

Results

Waste Characterisation

The results yielded a valuable insight into the variability of the chemistry of wastes. The bulk chemistries of the wastes are shown in Table 3. If attention is focused upon the primary constituent oxides (aluminium, calcium, potassium, sulphur, silicon), the variability within each group can be appreciated. This reflects variations in the raw materials used, operating conditions, plant age, and waste treatment methods.

Figure 1 illustrates the CO_2 capacity of the wastes. The total CO_2 values include the carbon present in the as-received material and that chemically bound as a result of carbonation. The net CO_2 values include only that chemically bound when the wastes are subjected to carbonation. The disparity between the total and net values should be noted. Thus, a waste that might be initially expected to be suitable for carbonation, based upon a preliminary assessment of its chemical properties, may in fact be non-reactive. As reflected in the oxide compositions, the CO_2 capacities both within and between the waste groups were also highly variable (see Figure 2).

The relationship between oxide composition and CO_2 capacity is being evaluated statistically to improve the prediction of CO_2 reactivity of the wastes. Early results indicate that an equation model developed from the dataset is more accurate previous models.[13]

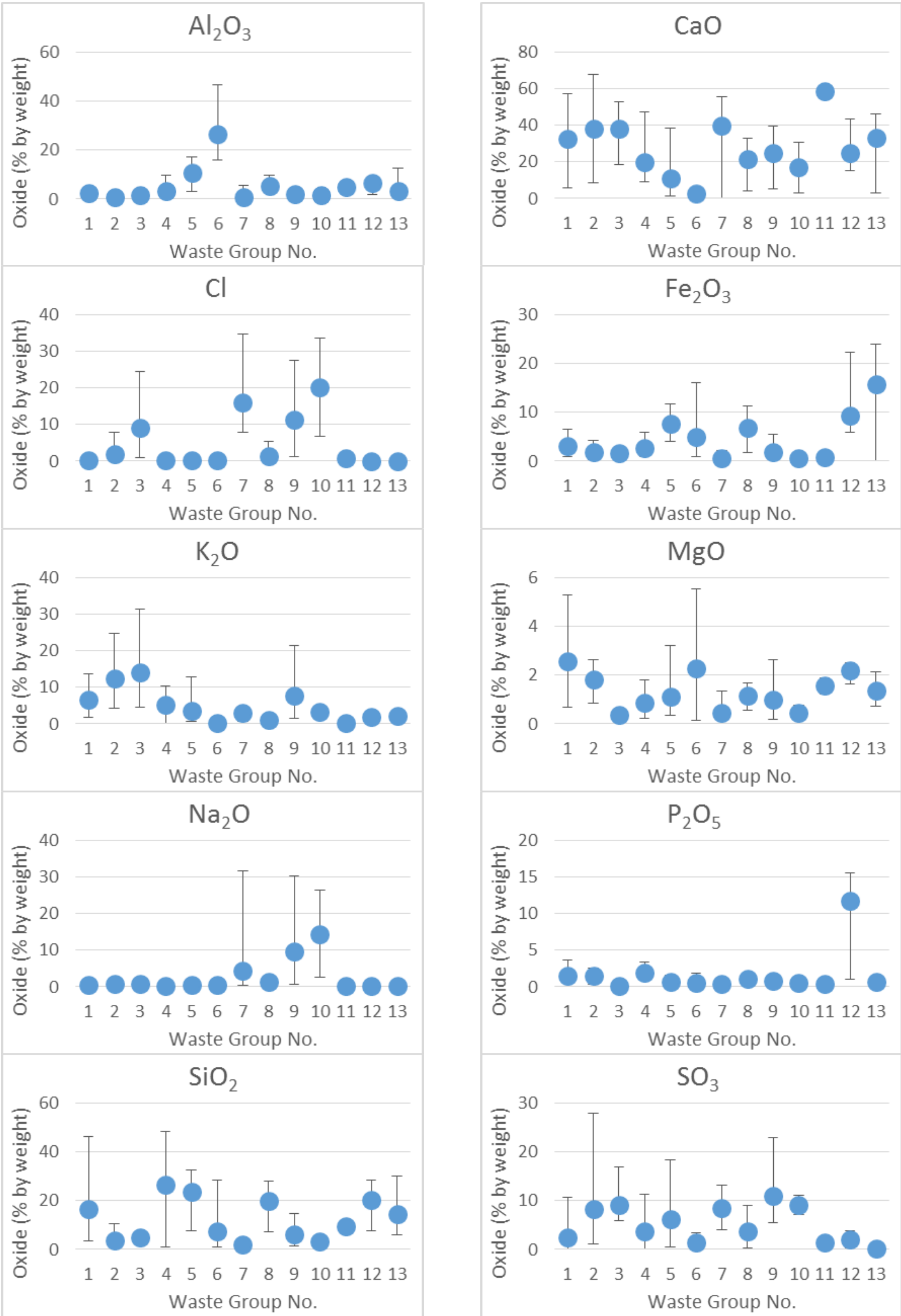

Figure 1: Bulk chemistry of waste groups (error bars denote minimum and maximum values in the group)

The next stage of analysis will employ more elaborate statistical analysis to explore further issues such as the fit for individual waste groups and possible interferences between variables (i.e. oxides).

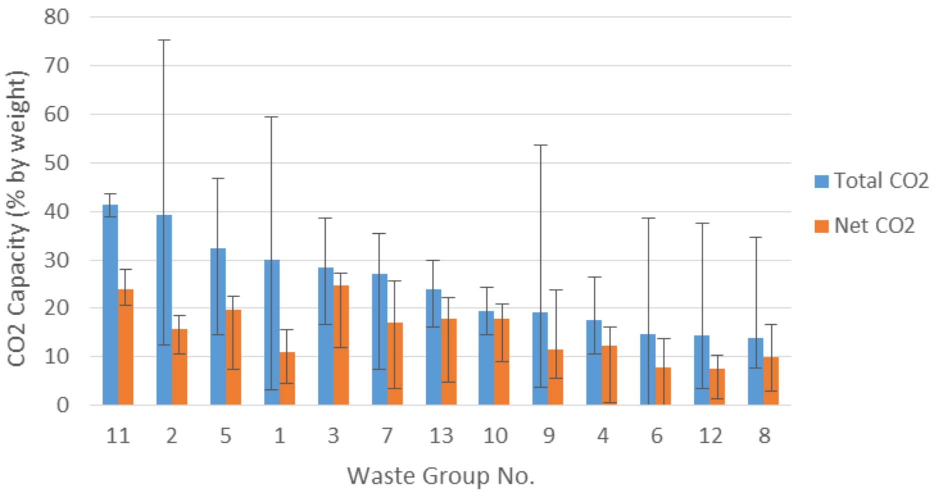

Figure 2: Carbon dioxide capacity of wastes (whiskers illustrate minimum and maximum values)

Aggregate Product Development

Aggregates produced from the wastes were tested against the product specifications developed by Carbon8. Aggregates derived from municipal solid waste incineration air pollution control residues (MSWI-APCr), paper sludge incineration ash (PSIA), and biomass bottom/fly ash (BBA/BFA), were selected for rigorous testing. Alongside the three prototypes, a control primary aggregate (flint gravel) and secondary aggregate (expanded clay) were also tested (see Table 3).

Table 3. Aggregate/concrete testing results

	Test	MSWI-APCr	PSIA	BBA/BFA	1° Aggregate	2° Aggregate
Aggregate	Apparent Density	2.6	2.5	2.5	2.7	2.0
	Bulk Density (kg/m^3)	1113	855	1050	1489	700
	Water Absorption (%)	16.1	24.1	17.8	<0.5	19.9
	Crushing Resistance (N/mm^2)	8.3	5.2	6.4	20.3	6.6
	Thermal Conductivity (W/m.K)	0.2	0.15	●	0.15	0.24
Concrete	Bulk Density (kg/m^3)	1956	1702	1898	2121	1558
	Flexural Strength (N/mm^2)	2.7	2.9	2.8	2.9	3.7
	Compressive Strength (N/mm^2)	12.5	14.3	12.2	28.4	11.1
	Thermal Conductivity (W/m.K)	0.7	0.6	●	0.9	0.6
	Specific Heat (J/kg.K)	755	828	●	815	739
	Thermal Effusivity (J/m^2.K.s1/^{2})	1031	943	●	1285	792

● *test results pending*

The prototypes exhibited bulk densities akin to the secondary aggregate, and were within BS EN 13055-1 requirements for lightweight aggregate. Crushing resistance was comparable to the secondary aggregate, but considerably less than that of the primary aggregate control. The density of the concretes produced from the prototypes fell between that of the secondary aggregate (1558 kg/m^3) and that of the primary aggregate (2121 kg/m^3). Compressive strength of the prototype aggregate concretes was commensurate to the secondary aggregate, but did not achieve the same flexural strength. The thermal properties of the concrete made from the prototypes was comparable to the secondary aggregate, thus was superior comparable to a standard concrete. These results indicate that the prototype aggregates have potential applications in the lightweight/medium-weight aggregate market.

A full end-use evaluation has been made for the MSWI-APCr aggregate, by validating its use in concrete construction block manufacture (see Table 4). The results show comparable properties between the standard product and MSWI-APCr aggregate substituted one in terms of strength (compressive and transverse failure), density, and geometry (flatness and parallelism). The MSWI-APCr aggregate has been granted end-of-waste status in the UK, and is now in full commercial production (currently 60,000 tonnes per year).

Table 4. Physical properties of MSWI-APCr aggregate and control concrete blocks

Property	Standard Aggregate	With APCr Aggregate*
Density (kg/m^3)	1660	1730
Compressive Strength (MPa)	11.8	11.2
Transverse Failure Load (kN)	7.75	7.78
Flatness (mm)	0.0	0.0
Parallelism (mm)	1.2	1.0
Drying Shrinkage (mm)	0.38	0.34
Moisture Expansion (mm)	0.13	0.11

**partial substitution*

Following a proof-of-concept trial planned to manufacture a bulk sample the BBA/BFA aggregate, an identical end-use evaluation for its use in concrete construction blocks will be undertaken. It is expected that the results of this work will be a major step forward in achieving end-of-waste status for this material.

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