Accelerated Carbonation of Hazardous Wastes

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ABSTRACT

Accelerated carbonation involves exposing a material to a concentrated atmosphere of carbon dioxide, and can be used to treat hazardous wastes and soils and create new construction materials. The present work examines the use of accelerated carbonation to reduce the hazardous properties of wastes as a means of reducing the costs of disposal to landfill, and then develops the process to manufacture aggregate from the waste removing it from landfill disposal completely .

A range of thermal wastes, including those from cement, metallurgical and paper processes, were found to be reactive with carbon dioxide. Many of these wastes are hazardous on account of their alkaline pH, which carbonation partially neutralizes, effectively allowing reclassification of the materials as stable non-reactive hazardous wastes under the Landfill Regulations. Cement and paper wastes were highly reactive with carbon dioxide, and were considered for use as cement substitutes to reconstitute non-reactive wastes into aggregate.

Previous work had suggested that carbonation and pelletising were not compatible due to differing optimum conditions. This issue was investigated by considering the effects of the mix formulations and machinery parameters. The pelletising and carbonation processes require widely different moisture contents. The disparity is due to the need for total saturation of the material to form bonds between grains during pelletising, and an open pore network for carbon dioxide to penetrate. To achieve the two simultaneously, several methods were investigated. Chemical catalysts including sodium hypochlorite and sodium sulfite increased carbonation in a saturated material. However, curing the formed aggregates in carbon dioxide was found to be the most economic solution.

A pilot scale process was developed based upon the laboratory results. A bespoke rotary carbonation reactor was developed to produce aggregate in bulk for commercial testing.

Aggregate which was subjected to accelerated carbonation, has enhanced strength and durability compared to aggregate exposed to natural carbonation. The aggregate was successfully used to produce lightweight concrete with comparable strength to concrete made from commercial lightweight aggregate. Aggregate was also supplied for a research project to investigate the use of recycled materials as a horticultural growing medium.

DECLARATION

I certify that this work has not been accepted in substance for any degree, and is not concurrently being submitted for any degree other than that of Ph.D Chemical Science, being studied at the University of Greenwich. I also declare that this work is the result of my own investigations, except where otherwise identified by references, and that I have not plagiarised another's work.

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ABBREVIATIONS

ACT	Accelerated Carbonation Technology
ALSF	Aggregate Levy Sustainability Fund
ASTM	American Society for Testing and Materials
BAA	British Aggregate Association
BGS	British Geological Survey
BS	British Standard
BSE	Backscattered Secondary Electrons
CBD	Cement Bypass Dust
CCS	Carbon Capture and Storage
CEM1	Ordinary Portland Cement
CKD	Cement Kiln Dust
CRM	Certified Reference Material
C-S-H	Calcium Silicate Hydrate
DEFRA	Department of the Environment, Food and Rural Affairs
DTI	Department of Trade and Industry
EA	Environment Agency
EDAX	Electron Dispersive X-Ray Analysis
EU	European Union
EU-ETS	European Union Emissions Trading Scheme
EWC	European Waste Catalogue
HMRC	Her Majesty’s Revenue and Customs
ICP-OES	Inductively Couple Plasma Optical Emission Spectroscopy
IPCC	International Panel on Climate Change
KCC	Kent County Council
LOI	Loss On Ignition
LWA	Lightweight Aggregate
Mpa	Megapascals
MSWI-BA	Municipal Solid Waste Incineration Bottom Ash
MSWI-FA	Municipal Solid Waste Incineration Fly Ash
PFA	Pulverised Fuel Ash
RPM	Revolutions per Minute
SEM	Scanning Electron Microscopy
S/S	Stabilisation/Solidification
SSA	Sewage Sludge Ash
TGA	Thermogravimetric Analysis
WAC	Waste Acceptance Criteria
WM2	Waste Management 2 (EA Guidance)
WRAP	Waste Resources Action Programme
W/S	Water/Solid Ratio
XRF	X-Ray Fluorescence
XRD	X-Ray Diffraction

Chapter 1: Introduction

1.1 Background

Industrial wastes can be treated with carbon dioxide gas in a process known as Accelerated Carbonation. The process has potential for the remediation of waste for disposal or their re-use as new construction materials.

The UK generates 335 million tonnes of waste each year (D.E.F.R.A, 2007c). Despite increased recycling, large amounts of waste cannot be effectively reused. Disposal to landfill continues to be the easiest and most economical waste management solution but is considered unsustainable and European legislation is a major driver for the development of other treatment options. In the UK, the landfill tax escalator is an additional driver for diverting waste from landfill.

Concerns about global climate change as a result of increasing levels of carbon dioxide in the atmosphere, has prompted attempts to mitigate emissions from particularly coal fired power stations but also other major point sources of carbon dioxide such as cement manufacture. Reducing emissions alone is unlikely to fulfill long-term targets amid a growing population and increasing demand for energy (I.P.C.C, 2005). The development of long-term storage of carbon is a necessary step. To date Carbon Capture and Storage (CCS) schemes remain highly experimental, and concerns have been raised over long term environmental impacts. Finding a safe, permanent storage solution for carbon dioxide remains a major challenge. Accelerated Carbonation Technology (ACT) is being investigated as a carbon capture solution since carbon dioxide is permanently bound into solid carbonate minerals.

Accelerated carbonation is an enhanced form of natural carbonation, which has previously been employed on a small scale as a rapid curing method for cement-bound products (Soroushian *et al.*, 2004, Sorochkin *et al.*, 1975). In the last ten years, ACT has been developed for the treatment of contaminated land and industrial wastes. The process promotes stability and strength development in materials with otherwise comparably poor cementitious properties, and can bind waste together into preformed shapes for use as construction materials (Fernández Bertos *et al.*, 2004). Waste can be formed into aggregate by agglomeration (also known as pelletising) in a rotating vessel. If the two processes are combined, it is feasible to produce hardened aggregate (Padfield *et al.*, 2004).

This project considers the use of the carbonation process to treat industrial wastes and to manufacture aggregates from them. Scaling up the process to produce material at a semi-commercial scale is also examined.

The project was set up as an EPSRC CASE studentship (G03303113) through the Knowledge Transfer Network (KTN). Knowledge Transfer Networks are managed by the UK government's Technology Strategy Board and are designed to improve and speed up knowledge exchange between businesses and academic institutions. In this case, the studentship was awarded to enable the University of Greenwich to develop ACT to provide solutions to the waste management problems of Gallagher (Aggregates) Ltd.

1.2 Aims and Objectives

The overall aim of this project was to develop accelerated carbonation as a treatment for industrial wastes, and produce new construction materials by improving their physical and chemical properties.

The primary objectives were:

- Examine the use of accelerated carbonation for the treatment of a range of industrial wastes to facilitate easier waste management and economic disposal.
- Examine the re-use potential of the wastes as aggregate using a pelletising process
- Investigate the pelletising method, and optimize the process.

- Scale up the process, to demonstrate the application of the technology on a commercial scale, and produce aggregate material for testing
- Test the aggregate to the regulatory standards, and consider potential end-uses

1.3 Report Structure of Thesis

This thesis is divided into 9 chapters describing the methods, materials and experiments undertaken during the work on this project.

The relevant literature and background to the project is examined in Chapter 2. Accelerated carbonation is explored in detail, including the variables affecting the chemical reaction, the chemical and physical effects of the process, and potential applications. Construction aggregates, their uses and market trends are examined. The literature surrounding the waste materials used and the legislation relevant to the management and disposal of waste is summarised.

Chapter 3 describes the analytical methods used as well as descriptions of the wastes materials utilised in the study.

The experimental work is divided into five chapters. In each, the relevant methods are detailed, and the results are presented and discussed, with general conclusions.

Chapter 4 describes the wastes selected and how they were tested for potential treatment with accelerated carbonation. The chemical and physical characterisation of the wastes is presented together with their reactivity with carbon dioxide. Those reacting with carbon dioxide are examined for chemical and mineralogical alteration, and changes in leaching behaviour. The results are compared against European legislation to evaluate the effectiveness of accelerated carbonation to reduce toxicity and facilitate cost-effective disposal and potential re-use.

Chapter 5 presents the investigation of the potential for reconstituting the fine grained wastes, using a pelletising technique, for use as aggregate. The manufacturing process is developed by optimising mix formulation and machinery variables. Wastes which are naturally reactive with carbon dioxide are investigated as binders for solidifying other non-reactive wastes.

Chapter 6 describes the methods examined to improve the efficiency of the carbonation reaction, to facilitate its use in an industrial process. These include alternative methods of agglomeration and carbonation, and the introduction of admixtures to alter the chemical and physical properties of the carbonating system.

Chapter 7 describes how the process was scaled up from the laboratory to a pilot scale process. A bespoke pilot plant for simultaneous carbonation and agglomeration is developed. Comparative experiments are conducted in the laboratory and on the pilot plant. A pilot scale process for manufacturing lightweight aggregate is devised.

The aggregate products from the pilot scale process are covered in Chapter 8. The aggregates are tested to the relevant British Standards alongside commercial lightweight aggregates. Product samples are also provided for pilot scale consumer trials, and the early results are evaluated.

Chapter 9 provides an overall discussion of the results and the final conclusions are drawn. Questions remaining unanswered and suggestions for further work are also outlined.

Included in the appendices are two papers published in the Journal of Waste Management: Accelerated carbonation treatment of industrial wastes, and Production of lightweight aggregates from industrial waste and carbon dioxide.

Chapter 2 : Background

2.1 Introduction

This chapter examines the relevant literature surrounding the legislation, technologies and technical specifications relating to the production of aggregate from waste. The accelerated carbonation process and its applications are explored.

Agglomeration is the technique used to produce pelleted products from fine grained wastes. The agglomeration process, including methods, applications and variables are reviewed. These pelleted products are to be used as aggregates. The different types of aggregates and their uses, the current market status and legislation are discussed.

The production of waste in the UK is examined. Production of aggregate from waste constitutes a treatment process, therefore the legislation on waste assessment and management is summarised.

2.2 Accelerated Carbonation

2.2.1 Introduction

Accelerated carbonation is a reaction occurring between carbon dioxide and alkali earth hydroxides, oxides and silicates. The process has been successfully used to treat waste materials to reduce toxicity, and improve mechanical properties to facilitate re-use (Fernandez Bertos *et al.*, 2004b, Padfield *et al.*, 2004).

2.2.2 Accelerated Carbonation

Natural carbonation is a slow process, taking years or decades, due to the low concentration of carbon dioxide in the atmosphere (Van Ginneken *et al.*, 2004). The carbonation process can be accelerated by exposing the reactive material (cement, lime or reactive waste) to an elevated concentration of carbon dioxide (Johnson *et al.*, 2003, Liu *et al.*, 2001, Maries *et al.*, 2001). The accelerated carbonation process can completed within several hours or even minutes (Roy *et al.*, 1999).

2.2.3 Applications

For several decades ACT has been considered as a method for rapidly hardening cement and concrete products. Applications include preformed blocks and slabs made from primary and recycled materials (Soroushian *et al.*, 2004, Sorochkin *et al.*, 1975, Bierlich, 1969).

More recently, ACT has been investigated for the treatment of contaminated land and wastes (Lange *et al.*, 1996a). The treatment of many industrial wastes allows improvement of their physical and chemical properties, offering the potential to produce a valuable product from waste normally destined for landfill (Fernández Bertos *et al.*, 2004). Many waste materials are reactive with carbon dioxide, particularly those derived from industrial thermal processes, e.g. incineration ashes (Baciocchi *et al.*, 2009; Arickx *et al.*, 2006), steel slags (Diener *et al.*, 2010; Chen *et al.*, 2007), and cement wastes (Huntzinger *et al.*, 2009; Johnson, 2000).

Contaminated soil can be treated by a stabilisation/solidification (S/S) process which involves mixing a cementitious binder (typically cement or lime) with the soil. This induces chemical fixation of the contaminants (stabilisation) and physical containment in the hardened mass (solidification) (B.C.A, 2004a, Bone *et al.*, 2004). ACT has been coupled with S/S to rapidly harden the cementitious binder and promote contaminant retention through material densification and chemical alteration. ACT also helps to overcome the deleterious effect of organics and heavy metals upon cement hydration (Soroushian and Hsu, 1999).

Several pilot scale trials using the accelerated carbonation process have been undertaken. In 2000, a small trial using ACT was conducted at a former pyrotechnics manufacturing site, heavily contaminated with heavy metals (Cutter *et al.*, 2003). ACT was also used as a trial treatment at a former coking works near Chesterfield (C.L:A.I.R.E, 2006) and at a heavily polluted site at Widnes, Cheshire (Barr *et al.*, 2003).

The production of aggregate from waste using an accelerated carbonation process was initially investigated by Padfield *et al.* (2004). The study focused upon finding a solution to by-products from quarrying known as quarry fines. These were mixed with a selection of different wastes arising from industrial thermal processes, pelletised to produce granules, which were then hardened by exposure to carbon dioxide. In conclusion, the work established that aggregates could be produced from carbonated wastes. However, the rate of carbonation was very low, and prolonged curing in a pressurised carbon dioxide atmosphere was necessary.

2.2.4 Reaction and Mechanisms

Carbonation involves a series of reaction stages (Arandigoyen *et al.* 2006, Domingo *et al.*, 2006, Li *et al.*, 2003, and Jiang *et al.*, 2000):

1) Diffusion of carbon dioxide and permeation into the solid.
2) Solvation of carbon dioxide in the aqueous film in the pores and hydration to form carbonic acid (H_2CO_3), which is a slow and usually rate-determining step.
3) The acid subsequently ionizes into $2H^+$ and CO_3^{2-} ions.
4) Leaching out Ca^{2+} ions and diffusion in the pore water.
5) Reaction of the dissolved Ca^{2+} and CO_2.
6) Precipitation of $CaCO_3$ which acts as a binder between particles.
7) H_2O produced.
8) A secondary carbonation phase during which hydrated cement products e.g. calcium silicate hydrate (C-S-H) is converted to calcium carbonate and silicate hydrate (S-H).

These steps can be summarised as three primary reactions equations 2.1-2.3 (Jiang *et al.*, 2000).

$$CO_{2\,(g)} + H_2O_{\,(l)} \leftrightarrow H_2CO_3 \tag{2.1}$$

$$CaO_{\,(s)} + H_2O_{\,(l)} \rightarrow Ca(OH)_{2\,(s)} \tag{2.2}$$

$$Ca(OH)_{2\,(s)} + H_2CO_{3\,(l)} \rightarrow CaCO_{3\,(s)} + 2H_2O_{\,(l)} \qquad (2.3)$$

The hydration of carbon dioxide to form carbonic acid is represented in equation 2.1. In materials where free lime is present, calcium oxide hydrates in water to form calcium hydroxide (equation 2.2). The calcium hydroxide and carbonic acid combine to form calcium carbonate (equation 2.3). In hydrated materials, such as cement, in which the primary hydration product is calcium silicate hydrate (C-S-H), the paste is decalcified to form calcium carbonate, leaving a residual silica gel. The hydration of carbon dioxide and the formation of calcium carbonate is exothermic (Bukowski and Berger, 1979).

2.2.5 Reaction Variables

The effectiveness of the carbonation reaction is controlled by the reactivity of the material and by the ability of carbon dioxide to diffuse into the solid material (see figure 2.1).

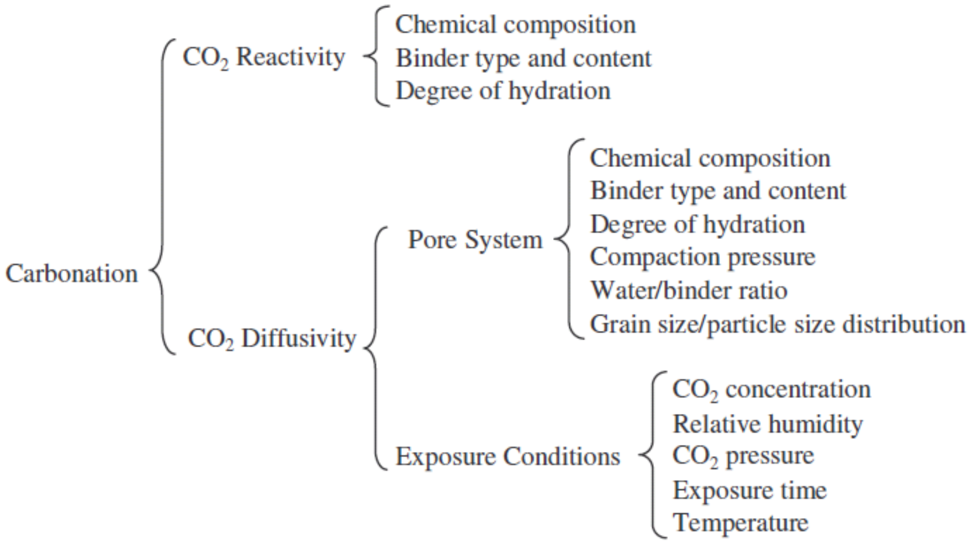


Figure 2.1: Variables affecting accelerated carbonation (modified from Fernandez Bertos *et al.*, 2004a

The former is affected by the chemical composition of the materials, the amount of any reactive binder added, and the degree of natural weathering or hydration. The rate of ingress of carbon dioxide into a material is controlled by the structure of the pore system, which is in turn affected by the particle size and grading of the material. Carbon dioxide penetration is also affected by the exposure conditions including gas concentration and pressure.

2.2.5.1 Water/solid ratio and humidity

The carbonation reaction is dependent upon moisture for carbon dioxide hydration, but in excess it has a limiting effect upon the rate of reaction (Rendek *et al.*, 2006a, Lange *et al.*, 1996a). The optimum water solid ratio is dependent upon the properties of the material and the binder used, which include grain size, particle size distribution and surface area (Johnson *et al.*, 2003, Barnard *et al.*, 2005).

Carbonation slows down substantially in a saturated material due to reduced diffusion, and only proceeds when the pores have dried sufficiently to allow CO_2 ingress (Cultrone *et al.*, 2005, Russell *et al.*, 2001). When pores are saturated, only the exterior rinds of materials are carbonated (Venhuis and Reardon, 2003). Calcium carbonate surfaces are less hydrophilic than the calcium hydroxide they replace, expelling water from the reacted zone (Beruto *et al.*, 2005). This may result in oversaturation of the adjacent pore network and decreased diffusion of carbon dioxide into the unreacted zones. In order to promote carbonation, continual removal of the reaction water as it is produced is necessary to maintain an open pore network (Venhuis and Reardon, 2001). Conversely, as the carbonation reaction is exothermic, the pore water may evaporate and cause premature drying of the material before the carbonation reaction reaches completion (Young *et al.*, 1974).

Relative humidity is recognized as an important controlling factor (Roy *et al.*, 1999). A humidity range from 50-65% is optimum for effective carbonation (Russell *et al.*, 2001, Shaffique *et al.*, 1998), whilst below 30% and above 80%, little or no reaction takes place (Criado *et al.*, 2005, Dheilly *et al.*, 2002). If the reaction occurs in a sealed vessel, the atmosphere may become saturated, leading to pore blocking and reduced reaction efficiency (Bukowski and Berger, 1979)

2.2.5.2 Carbon Dioxide Concentration

The rate of carbonation is limited by diffusion of carbon dioxide gas into the liquid phase, which is in turn is dependent on the concentration gradient of free carbon dioxide (Steffens *et al.*, 2002). Carbonation proceeds more rapidly at a higher carbon dioxide concentration (Anstice *et al.*, 2005, Jerga, 2004, Dheilly *et al.*, 2002, Ecke, 2003, Vucak *et al.*, 1998). Decreasing the concentration below 100% reduces the rate and extent of the carbonation reaction. However, significant reaction still takes place at 70% concentration and effective treatment of materials has been demonstrated as low as 10% (Van Gerven *et al.*, 2005, Johnson, 2000, Sanjuan and del Olmo, 2001).

Conversely, at high concentration, the rate of reaction is often so great that the heat generated causes premature drying (Cultrone *et al.*, 2005). This may also be associated with the development of an impermeable reaction rim on the surface of grains, which prevents further carbonation (Dunster, 1992).

Elevating the concentration and the system pressure are necessary to complete the carbonation process within an industrially acceptable timescale (Teramura *et al.*, 2000). However, dilute gas is more economical to use and may be more suitable for treating certain materials as well as avoiding problems associated with the vigorous reaction with concentrated gas (Soroushian and Ostovari, 1998).

2.2.5.3 Pressure

Penetration of carbon dioxide into the material and its solubility in the pore solution is enhanced by increasing pressure (Anthony *et al.*, 2000). Increasing the pressure of a carbon dioxide atmosphere up to 2 bars has been found to promote the rate of carbonation (Barnard *et al.*, 2005).

Higher pressure increases the reaction rate, but is accompanied by other undesirable effects. The growth of larger calcite crystals at high pressure can disrupt the existing structure, resulting in a weaker bond between grains (Domingo *et al.*, 2006, Bukowski and Berger, 1979). Secondly, the rapid reaction due to high-pressure treatment often results in thermal fracturing and micro-cracking of the crystallised calcium carbonate (Liu *et al.*, 2003). A slower reaction allows heat to dissipate (Berger *et al.*, 1972).

2.2.5.4 Exposure time

Extending the time of exposure to carbon dioxide allows greater conversion of reactive minerals to calcium carbonate (Sulapha *et al.*, 2003, Balayssac *et al.*, 1995). Prolonged exposure increases the penetration of carbon dioxide into the material, and the depth of the carbonated layer (Tam *et al.*, 2005, Jerga, 2004, Jiang *et al.*, 2000). Shorter treatment times may result in the development of poorly formed crystals (Domingo *et al.*, 2006).

The rate of the carbonation reaction is not constant, but decreases with time as the proportion of reactive material decreases (Barnard *et al.*, 2005). The subsequent behaviour depends upon the reaction conditions, but strength development typically continues up to a few hours, after which further exposure has little or no further effect (Soroushian *et al.*, 2004).

2.2.5.5 Temperature

The effect of temperature upon the carbonation reaction is highly complex. Firstly, a higher temperature improves the dissolution of the reactive phases (Garcia-Carmona *et al.*, 2003). However, this is offset by suppression of calcium carbonate precipitation (O'Connor *et al.*, 2005), and dissolution of edges and corners of the formed crystals (Domingo *et al.*, 2006). Stable calcium carbonate in the form of calcite preferentially forms below 10^{o}C. At higher temperatures, there is a shift towards the precipitation of meta-stable forms of calcium carbonate such as vaterite and aragonite (Fernandez Bertos *et al.*, 2004b). Higher temperatures also promote decomposition of carbonic acid (Abu-Eishah *et al.*, 2004). Carbonation typically increases up to 60^{o}C probably due to leaching of Ca^{2+} ions, but above 60^{o}C uptake drops due to decreased CO_2 solubility (Cultrone *et al.*, 2005, Dheilly *et al.*, 2002, Liu *et al.*, 2001, Molenaar and Venmans, 1993). As the carbonation reaction itself is exothermic, an immediate temperature rise of up to $10\text{-}20^{o}$C can be expected (Maries, 1992, Klemm and Berger, 1972).

2.2.5.6 Porosity, Grain Size & Surface Area

The diffusion of carbon dioxide is controlled by the pathways into the material e.g. cracks or pores, and the reaction surface available. High porosity materials are associated with a higher rate and extent of carbonation (Khunthongkeaw *et al.*, 2006, Castroa *et al.*, 2000, B.R.E, 1995). The reaction is also promoted by the presence of a large reaction surface (Klimesch and Ray, 1997, Arandigoyen *et al.*, 2006). However, in very fine grained materials, the reaction is inhibited due to tighter particle packing restricting carbon dioxide permeation (Johnson, 2000, Zhang *et al.*, 2004). Similarly, low porosity materials will readily suffer from pore blocking as reaction products precipitate in the pore space (Johnson *et al.*, 2003). Conversely, fine grained materials may benefit from improved binder dispersion, increased particle contact, and improved cementation due to closer packing (Barnard *et al.*, 2005, Molenaar and Venmans, 1993, Huang and Airey, 1998). The ideal material for carbonation will exhibit a small particle size, high porosity and a large surface area (Cultrone *et al.*, 2005, O’Connor *et al.*, 2005, Khan and Lynsdale, 2002).

2.2.5.7 Chemical Composition

The magnitude of the carbonation reaction is directly related to the amount of reactive minerals present in the material (Balayssac *et al.*, 1995). Calcium oxide and calcium silicate are the primary reactive component in unhydrated materials. Calcium may also be present in the form of silicates, which are also reactive (Johnson, 2000, Bukowski and Berger, 1979, Young *et al.*, 1974). Johnson (2000) found a direct relationship between total calcium content determined by XRF and carbon dioxide uptake.

Steinour devised a formula (equation 2.4) to estimate the maximum theoretical uptake of a material based upon the oxide weights of calcium, sulfur, sodium and potassium (Fernandez Bertos *et al.*, 2004b).

$$CO_2(\%) = 0.785(CaO - 0.7SO_3) + 1.09Na_2O + 0.93K_2O \qquad (2.4)$$

The reaction can be hindered by the presence of organics and anions, which may react with the cementitious phases and influence the diffusion of carbon dioxide (Garcia-Carmona *et al.*, 2003, Lange *et al.*, 1996a). Conversely, carbonation may be promoted by the presence of certain metals due to the precipitation of metal carbonates (Lange *et al.*, 1996b).

2.2.6 Reaction Effects

Carbonation affects the physical, microstructural and chemical properties of the reactive material. The reaction promotes accelerated curing and improved mechanical properties of cementitious systems, alteration of the solid and pore water chemistry, and modification of contaminant mobility (Fernández-Bertos *et al.*, 2004b).

2.2.6.1 Physical

Carbonation results in a reduction in porosity due to the formation of voluminous calcium carbonate in the pore space (Van Gerven *et al.*, 2005, Ngala and Page, 1997). Calcite occupies a volume 17% larger than Portlandite (calcium hydroxide), and reduces porosity by 5-15% and permeability by three to five orders of magnitude (Russell *et al.*, 2001, Jerga, 2004, Dias, 2000). This aids the retention of contaminants through improved physical containment (Lange *et al.*, 1996b), increases weight and bulk density, and improves strength (Aguilera *et al.*, 2003, Sanjuan and del Olmo, 2001). However, microcracking may occur if the material is insufficiently deformable to accommodate the expansion e.g. in hardened concrete (Johannesson and Utgenannt, 2001, Lange *et al.*, 1996a).

Exposing a material to carbon dioxide initially causes alteration of the surface layer. Densification of the surface structure leads to the development of an impermeable reaction rim, which restricts diffusion of carbon dioxide into the core (Jerga, 2004) (see figure 2.2). As more surface pores close, CO_2 penetration slows, and carbonation shifts to an advancing front (Venhuis and Reardon, 2003). This leads to the development of three carbonation zones; an outer fully carbonated zone at the surface, a zone of decreasing carbonation terminating at a front, followed by an uncarbonated zone (Saetta and Vitaliani, 2005, Houst and Wittmann, 2002). Infilling of the pore structure as the carbonation front progresses is also accompanied by an increase in porosity just ahead of the carbonation front, resulting from decalcification (Bary and Sellier, 2004)..

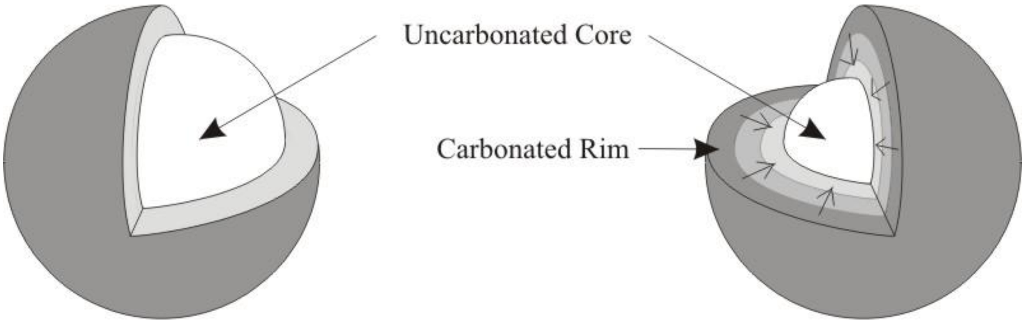


Figure 2.2: Growing rind model (based upon Shaffique *et al.*, 1998)

2.2.6.2 Microstructure

Microstructural alteration occurs due to the precipitation of voluminous calcium carbonate. The carbonated structure is considerably less porous than the original hydrated matrix (Beruto *et al.*, 2005). Crystals of calcium carbonate join together into an interlocking lattice, forming an unimpaired bond between grains (Arandigoyen *et al.*, 2006).

The carbonation reaction occurring in cement causes decalcification of the C-S-H gel as calcium is consumed in the reaction (Hills *et al.*, 1999). Removal of calcium from C-S-H forms a polymerized hydrous silica gel (Valls and Vazquez, 2001, Klimesch and Ray, 1997, Lange *et al.*, 1997). The decalcification of C-S-H increases the proportion of nano-pores, whilst calcite precipitation results in closure of micro-pores (Teramura *et al.*, 2000, Dias, 2000, Ngala and Page, 1997).

2.2.6.3 Chemical

The carbonation reaction alters pH, which has an influence on the stability and leaching of constituents (van der Sloot, 2002). A decrease in pH of up to 4 units may be observed for a completely carbonated sample due to the conversion of alkaline hydroxide to neutral carbonate (Li *et al.*, 2003). This is particularly important for the solubility of regulated hazardous metals, which may be either increased or decreased depending upon their solubility with respect to pH (Van Ginneken *et al.*, 2004).

Stabilisation by pH alteration is accompanied by changes to the chemistry of the material which also affect contaminant retention (Chen *et al.,* 2003). Under optimum conditions the heavy metal concentration in the leachate can be reduced by up to 80% (Fernández-Bertos *et al.*, 2004b). This can be attributed to changes in metal solubility due the precipitation of metals as low solubility carbonates and the formation of solid solutions in the precipitated calcium carbonate (Van Gerven *et al.*, 2004a, Shaffique *et al.*, 1998).

2.2.7 Carbon Capture

Carbonation of waste has been proposed as a method for carbon capture. In recent years there has been a focus upon the reduction of global carbon dioxide emissions. Major climate change is predicted within the next century if the atmospheric carbon dioxide concentration doubles from its present level (D.T.I., 2002). The 1990s was the warmest decade since records began, and climate temperature could rise by a further 6^{o}C by the end of the 21st century (A.B.I., 2005). UK emissions in 2001 totalled 0.55Gt of which 0.2Gt was derived from power generation. Despite a 20% drop in emissions in the last 30 years through decarbonisation of the energy system, improved energy efficiency and a general shift from primary to the service industry, they are now rising due to increased electricity production (Eyre, 2001). Between 1990 and 2004, emissions fell by 5.6%, but 2004 saw a 0.5% increase over 2003 (D.E.F.R.A, 2006).

Carbon capture and storage (CCS) is the process of capturing the carbon dioxide produced from industrial processes. The carbon dioxide is captured, transported, and stored in a long-term repository. A regulatory framework recognising the importance of CCS was included in the Energy Act 2008, and the technology is being actively debated for inclusion in the EU Emission Trading Scheme (ETS) (D.E.C.C, 2008).

Improvements in energy efficiency and adopting more renewable energy sources are important methods for reducing carbon dioxide emissions, but they are unlikely to be sufficient alone. Recycling and the concept of ‘industrial ecology’, whereby by-products from one industrial process are used as feedstocks for another are an ideal solution, but offer only niche opportunities (I.P.C.C, 2005, Herzog *et al.*, 1997, Moomaw, 1996).

Consequently, a cheap and efficient method of carbon dioxide sequestration is needed. A variety of methods have been proposed, which include storage in deep geological depositories or dissolving carbon dioxide into the ocean (D.T.I., 2003). However, there are concerns over the long-term stability of carbon storage, particularly the possibility of escape and the environmental impact (I.P.C.C, 2005). This is compounded by the projected financial costs, and the low number of large point sources in close proximity to suitable disposal sites (I.P.C.C, 2005, Sims *et al.*, 2003, Grimston *et al.*, 2001).

As an alternative, many waste materials are reactive with carbon dioxide, particularly those derived from industrial thermal processes. Accelerated carbonation of industrial wastes provides a low cost method of sequestering carbon dioxide, albeit on a relatively small scale (Van Gerven *et al.*, 2004b).

2.3 Agglomeration

2.3.1 Introduction

Agglomeration is a process used to improve bulk powder properties by grain size enlargement. The process reduces dust, improves flow properties, elevates bulk density and produces a more valuable product (Blandin *et al.*, 2005, Samimi *et al.*, 2003, Schaafsma *et al.*, 1998). Agglomeration is used in this study to produce aggregate-sized spherical pellets from fine grained waste materials.

2.3.2 Agglomeration Mechanisms

Agglomeration is achieved by sticking particles together through physical or chemical forces under direct or in-direct agitation (Pietsch, 2003). Particle adhesion can occur by natural electrostatic and frictional forces, or a liquid binder can be added. Initial particle bonding may be permanent in the form of cement or temporary prior to further treatment e.g. application of heat to form a sinter bridge (see figure 2.3).

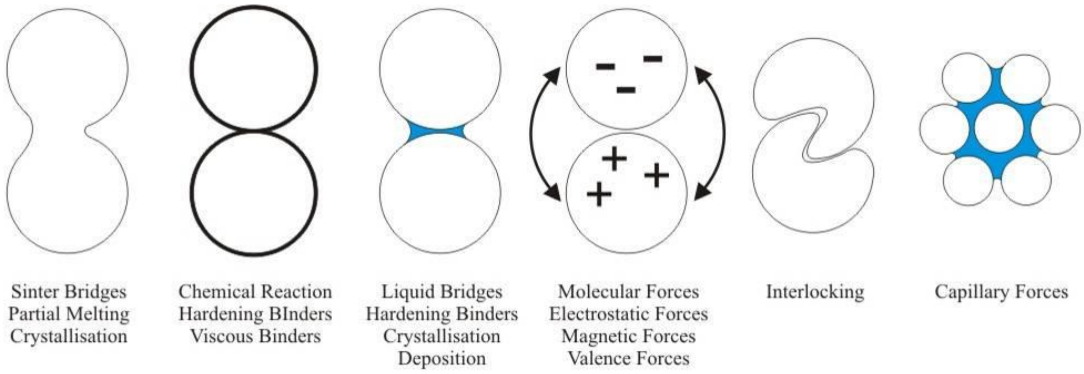


Figure 2.3: Binding mechanisms employed in agglomerating systems (modified from (Pietsch, 2003)

The binding strengths of interlocking and molecular forces are comparatively weak. Strong permanent bonds are formed by sintering, chemical binding, or the formation of an inter-grain cement. Sintering and chemical binders introduce additional costs through the use of large amounts of energy or chemical reagents. Alternatively, accelerated carbonation can be employed to bind particles through the crystallisation of calcium carbonate cement in pore space between grains, relying upon the reaction between the material and carbon dioxide.

2.3.3 Agglomeration Methods

Particle binding is achieved by bringing grains into close contact. A range of processes have been devised for this purpose, which rely upon thermal, compression, liquid binding or mechanical agitation (see table 2.1).

Agitation by mechanical mixing is suited for heavy-duty agglomeration of voluminous materials, such as wastes (Ennis, 1996). Mechanical mixers are described as being high shear or low shear depending upon the force of agitation applied.

Table 2.1: Agglomeration processes (adapted from Mak, 2001)

Process	**Subdivision**	**Description**	**Applications**
Thermal	Sintering	Agglomeration of particles is achieved by heating which results in drying, fusing, chemical reaction or crystallisation (Mak, 2001).	Used as a secondary step after forming agglomerates by another process.
Compression	Compaction	Force is applied to compact the material into a mould e.g. briquetting	Heavy duty applications
	Extrusion	Extrusion involves premixing the material into a paste, and forcing it under pressure through an aperture or die to form continuous rods or bars that are cut to the required length	Food and pharmaceutical industries (Keleb, 2004)
Liquid Systems	Spray Drying	The liquid is atomised in stream of hot gas which instantly dries to a powder. The powder is commonly subjected to a second pelletising step in a fluidised bed to improve handling properties (Gharsallaoui *et al.*, 2007).	Food industry for producing dried powders from liquid feeds, such as powdered milk.
	Hot Melt Cooling	Molten binder binds particles together by capillary force whilst still in a liquid phase, and hardens upon cooling to form a permanent bond. (Vilhelmsen and Schaefer, 2005).	Used as a secondary step after forming agglomerates by another process.
	Flocculation or Coagulation	Coagulation reduces the repulsion of particles to induce agglomeration. Flocculation is the clumping of particles by the addition of a polymer solution (Simons, 1996).	Filtration systems
Agitation	Mechanical Mixing	Further subdivided into low shear rotating drums or discs and high shear rotary processors.	Low shear for heavy duty applications. High shear for pharmaceuticals and detergents etc
	Pneumatic Mixing	A gas stream is the source of agitation, as in fluidised beds. The drying action of the hot gas solidifies the binder to form a permanent bridge (Vervaet and Remon, 2005)	Food and detergent products

2.3.3.1 High shear

In high shear mixers, particle motion is induced through mechanical agitation by a spinning impeller or blade within a closed chamber (Faure *et al.*, 2001). Initial powder mixing and agglomeration takes place within the same apparatus, precluding a separate premixing stage (Keleb, 2004). The intense agitation generated produces regular shaped agglomerates with a high degree of compaction in short timescales (Kristensen, 1996). Hoornaert *et al.* (1998) studied processing variables when agglomerating polymer bound enzyme pellets in a Lödige-type mixer. These mixers feature a high speed ‘chopper’ blade mounted near the top of the chamber, and a slower ‘Ploughshare’ impeller at the base of the chamber. This research revealed the importance of optimising both the binder content and viscosity as well as the mixing duration, speed and temperature.

2.3.3.2 Low Shear

These rotating vessels rely upon the force of gravity to keep particles in motion, and impart low shear stress to the agglomerates through gentle tumbling and rolling (Mills *et al.*, 2000). Rotating drums are able to handle a variety of feedstocks including slurries and granules, although optimisation of numerous operating variables is necessary to achieve a satisfactory process (Yang *et al.*, 2003).

Disc (or pan) pelletisers are rotating inclined shallow dishes. The inclination of the dish can be adjusted, which controls the mixing pattern of the material. As particles grow in the pan, they migrate to the surface and eventually spill over the lip of the pan. Consequently, the product from pan pelletisers tends to be more uniform and consistent than that from a drum, which will often require the pelletised product to be screened and crushed if necessary (Zed, 2001).

Low shear pelletisers are suited to processing mineral and metalliferous materials, and have been used to process wastes in previous research (see table 2.2).

2.3.4 The Agglomeration Process

Three stages are recognized in the agglomeration process, which may occur sequentially or simultaneously; wetting and nucleation, consolidation and growth, breakage and attrition (see figure 2.4) (Forrest *et al.*, 2003). The transition between the three stages depends on the physico-chemical properties of the feed and the machinery operating conditions (Saleh *et al.*, 2005).

Table 2.2: Summary of selected recent studies using drum and disc pelletising processes

Author	**Type**	**Material**	**Binder**	**Speed & Angle**	**Time**	**Key Points**
(Albert and Langford, 2007)	Disc	Limestone fines	8-14% water	NS	NS	Spray agglomeration / fluidised bed drying
(Amaratunga and Hmidi, 1997)	Drum	Gold mine Tailings	Portland cement, gypsum & water	33rpm	30mins	Water sprayed into drum / Higher moisture content improved green strength
(Arslan and Baykal, 2006b)	Disc	Fly ash	10-30% cement & water	42-48rpm 42-45°	20mins	Production of pellets with crushing strengths up to 1.5MPa.
(Baykal and Doven, 2000)	Disc	Fly ash	Cement/Lime & water	35-55rpm 35-50°	20mins	Agglomeration controlled by the mechanical properties of the feed / Bond between pellets and cement paste needs improvement
(Davis *et al.*, 2006)	Drum	Limestone fines	Cement & $MgCO_3$	50rpm	NS	Production of pellets with different binder mixes to treat metal contaminated water
(Dutta *et al.*, 1997)	Disc	Iron ore fines & slimes	Cement/Silica fume & water	32rpm 45°	NS	Increasing surface area of the binder improves pellet strength
(Gluba, 2003)	Drum	Dolomite flour	Water	20rpm	NS	Coarse spray beneficial for pellet growth
(Harikrishnan and Ramamurthy, 2006)	Disc	Fly ash	Water	20&40rpm 40&70°	NS	High speed improves strength / Angle controls flow pattern / Relationship between angle & moisture content also important
(Holuszko and Laskowski, 2004)	Disc	Coal fines	Water	25rpm	30mins	Difficulties of agglomerating hydrophobic materials
(Iveson, 2002)	Drum	Glass ballotini	Water & glycerol	30rpm	2.7hrs	Porosity decreases with time / More binder improves consolidation / Higher viscosity binder decreases consolidation
(Iveson and Litster, 1998a)	Drum	Glass ballotini	Glycerol	30rpm	2hrs	Decreasing particle size and increasing binder viscosity reduces consolidation

(Kawatra and Ripke, 2002)	Drum	Steel slag	1% fly ash & water	25rpm	NS	High shear premixing / Spray agglomeration / Sintering formed pellets
(Mehta *et al.*, 1996)	Disc	Reactive mine tailings	Cement	15-45rpm 25-45°	60mins	Higher moisture content, lower inclination & higher speed improves growth
(Mills *et al.*, 2000)	Drum	Silica sand	Silicone oil	29rpm	NS	Increase in viscosity of binder slowed growth, but reduced caking
(Orava *et al.*, 2006)	Disc	Municipal & sewage compost	30% fly ash & water	40rpm & 58° (pilot) 60rpm & 55° (lab)	NS	Optimum conditions developed at laboratory scale and applied to pilot scale production / Feed material heterogeneity has a major influence upon agglomeration
(Qui *et al.*, 2004)	Disc	Iron ore Concentrate	Organic binder	45°	NS	Size increase with time / Increase in strength with increasing binder content
(Sastry *et al.*, 2003)	Drum	Iron ore Concentrate	Bentonite & water	NS	NS	Moist feed continuously added to create layered agglomerates
(Venkataramanaa *et al.*, 2002)	Drum	Iron ore Concentrate	Calcined lime & water	5.2rpm (pilot)	NS	Comparison between lab and pilot scale / Pilot pellets smaller and poorer growth / Pilot residence time is pellet size dependent
(Ververka and Hinkle, 2001)	Disc	Limestone	Lignosulfonate, starch, molasses	20rpm 54°	30mins	Development of a continuous pilot scale process / fludised bed drying of pellets
(Wauters *et al.*, 2002a)	Drum	Copper Concentrate	37.8-45.4% water	21.4rpm	NS	Spray parameters investigated / Size segregation in drums
(Wauters *et al.*, 2002b)	Drum	Copper Concentrate	37-43.4% water	21.4rpm	NS	Spray agglomeration / Increase in size with time / Increased water speeds growth
(Zed, 2001)	Drum & disc	Zinc oxide & copper ore	Water	NS	NS	Drum pelletiser more efficient in terms of growth and reduced breakage

NS ~ Not specified

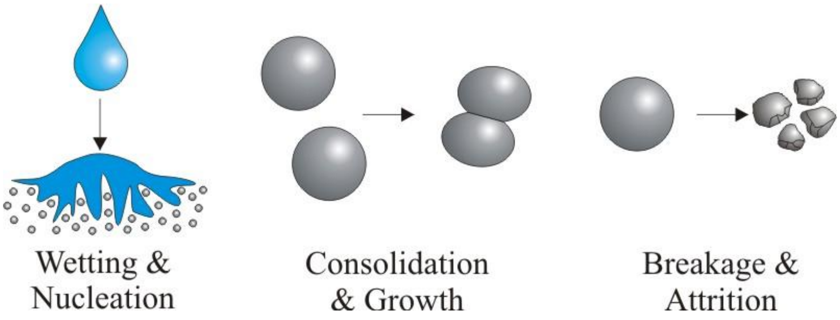


Figure 2.4: Agglomeration stages (modified from Litster, 2003)

2.3.4.1 Wetting and Nucleation

The initiation phase of agglomeration involves the contact between the liquid binder and the dry powder (Wildeboer *et al.*, 2005, Ceylan and Kelbaliyev, 2001). The wetting phase occurs as a droplet is drawn into the powder by capillary force, dissipating through the particles and forming nuclei (Iveson *et al.*, 2003, Schaafsma *et al.*, 1998). This process may occur via immersion whereby a comparatively large droplet engulfs a particle, or where a smaller droplet disperses itself over the particle surface (Iveson *et al.*, 2001a). Under the correct conditions, capillary interactions between moist particles will give rise to accretion of agglomeration nuclei (Sastry *et al.*, 2003).

Nucleation proceeds when there is sufficient surface saturation (Kristensen, 1996). Effective binder distribution throughout the mixture is essential to ensure the homogeneity of the final product, otherwise highly variable and undesirable characteristics may be incurred. The method of material wetting has a major influence upon the pelletised product. Poor wetting and liquid distribution can lead to a broad range of formed granule sizes and the process becoming increasingly difficult to control (Gluba, 2003, Litster *et al.*, 2002). If the degree of wetting of the powder is too low, pockets of dry material (dead zones) may remain and growth cannot be sustained beyond the nucleation phase, producing a ‘crumb’ product (Bardin *et al.*, 2004, Goldszal and Bousquet, 2001). Nuclei exhibit brittle behaviour at low liquid concentration, but start to behave plastically at higher levels of saturation facilitating growth by coalescence (Farag Badawy and Hussain, 2004). However, increased saturation may lead to overwetting and caking of the material to the machine, and requires removal by mechanical breaking

(Litster *et al.*, 2001). Conversely, careful control during this initial phase allows the density and size of the pelletised product to be regulated (Iveson *et al.*, 2003).

2.3.4.2 Liquid Saturation

Wet agglomeration occurs when particles which are surface wet come into contact with one another and form a liquid bridge (Farag, Badawy and Hussain, 2004). These nuclei continue to grow as further interactions with other particles generate more bridges. These bonds hold the particles together through a combination of capillary pressure, surface tension and viscous forces until more permanent bonds are formed by drying or curing (Jorgensen, 2004, Iveson and Litster, 1998b).

The six saturation states occurring in granular materials are shown in figure 2.5. The pendular state develops when there is sufficient moisture to generate liquid bridges at the particle contacts. Partial saturation of the pores is characteristic of the funicular state. Total pore saturation without any surface wetting is characteristic of the capillary state. At this point, capillary forces are at their strongest, but saturation of the pores lowers interparticle friction (Iveson and Litster, 1998b). Total saturation forms a suspension of particles (droplet), which may contain unsaturated pockets (Vilhelmsen and Schaefer, 2005). The latter two states are associated with the immersion growth mechanism, in which particles are engulfed by large droplets. Saturation up to the capillary state are typical of a drop-controlled regime (Iveson *et al.*, 2001b).

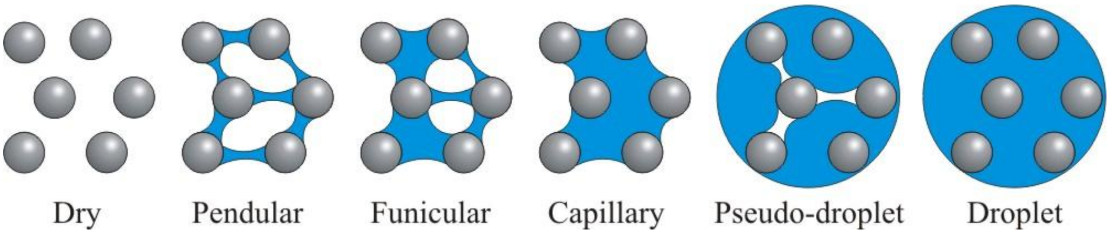


Figure 2.5: Saturation states in granular materials (modified from Iveson *et al.*, 2001a)

The formation of a liquid bridge is determined by the complex interrelationships between the processing conditions and the properties of the mixture (Rossetti and Simons, 2003). Successful bridge formation is achieved by increasing the saturation of the mixture, or by increasing the energy input. The former is a function of the moisture content, particle size and wetting characteristics of the raw feed, whilst the latter is controlled by the intensity, duration and pattern of mixing.

2.3.4.3 Consolidation and Growth

Following nucleation, the newly formed agglomerates begin to grow and consolidate. Consolidation is the expulsion of water from a material, whereas compaction refers to the expulsion of air. Growth takes place by coalescence or layering processes (Iveson *et al.*, 2001a). Coalescence occurs when two well formed agglomerates collide and form a single agglomerate. Layering is when fines adhere to the surface of a larger particle (Sastry *et al.*, 2003).

Successful coalescence is determined by the newly formed bond strength between the particles compared to the disruptive forces of the collision (Mills *et al.*, 2000, Tardos *et al.*, 1997, Ennis, 1996). Highly energetic collisions may result in rebound. Deformable granules dissipate most of the collision energy, forming a dumbbell shaped particle which will eventually consolidate into a single spherical granule if it survives stresses from subsequent collisions (He, 1999, Iveson *et al.*, 1996). Survival of these forces and subsequent growth is dependent upon the degree of saturation and the extent of consolidation of the agglomerate (van den Dries *et al.*, 2003). The ability of agglomerates to deform under stress is important for effective coalescence, which can only occur if there is sufficient moisture present in the agglomerate (Farag Badawy and Hussain, 2004, van den Dries *et al.*, 2003, Kristensen, 1996).

Agglomerate growth is dependent upon consolidation. Growth can only occur when the agglomerate surface is wet (Ceylan and Kelbaliyev, 2001). Consolidation and compaction of the agglomerate structure reduces porosity and squeezing out entrapped air and binder onto the surface of the granule (Oulahna *et al.*, 2003, Faure *et al.*, 2001, Adetayo and Ennis, 2000).

Growth may be delayed whilst consolidation takes place and nucleates become surface wet. This induction phase growth is typical of stronger nucleates which require greater force to consolidate (see figure 2.6). However, coalescence may occur without a consolidation phase. These steady growth systems occur if the agglomerates are sufficiently deformable to coalesce immediately from the point of nucleation, and size enlargement proceeds from the start of agitation (Wauters *et al.*, 2002a).

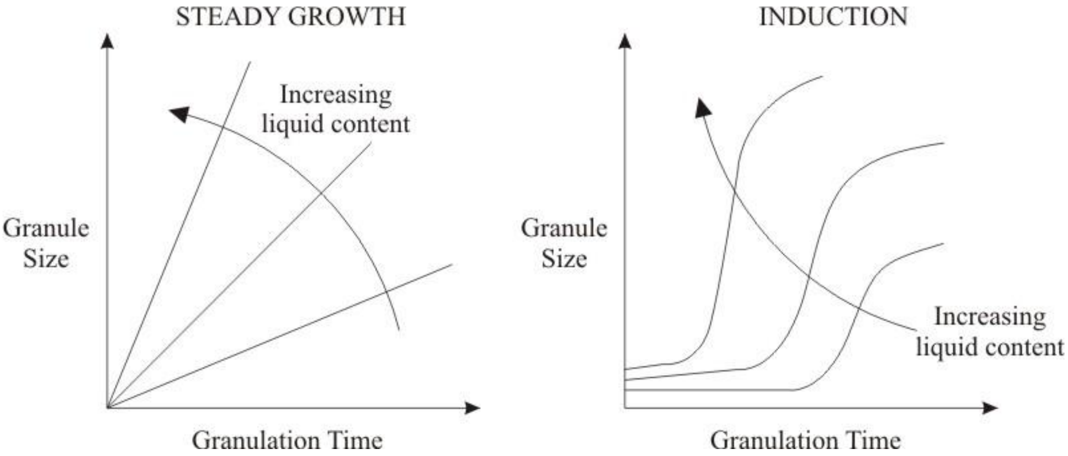


Figure 2.6: Growth rates in steady growth and induction growth systems (modified from Wauters *et al.*, 2002a).

The extent of consolidation depends upon the amount of deformation occurring during collisions (Litster, 2003). This is controlled by the processing parameters such as the intensity of the agitation and the processing time (Oulahna *et al.*, 2003). Consolidation is also controlled by the physical characteristics of the powder e.g. morphology and size distribution, and the amount of moisture which acts as a particle contact lubricant (Iveson and Litster, 1998a, Hjemstad and Schneider, 1996). Agglomerates will consolidate until they are strong enough to resist further consolidation, and growth will cease when surface saturation can no longer be achieved (see figure 2.7) (Iveson and Litster, 1998b). The critical size of the agglomerates is controlled by the amount and viscosity of the binder (Mackaplow *et al.*, 2000).

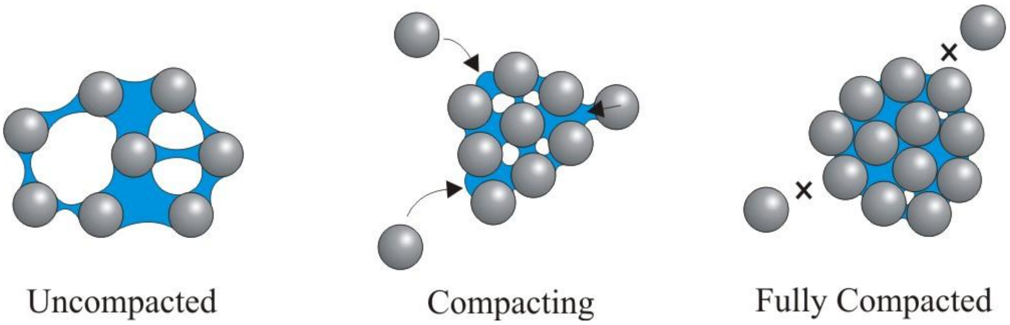


Figure 2.7: Consolidation and growth (based upon Schaafsma, 1998)

2.3.4.4 Breakage and Attrition

The final transition of the agglomeration regime is marked by a change from growth to breakage and attrition. Three mechanisms of breakage have been identified; fracture, attrition and abrasion (see figure 2.8).

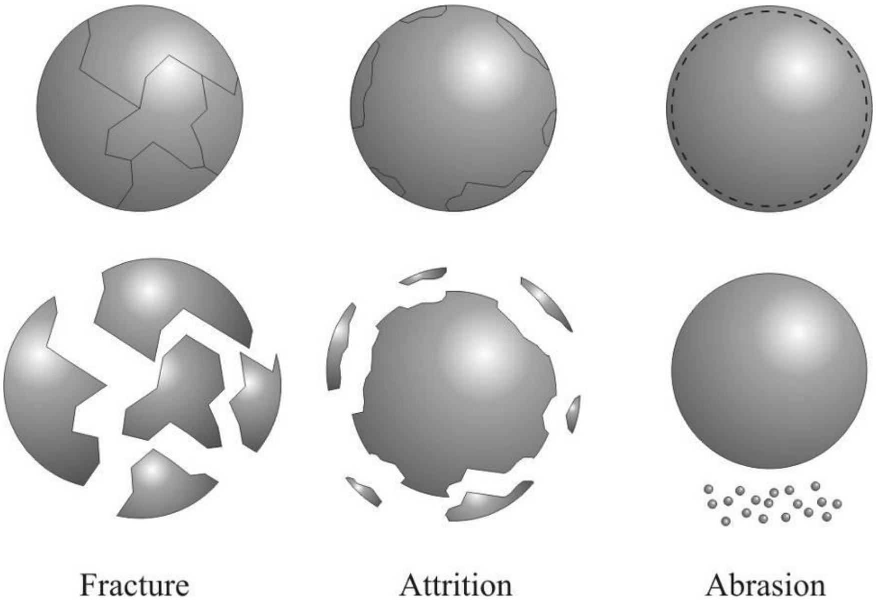


Figure 2.8: Breakage and attrition mechanisms (modified from Arslan, 2003)

This transition to a breakage-dominated environment is marked by a static phase of slow decay and growth which is probably controlled by abrasion transfer. The extent of breakage increases with time and results in the generation of fines (Venkataramanaa *et al.*, 2002, Litster and Sarwono, 1996). The extent of granule breakage and attrition is controlled by the velocity of the impact, and in turn by the force of the mixing motion (Horio, 2003, Mishra *et al.*, 2002). Excessive deformation during impact stunts growth or causes the granules to continuously break apart and form a weak crumb (Iveson *et al.*, 2003). Fracturing of granules in a low shear mixer is often due to collisions with the drum wall (Mishra *et al.*, 2002). Mixtures bound with low viscosity binders e.g. water may be expected to suffer more breakage (van den Dries *et al.*, 2003). These materials may also suffer from rapid breakage at low moisture contents, whilst at higher moisture contents attrition is dominant (Verkoeijen *et al.*, 2002).

2.3.5 Mixing Patterns

Effective mixing is critical to the efficiency of the agglomeration process. Modeling the growth patterns during the agglomeration process has been the subject of a great deal of research. However, this remains a complex task due to the influence of the processing parameters along with the properties of the material.

Particle motion in a low shear environment is highly complex and may comprise of one or more of a centrifuging, cataracting, cascading, rolling, slumping or slipping action (see figure 2.9) (Weir *et al.*, 2005).

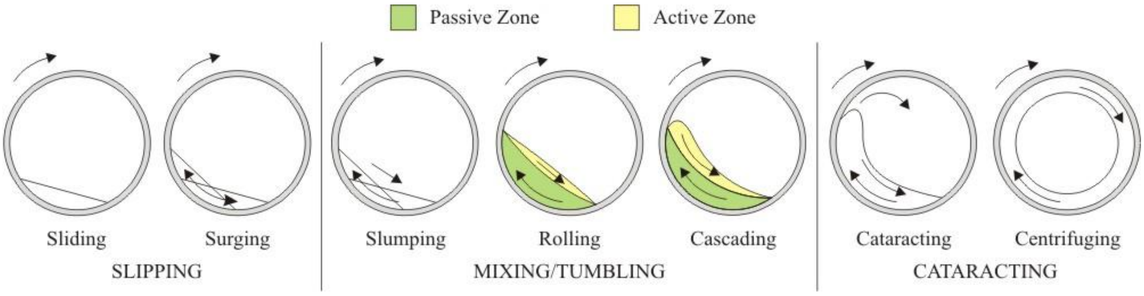


Figure 2.9: Mixing regimes in a rotating drum (modified from Sherritt *et al.*, 2003)

The pattern of growth may switch from one mechanism to another as pellets grow in size (Kapur and Runkana, 2003). The transition between mixing regimes is controlled by the rotation speed of the drum, and the friction between the powder and the drum which can be affected by the extent of fill (see figure 2.10) (Santomaso *et al.*, 2005, Félix *et al.*, 2002).

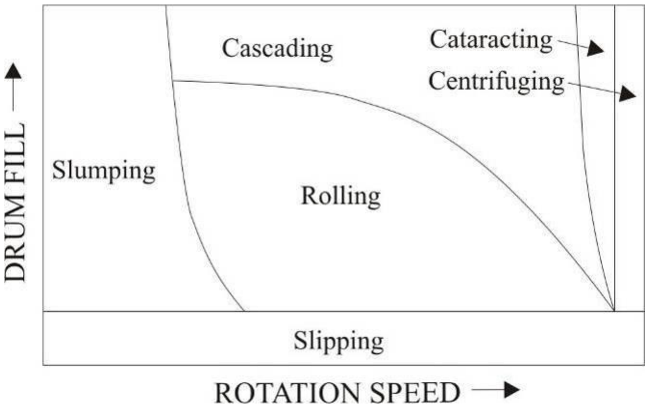


Figure 2.10: Effect of drum fill and rotation speed upon mixing patterns (modified from Mellmann, 2001)

At slow speeds, low friction results in an undesirable slipping motion when the powder remains as a solid mass and skates upon the drum surface. Slumping occurs when there is sufficient friction to partially carry the powder body up the drum before gravity causes an avalanche back down to the drum base. These regimes are indicative of little or no mixing, due to minimal bed turnover, which is unsuitable for inducing particle coalescence or layering (Sherritt *et al.*, 2003).

At higher friction/speed, mixing of the powder bed begins to take place, with two distinct horizons developing. A solid bed layer remains at the base of the powder mass (passive zone), which is overlain by a lower density dynamic flow layer (active zone) (Sudah *et al.*, 2002). In the passive region, material in contact with the drum wall is carried upwards until an angle of repose is reached and the particles flow down the contact zone with the solid bed (Ding *et al.*, 2002). In a slumping mode, the avalanching behaviour characteristic of a surging regime remains, but the development of a continuous flow layer is evident as the material carried up the drum wall periodically collapses forward and tumbles over the solid bed. The rolling regime is indicative of the evolution of the slumping action to a continuous flow (Mellmann, 2001).

A continued increase in mixing speed causes the powder bed to dilate, and an increase in the angle of repose, as the dominant force begins to shift from a gravity-controlled regime to a centrifuging regime (Arslan and Baykal, 2006b, Yang *et al.*, 2003, Ding *et al.*, 2002). Consequently, the powder mass is subjected to increased friction with the drum, which in turn gives the particles higher inertia and a tendency to cascade or cataract. Cataracting behaviour results when the energy imparted into the particles is so great that they are able to separate from the powder mass and are thrown through the air (Santomaso *et al.*, 2005). Centrifuging occurs when the material is constantly in contact with the drum wall, therefore mixing and agglomeration is impossible (Ryou, 2004, Mellmann, 2001).

Normal particle motion in rotating drums typically involves rolling or slumping, although optimum agglomeration occurs when the bed is either rolling or cascading, and efficient mixing of dry powders occurs in a cataracting regime (Santomaso *et al.*, 2005; Ding *et al.*, 2001). The integrity of a pelletised product is compromised if either gravitational or centrifugal force becomes dominant (Baykal *et al.*, 2000).

2.3.6 Process Variables

Agglomeration is an intricate process involving a number of parameters that influence the properties of the product (Goldszal *et al.*, 2001). It may be difficult to control the process and produce a product with the desired properties (Oulahna *et al.*, 2003, Mort *et al.*, 2001). A trial and error approach is often required for product development by adjusting and refining mix designs, binder properties and pelletising conditions (Knight, 2004, Faure *et al.*, 2001).

Previous research has shown that the pelletising process is fundamentally controlled by the engineering properties of the material, the moisture content of the mixture and the processing parameters such as the rotation speed (Wang and Cameron, 2002, Baykal and Doven, 2000). The desired attributes are controlled by the formulation of the raw material and the process design (machinery and operating variables) (Iveson *et al.*, 2001b). Saleh *et al.* (2005) highlighted that it is still not possible to reliably predict the effect of formulation properties upon the final product. This is largely due to the complex interrelationships between mix and processing variables. Figures 2.10 & 2.11 illustrate the effect of rotation speed (deformation), drum fill and moisture content. Table 2.3 summarizes the key variables associated with low shear agglomeration.

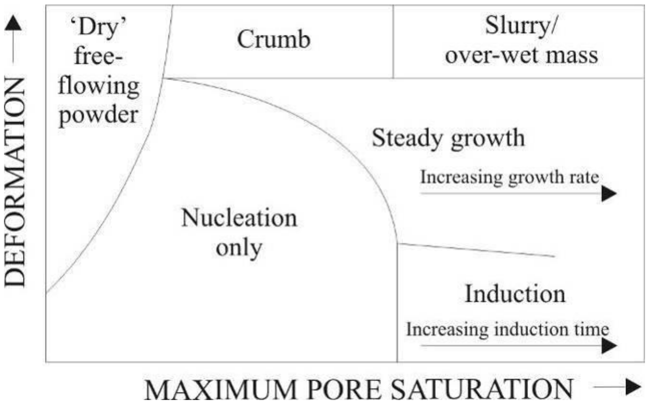


Figure 2.11: Effect of pore saturation and deformation upon agglomerate growth (modified from Iveson *et al.*, 2001)

Table 2.3: Summary of the key drum agglomeration variables

Variable	**Description**
Moisture Content	Increasing moisture content increases the growth rate and size of the pelletised product (Zed, 2001; Mackaplow *et al.*, 2000). Insufficient moisture will only form nucleates or a crumb, whilst excess will produce a slurry (Arslan and Baykal, 2006, Gluba *et al.*, 2001; Iveson and Litster, 1998b). Moisture requirement is material specific due to differences in particle size and wetting characteristics, and may vary between batches (Keleb, 2004, Gluba *et al.*, 2001).
Particle Size	Agglomeration of both small (<10μm) and large particles are difficult (Keleb, 2004). Interparticle friction is important for pellet strength. Coarse, narrowly-sized particles produce weak pellets (Iveson, 2002). Increasing particle size increases the mean pore size, requiring more moisture to form liquid bridges (Iveson and Litster, 1998b). Particle size distribution of the feed directly affects the product (Venkataramana *et al.*, 2002)
Material Properties	Particle shape, wettability, reactivity & porosity influence agglomeration behaviour (Pietsch, 2003). The morphology and size distribution of particles determine the frictional forces between particles, affecting pellet strength (Palzer, 2005). Hydrophobic materials form weak capillary bonds between particles (Holuszko and Laskowski, 2004).
Speed	Agglomeration at higher speeds increases the extent of consolidation, improves growth, and reduces the porosity which increases the strength of the pellets (Jorgensen, 2004, Iveson, 2002, Mehta *et al.*, 1996, Harikrishnan and Ramamurthy, 2006). The rotation speed must also be sufficient to induce optimal particle flow inside the drum (Santomaso *et al.*, 2005).
Duration	An increase in agglomeration time increases the energy input to the pellets, promoting further consolidation and increased growth (Qui *et al.*, 2004, Iveson, 2002).
Operating Conditions	Ambient temperature and humidity can have a major effect upon the finished product (Oulahna *et al.*, 2003). Temperature may affect binder viscosity and in turn growth, or chemical reactions within the system (Hoornaert *et al.*, 1998).

2.3.7 Process scale-up

Schaafsma *et al.*, (1998) stated that the mechanics of a laboratory experiment are rarely indicative of a full-scale industrial process. Effective scaling-up requires accurate experimental design through a comparison of variables and interactions of materials and machinery at one scale with another (Iveson *et al.*, 2001a). This was highlighted by Arslan (2006a), who calculated the rotation speed required for pan pelletisers at progressively larger scales, but determined experimentally that the optimum operating speeds were considerably different.

Research has shown that slower growth rates occur in larger drums due to reduced consolidation efficiency and higher breakage and attrition, whilst scaling up of a high shear process is associated with decreasing mixing efficiency (Faure *et al.*, 2001). This in turn has implications for liquid binder distribution, resulting in the development of a broader size distribution of agglomerates, and rapid growth of the larger pellets (Iveson, 2002). The decreasing efficiency of liquid distribution in larger mixers necessitates energetic mechanical mixing to achieve uniformity (Knight *et al.*, 1998).

The segregation of agglomerates according to size occurs in pelletisers due to the lower bulk density of the larger pellets. Segregation results in the development of inefficient flow patterns and limited interaction between different sized agglomerates (Venkataramanaa *et al.*, 2002, Litster and Sarwono, 1996). Stationary regions develop within the flow structures of drum, pan and high shear mixers where agglomerates have lower collision velocities and slower growth rates (Iveson, 2002). Figure 2.12 shows typical particle segregation patterns in a drum, with the development of an axial core of fines and the congregation of larger agglomerates near the drum walls. In a pan pelletiser, larger agglomerates remain almost static on top of a larger bed of tumbling fines (Iveson, 2002).

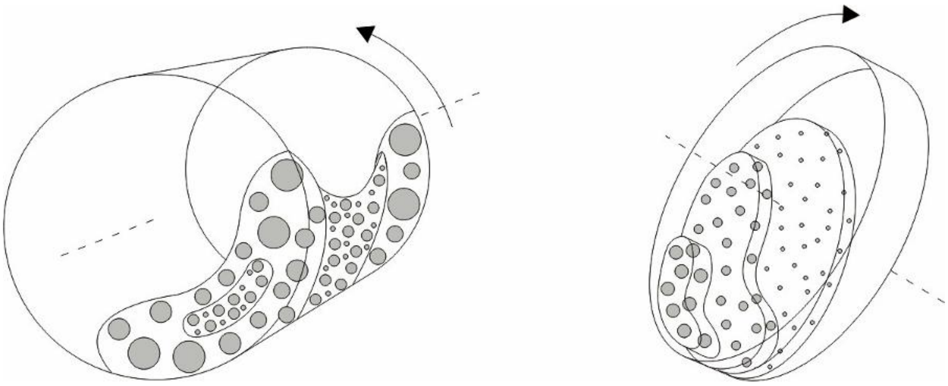


Figure 2.12: Particle segregation in rotating drums and pans (based on Iveson, 2002)

Agglomeration processes may operate on a batch or continuous basis. Continuous agglomeration permits high production rates, minimal user input, and consistent product properties. Alternatively batch processing is suitable for producing small quantities or a wide range of products, at the expense of the increased maintenance and cleaning required. The latter also allows easy separation of any sub-standard product (Gantner, 2003). Batch processing is particularly useful for developing an optimised product for continuous processing (Miller, 2005).

An industrial-scale process incorporates a number of stages. A typical system for the production of granulated fertilizer is shown in figure 2.13. Raw materials are batched by weighing, and conveyed to a premixer. Some processes negate the need for a premixer, and the raw feed is added directly to the granulating drum along with the binder. From the premixer the material is fed to the granulation drum. The product is graded to separate out the required size fraction. Oversize material is passed through a crusher and

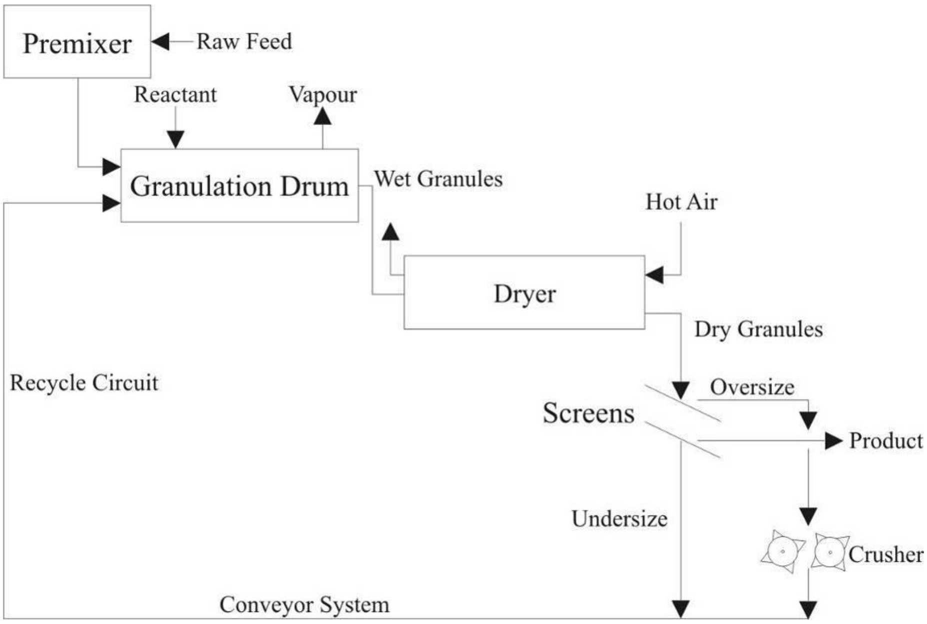


Figure 2.13: Schematic of a typical fertiliser manufacturing agglomeration process (modified from Wang and Cameron, 2002)

combined with the undersize agglomerates to be recycled back into the process. Depending upon the pelletising method, the graded product is cured either by drying, sintering or firing (Degreve *et al.*, 2006, Pottmann *et al.*, 2000). Conveyers will be required to move material from one stage to the next, dust collection systems to minimise waste, and silos and tanks for storing solids and liquids respectively (Albert and Langford, 2007).

2.4 Aggregates

By combining a pelletising technique with accelerated carbonation, it is possible to produce cemented pellets suitable for use as aggregate.

Aggregates are widely used in construction as a major constituent of concrete, tarmac, engineering fill and landscaping materials. As a major component in all aspects of construction, and with a broad range of uses, producing an aggregate from waste was the aim of this study.

2.4.1 Classification of Aggregates

Aggregates are particles of rock which form part or an entire building or engineering structure in a bound or unbound condition (Smith and Collis, 2001). Aggregates may be classified according to particle size, bulk density and source. For practical purposes, aggregates are divided by the mode of production into sands and gravels, and crushed rock. Primary class material is won from a natural source, whilst secondary aggregate is derived from recycled material. In civil engineering, fine aggregate refers to particles below 4mm in size, and coarse aggregate to those above 4mm in size (BS EN 12620, 2002).

Aggregates are sub-divided by bulk density into lightweight, normal-weight and heavyweight classes. Most natural aggregates fall into the normal-weight category (Smith and Collis, 2001). Lightweight aggregates have a bulk density less than 1200kg/m^3 (BS EN 13055, 2002). These may be naturally occurring in the form of low-density rock such as pumice, or manufactured e.g expanded clays or shales. Heavyweight aggregates (typical weight 2400kg/m^3), such as steel ball-bearings and hematite are used for the production of high density concretes for specialised applications e.g. nuclear shields (Mehta and Monteiro, 2006).

2.4.2 Lightweight Aggregates

Lightweight aggregates are premium products used in specialist applications including in lightweight structural concrete and in horticulture as plant substrates (Chandra and Berntsson, 2003). It was the intention to produce lightweight aggregates from wastes.

Lightweight aggregates may be found naturally e.g. pumice, or manufactured from mineral raw materials, by expanding clays, shales and slates. Secondary lightweight aggregate is manufactured from industrial by-products or waste e.g. foamed blastfurnace slag or pelletised pulverized fuel ash.

Lightweight aggregates are normally manufactured in energy intensive processes by agglomeration and expansion. Expansion is achieved by heating the raw materials to a pyroplastic state, which results in bloating of the structure as gases are evolved. When rapidly cooled, the aggregates retain their expanded structure, giving them a low density. Many trade names exist for lightweight aggregates. Table 2.4 summarises the manufacturing processes for several lightweight aggregate products.

Table 2.4: Summary of selected lightweight aggregates manufacturing processes

Aggregate	**Manufacturing Process**	**Advantages**	**Disadvantages**
Aardelite	A mixture of lime and fly ash is pelletised and cured at 90°C (Aarding, 2007).	Relatively low energy input	Use of lime as a binder
Carbolite	Fine grained thermal residues e.g. coke breeze are pelletised with an organic or inorganic binder and cured at 90°C (Aarding, 2007).	Use of waste materials	Use of commercial binder
Foamed Slag	Molten blastfurnace slag is quenched with jets of water on a foaming bed causing bloating by steam expansion (Chandra and Haber, 2002).	Relatively low energy input / use of waste materials	
Granulex	Crushed slate is bloated in a rotary kiln at 1150°C (Owens, 1993).	Low density aggregate	High energy input / raw material use
Leca/ Fibo	Natural clay, pelletised and expanded in a rotary kiln at 1050°C (Maxit Group, 2008).	Low density aggregate	High energy input / raw material use
Liapor	Natural shale is ground to powder and pelletised. The pellets are dusted with limestone and fired (Owens, 1993).	Low density aggregate	High energy input / raw material use
Lytag	Pulverised fuel ash is pelletised and sintered at 1000-1250°C (Lytag Ltd, 2007).	Use of waste materials	High energy input
Pellite	Molten blastfurnace slag is bloated by spraying with water, then drum pelletised and sprayed further to induce expansion (Owens, 1993)	Relatively low energy input / use of waste materials	
Perlite	Natural Perlite rock is heated to 790-1090°C causing it to expand (Perlite, 2009)	Very low density aggregate	High energy input / raw material use
Poraver	Glass powder is mixed with water and pelletised. The granules are expanded by heating to 900°C (Poraver, 2009).	Low density aggregate	High energy input
Solite	Natural slate is crushed and expanded in a rotary kiln (Solite LLC, 2008).	Low density aggregate	High energy input / raw material use
Ulopor	Expanded shale/slate (VTS, 2009).	Low density aggregate	High energy input / raw material use

2.4.3 Aggregate Specification

The regulation, specification and testing requirements for aggregates are covered in several European standards (see table 2.5).

Table 2.5: Summary of European standards covering lightweight aggregates

Standard	**Description**
BS 812	Testing aggregates (partially superseded)
BS 8500	Concrete (complimentary to BS EN 206)
BS EN 206	Concrete – specifications and performance, including aggregate requirements
BS EN 932	Tests for the general properties of aggregates
BS EN 933	Tests for the geometric properties of aggregates
BS EN 1097	Tests for the physical and mechanical properties of aggregates
BS EN 1367	Tests for weathering and thermal properties of aggregates
BS EN 1744	Tests for the chemical properties of aggregates
BS EN 12620	Aggregates for concrete
BS EN 13055	Specifies the properties for lightweight aggregate
BS EN 13242	Aggregates for unbound and hydraulically bound mixtures

2.4.4 UK Aggregate Industry

Since 1980, the UK has consistently consumed around 300 million tonnes each year. This trend is anticipated to continue for the duration of the current forecasts to 2016 (B.G.S, 2008c). Usage of secondary aggregate has increased steadily since the mid 1980s, and now accounts for 25% of the total. Total reserves of sand and gravel have declined from 907 million tonnes in 1995 to 650 million tonnes in 2004. Regional reserves have declined disproportionately, with the south-east suffering a decrease of 61% (B.G.S, 2006). Crushed rock reserves have remained largely constant since the early 1990s. However, the East Midlands and South-west hold 70% of the reserves, necessitating transport of large amounts of rock to the areas of high demand in the South-east (B.G.S, 2008a, 2006)

Aggregate production is increasingly constrained by environmental pressure, remoteness and issues with obtaining planning permissions from landowners as well as conflicts with other services or amenities (B.G.S, 2008b). Extraction is becoming increasingly costly, as the number of prime extraction sites with minimal overburden are being exhausted (A.A.S, 1999a).

2.4.4.1 Aggregate Levy

The Aggregates Levy was introduced in 2002 as a tax upon the extraction of primary materials. By increasing the cost of primary material, the levy aimed to promote the use of secondary and recycled aggregate (A.L.S.F, 2008). Initially set at £1.60 per tonne, it was increased to £1.95 in 2008, and £2.00 in 2009 (H.M.R.C, 2009a).

Proceeds from the levy are invested in the Aggregates Levy Sustainability Fund (A.L.S.F). The A.L.S.F was used to set up W.R.A.P (Waste and Resources Action Plan) to ensure quality of secondary materials, and to educate and assist in overcoming regulatory barriers for their use. W.R.A.P in turn set up the Aggregain resource to provide information on recycled aggregates (W.R.A.P, 2008).

The effectiveness of the levy is constrained by the limited proportion of primary aggregate that can be replaced by alternative materials. Similarly, the levy has had the reverse effect with respect to many wastes. Many quarry wastes, being derived from mineral exploitation, are subject to the levy, creating a market barrier (A.L.S.F, 2008). Many quarry wastes found a market as low priced, low-quality materials. The levy has priced these materials out of the market, resulting in an additional 20 million tonnes of waste per year, presenting a further disposal problem (B.A.A, 2007). This problem has affected the project sponsors, Gallagher (Aggregates) Ltd.

2.5 Waste in the UK

The UK currently generates around 335 million tonnes of waste per year (see figure 2.14). Over 60% arises from construction and demolition, and from mining and quarrying operations. Commercial and industrial activities combined are responsible for 25%, and household waste for a further 9%. Dredging waste accounts for 5%, whilst less than 1% is derived from agricultural activity and sewage treatment (D.E.F.R.A, 2007c).

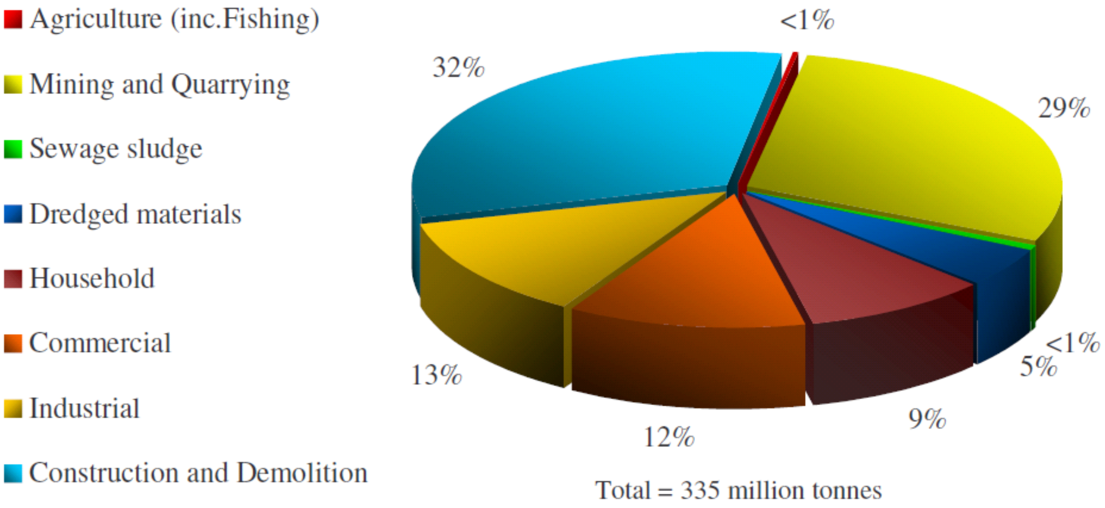


Figure 2.14: Waste generation in the UK (D.E.F.R.A, 2007c)

Waste disposal practices have shifted towards re-use and recycling over the last decade (see figure 2.15). Between 1998/99 and 2002/03 waste production increased from 195 to 221 million tonnes. Over the same period, landfill dependency remained constant at around 100 million tonnes, with the increase accommodated by increased recycling. Around 43% of the waste arising was disposed to landfill.

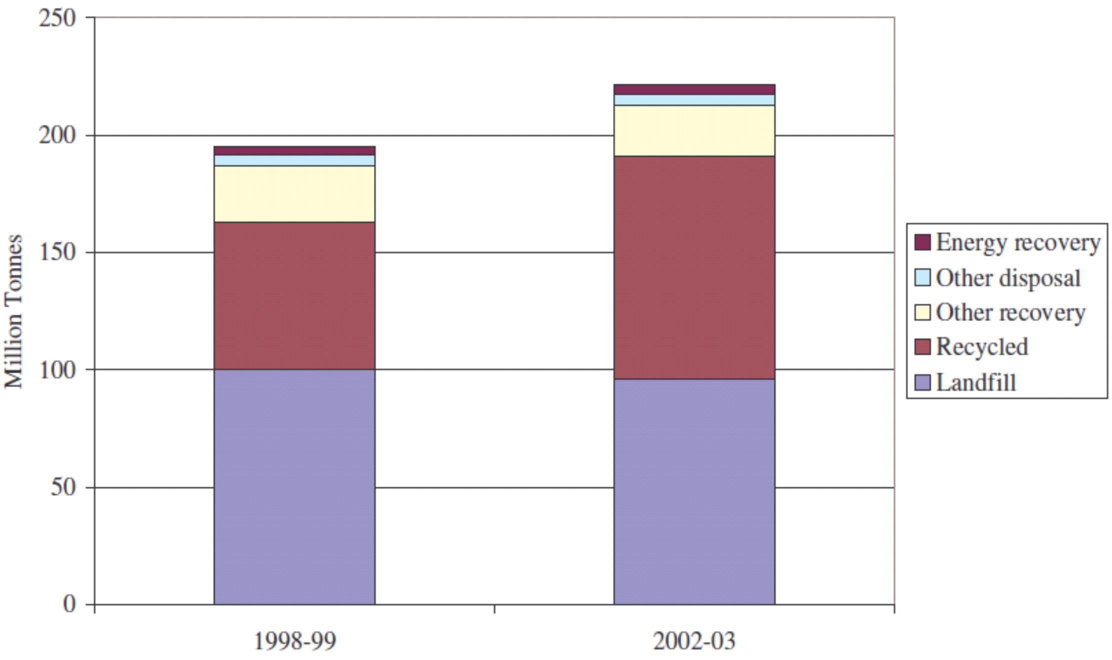


Figure 2.15: Waste arisings by disposal in the UK, 1998 – 2003 (D.E.F.R.A, 2007c).

2.5.1 Waste Regulation

Waste handling, movement, treatment, disposal, and re-use practices must adhere to a series of waste regulations. Waste generated in the UK is broadly classified into three categories; inert, non-hazardous, and hazardous. These classifications are based upon the severity of designated hazardous properties. UK waste practices are primarily covered in several pieces of legislation:

- The Landfill Directive
- The Waste Framework Directive
- The European Waste Catalogue
- The Hazardous Waste Regulations

A flowchart summarising the use of the legislation and the identification of waste is shown in figure 2.16. This process is also summarised in the WM2 (Waste Management 2) guidance published by the Environment Agency.

Inert waste, relates only to those materials listed in the Landfill Directive, including soil, glass, bricks and tiles. These listed wastes can be directly disposed to inert landfill without testing, subject to a visual assessment and checking the relevant documentation. The Waste Framework Directive contains a list of potentially hazardous wastes, and those not identified are deemed non-hazardous. Nearly all household, commercial and industrial waste is listed and should be assessed to determine if it should be designated as hazardous. The European Waste Catalogue is a directory classifying wastes by mode of production, which also separates wastes as hazardous or non-hazardous. Each waste has a unique six-digit identification code, with the first two digits denoting the European Waste Catalogue Chapter (see table 2.6).

Some wastes are listed as ‘mirror entries’, reflecting their tendency to fall into either class. These mirror wastes are classified either way by identifying hazardous properties (see table 2.7), through comparing the chemical composition against a series of thresholds listed in the Hazardous Waste Regulations (O.P.S.I, 2010).

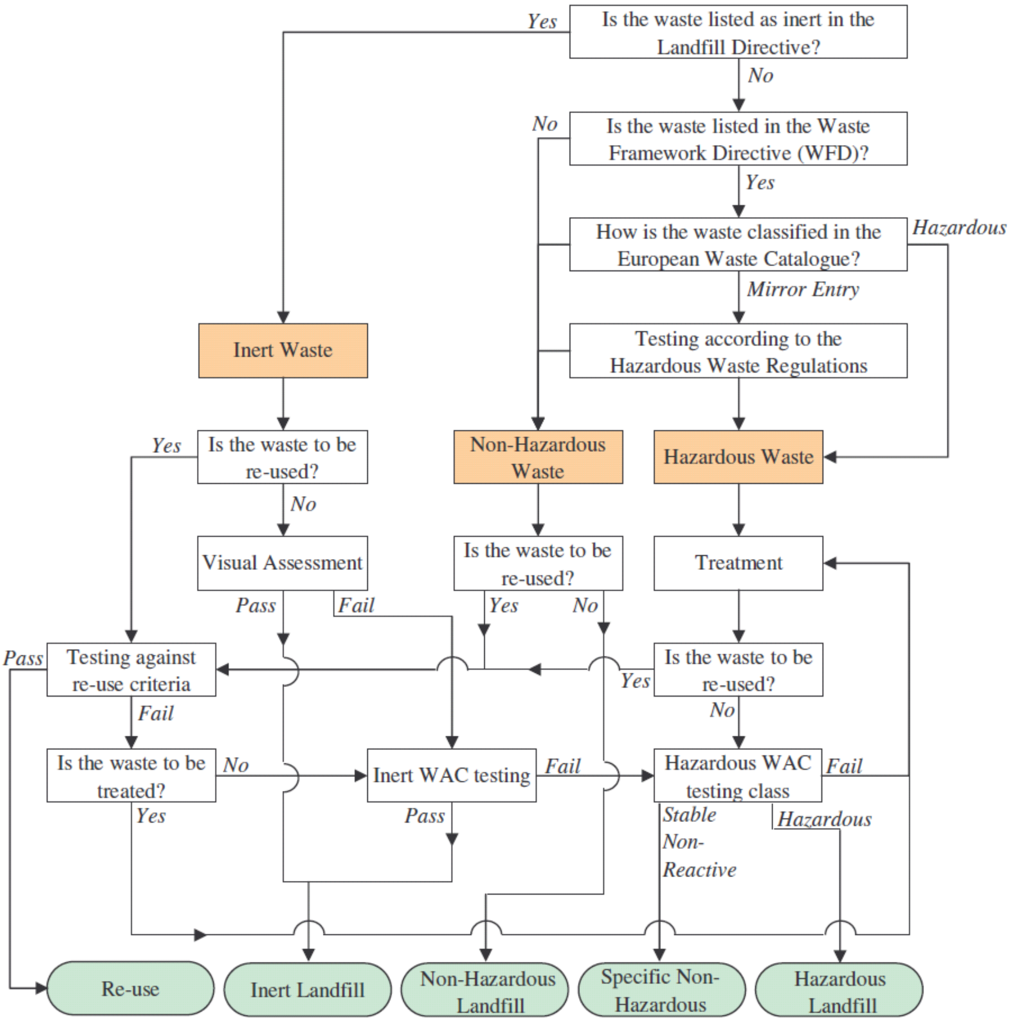


Figure 2.16: Waste management flowchart

Table 2.6: European Waste Catalogue summary

Chapter	Waste Type
01	Exploration, Mining, Quarrying, and Physical and Chemical Treatment of Minerals
02	Agriculture, Horticulture, Aquaculture, Forestry, Hunting and Fishing, Food Preparation
03	Wood Processing and the Production of Panels and Furniture, Pulp, Paper and Cardboard
04	Leather, Fur and Textile Industries
05	Petroleum Refining, Natural Gas Purification and Pyrolytic Treatment of Coal
06	Inorganic Chemical Processes
07	Organic Chemical Processes
08	Manufacture, formulation, supply and use of Coatings, Adhesives, Sealants, Printing Inks
09	Photographic Industry
10	Thermal Processes
11	Chemical Surface Treatment and Coating of Metals
12	Shaping and Physical and Mechanical Surface Treatment of Metals and Plastics
13	Oil Wastes and Wastes of Liquid Fuels
14	Waste Organic Solvents, Refrigerants and Propellants
15	Waste Packaging; Absorbents, Wiping Cloths, Filter Materials and Protective Clothing
16	Wastes not otherwise specified in the list
17	Construction and Demolition Wastes (including excavated soil from contaminated sites)
18	Human and Animal Health Care and/or Related Research
19	Waste Management Facilities, Off-site Waste Water Treatment Plants
20	Municipal (household waste and similar commercial, industrial and institutional wastes)

Table 2.7: Hazardous Waste Regulation Categories

ID	**Hazardous Property**
H1	Explosive: substances which may explode under the effect of flame, shocks or friction
H2	Oxidising: highly exothermic reactions when in contact with other substances
H3	Flammability
H4	Irritant: non-corrosive substances and preparations which, through immediate, prolonged or repeated contact with the skin or mucous membrane, can cause inflammation.
H5	Harmful: limited health risks by inhalation, ingestion or skin contact
H6	Toxic: serious health risks and even death by inhalation, ingestion or skin contact
H7	Carcinogenic: may induce cancer by inhalation, ingestion or skin contact
H8	Corrosive: substances and preparations which may destroy living tissue on contact
H9	Infectious: containing viable micro-organisms or their toxins which cause disease
H10	Teratogenic: non-hereditary congenital malformations by inhalation, ingestion or skin contact
H11	Mutagenic: hereditary genetic defects by inhalation, ingestion or skin contact
H12	Substances and preparations which release toxic gases in contact with water, air or an acid.
H13	Substances and preparations capable of yielding another substance, e.g. a leachate, which possesses any characteristics listed above.
H14	Ecotoxic: substances and preparations which present or may present immediate or delayed risks for one or more sectors of the environment.

Inert and non-hazardous waste can be readily re-used, subject to meeting any risk assessments for the environment in which they are placed. Alternatively, treatment to reduce toxicity may be an option to allow re-use. Treatment of hazardous wastes is now mandatory prior to disposal.

Wastes sent for landfill are tested by comparing water leachate concentrations against Waste Acceptance Criteria (WAC) for the appropriate class of landfill (see table 2.8). Only wastes meeting the criteria for the particular landfill class are permitted to be disposed. In the case of failure, the waste will have to be disposed in a higher landfill class, or treated before re-testing. Only wastes meeting the criteria specified in the Waste Framework Directive, the EWC, or the Hazardous Waste Regulations are permitted to enter a non-hazardous landfill. Hazardous wastes are subjected to WAC assessment to determine if they have lower levels of toxicity and can be landfilled in specially engineered non-hazardous facilities as stable non-reactive wastes, or can only be disposed at a hazardous landfill.

Tax is levied upon waste sent to landfill. The tax was introduced in 1996, and has been increased annually in an attempt to reduce landfill dependency. Inert waste is imposed with an ‘inactive rate’ of £2.50 per tonne, whilst non-hazardous and hazardous rate has an ‘active rate’ of £48 per tonne. Active rate tax will continue to increase by £8 per year until at it reaches at least £72. This increasing economic burden is inspiring interest in new treatment technologies.

Table 2.8: Waste Acceptance Criteria (WAC) for granular wastes at landfill

Component	**Hazardous**	**Hazardous (stable non-reactive)**	**Inert**
TOC (%)	6	5	3
BTEX (mg/kg)	6	Not specified	Not specified
PCBs (mg/kg)	1	Not specified	Not specified
Mineral Oil (mg/kg)	500	Not specified	Not specified
PAHs (mg/kg)	100	Not specified	Not specified
Limit values (mg/kg) for compliance leaching tests			
Arsenic	25	2	0.5
Barium	300	100	20
Cadmium	1	0.1	0.04
Chromium	70	10	0.5
Copper	100	50	2
Mercury	0.4	0.02	0.01
Molybdenum	30	10	0.5
Nickel	40	10	0.4
Lead	50	10	0.5
Antimony	5	0.7	0.06
Selenium	7	0.5	0.1
Zinc	200	50	4
Chloride	25,000	15,000	800
Sulfate	50,000	20,000	1,000
Fluoride	500	150	10
Phenol Index	1	Not specified	Not specified
DOC	1,000	800	500
TDS	100,000	60,000	4,000

2.6 Conclusions

This chapter examined the literature relating to the production of aggregate for construction from waste using an accelerated carbonation technique. This included legislation pertaining to aggregate, accelerated carbonation and agglomeration.

Accelerated carbonation technology (ACT) is a technique to induce rapid reaction between mineral or waste materials with carbon dioxide. ACT is controlled by a number of reaction variables including those affecting the pore structure and permeation of gas into a solid. ACT promotes enhanced physical and chemical properties. ACT can be used for the treatment of wastes and contaminated soils. The application of carbonation to treat certain wastes, primarily municipal solid wastes incineration ashes, has previously been explored. However, the wider use of the technology to treat other wastes from thermal processes has not.

Agglomeration is a technique for increasing the grain size of powdered or granular materials. Grain size enlargement can be achieved by various means including pressure forming, thermal fusing or mechanical agitation. Mechanical agitation by drum or disc pelletising is a technique suited to the agglomeration of ‘heavy’ materials such as those derived from mineral and mining processes. Drum pelletising is controlled by numerous variables, primarily the physical properties of the material, and the operating conditions of the machine. Drum pelletising can be effectively scaled up.

Aggregate usage in construction is increasingly being supplemented by using secondary or recycled materials. Aggregate reserves are diminishing, and new sources must be identified. Lightweight aggregates are commonly manufactured using high temperature, energy intensive processes.

An aggregate product can be manufactured using a pelletising process which employs accelerated carbonation as the binding mechanism. The product will effectively divert waste from landfill and may be able to permanently sequester carbon dioxide. This has previously been explored, and it was found that carbonation and agglomeration are not directly compatible. A study of the variables affecting both carbonation and agglomeration is needed to ascertain the issues involved. As yet, the production of aggregate using a carbonation process on a large scale has not been pursued.

Chapter 3 : Materials and Methods

3.1 Introduction

In the previous chapter, the current state-of-the-art of the key methods of carbonation and agglomeration were reviewed. The relevant legislation pertaining to carbonation including climate change was also examined.

This chapter presents the standard analytical methods used in this work, including x-ray diffraction, x-ray fluorescence, scanning electron microscopy and thermogravimetry. The methods of producing the aggregate and subsequent development of the process are discussed in the later chapters. The materials used in this study are also discussed.

3.2 Materials

Several industrial and commercial residues generated in the UK were sourced for trials with carbonation, and potential for re-use as aggregate. Wastes from quarrying activity, industrial and commercial processes, and domestic sources account for 63% of the total wastes produced. A further 5% is contributed by dredging, agriculture and sewage treatment. Samples of wastes from each of these groups were selected to evaluate the wider applicability of a carbonation treatment process. Construction and demolition waste is readily reused as new building materials, and was not considered for the project.

The wastes are examined for their modes of generation, the issues associated, methods of disposal, and the volumes generated in table 3.1.

Table 3.1: Summary of waste streams examined in this study

Waste	Description	Issues	Current Uses/Disposal	Volume (UK Annual)
Bauxite	Also known as 'Red Mud', is the by-product of the Bayer aluminum manufacturing process (Brunori *et al.*, 2005). Red mud production varies with bauxite grade (0.3-2.5 tonnes per tonne of aluminium) (AL.FED, 2007).	Alkalinity, volume generated creating storage issues (Brunori *et al.*, 2005, Yalcin and Sevinc, 2000).	Mostly stockpiled or landfilled. Proposed re-use in bricks, ceramics and specialized cements and concretes (Kalkan, 2006).	340,000 tonnes aluminium production (I.A.I, 2007).
Biomass Ash	Ash from the incineration of the pressed plant fibre residue (Rape Cake) after oil extraction. Wood by-products and biofuels are increasingly being used in small scale power stations and local district heating schemes (Pitman, 2006).	Alkalinity & handling problems (Pitman, 2006). Applying copious amounts to soil as a fertilizer can have a deleterious effect (Gorecka *et al.*, 2006).Disposal issues with increasing use of biomass as fuel.	Primarily destined for landspreading. Use of wood ash as a cement replacement was investigated by Abdullahi, (2006).	31,000 tonnes (estimate) (McKay, 2003)
Cement Kiln Dusts	Cement kiln dusts (CKDs), including bypass dusts (CBDs) consist of alkali-rich particulate matter removed from cement kiln exhaust gasses (Sreekrishnavilasam *et al.*, 2006, Singh *et al.*, 1995). Production of one tonne of cement produces between 6,000 to 14,000m^3 of dust-laden air containing 0.7 to 800g/m^3 (Buchwald and Schulz, 2005).	Highly variable composition, containing calcined and uncalcined feed materials along with cement clinker and condensed alkali compounds (Konsta-Gdoutos and Shah, 2003). CKD is regarded as being a health hazard (Baghdadi *et al.*, 1995).	Traditionally landfilled, but are increasing being recycled back into the cement feed (Ryou, 2004, Taha *et al.*, 2002). Also used in solidification/stabilisation applications, and for partial cement replacement in concrete (Udoeyo and Hyee, 2002, Heikal *et al.*, 2002).	110,000 tonnes (B.C.A., 2004)
Clinical Incineration Ash	Ash from the incineration of hazardous medical materials (human tissue, dressings, sharps, drugs etc) in specialized incinerators at temperatures exceeding 1000°C (Blenkharn, 2005).	Heavy metal content of the ash, which may include arsenic, mercury, nickel, chromium, cadmium and lead (Delay *et al.*, 2001).	Bottom and fly ashes are classified as hazardous waste and sent to landfill (Wheatley and Sadhra, 2004).	400,000 tonnes (C.I.W.E.M., 2001).
Metal Dust	Metallic dust obtained by blast cleaning of metal.	Heavy metals including lead.	Disposed to hazardous landfill.	Not available
MSWI Bottom Ash (-BA) and Fly Ash (-FA)	Municipal waste generation is increasing annually by 3-4%. Incineration as a method of dealing with the additional waste is increasing as dependence upon landfill decreases. The process heats the waste to 850°C, generating bottom ashes (residue remaining in the incinerator) consisting 25-30% of the original mass, and fly ash (airborne particulate matter collected in the emissions filtration system), 3% of the original mass (C.I.W.E.M, 2007, E.A, 2002).	Bottom ash is highly variable, and contains metals (including heavy metals), glass, ceramics and unburnt material (Arickx *et al.*, 2006, Bethanis *et al.*, 2002). It is classified as non-hazardous. Fly ashes are highly alkaline and contain much higher concentrations of heavy metals. The fly ash is considered hazardous, therefore requires pre-treatment before disposal (Ecke, 2003).	Fly ashes are landfilled. 38% of bottom ashes are landfilled, with the remainder used as substitute aggregate and bulk fill (E.A, 2002).	727,000 tonnes of bottom ash, 112,000 tonnes fly ash (H.O.C, 2002).

Quarry Wastes	These include a variety of residues (sands, silts, dusts etc) or other non-valuable materials produced after the extraction and processing of material to form mineral products (Mitchell *et al.*, 2004).	The aggregates levy has depressed the market in low-quality fill materials, rendering most quarry fines unsaleable (Goodquarry, 2007). Quarry silts and sludges are largely useless.	44.6% of all construction, demolition and excavation waste generated was recycled, the rest disposed to landfill or used to backfill quarry voids.	22.8Mt (waste), 53.9Mt (fines) (D.E.F.R.A, 2007a).
Paper Sludge Ash (PA)	Large volumes of wastewater are generated during the production of paper from virgin pulp and recycled fibre. The dewatered sludge contains residual fibres, a mixture of fillers (kaolin, calcite), and chemicals (bleaching agents, de-inking compounds) (W.R.A.P, 2007a, Boni *et al.*, 2004, D.O.E, 1996). The sludge is often incinerated prior to disposal.	Sludges may contain a variety of chemicals and traces of heavy metals. Incineration ashes are also highly alkaline (Xiao *et al.*, 1999).	Sludge disposal by landspreading (unlikely to continue in the UK), incineration or landfilling (W.R.A.P, 2007b). Potential use in s/s applications, lightweight aggregate, block manufacture and cement replacement (Mozaffari *et al.*, 2006, Liaw *et al.*, 1998).	1 Mt (sludge) (ENDS, 2005).
Pulverised Fuel Ash (PFA)	Coal-fired power stations burn pulverized coal in a fluidized bed furnace. Agglomerated particles of coal fall through the boiler as furnace bottom ash (FBA), comprising 20% of the total waste. Lighter particles are carried by the exhaust gases and collected by electrostatic precipitators in the flue stack (80% of total waste) (D.O.E, 1995a).	Both PFA and FBA are considered non-hazardous (C.I.R.I.A, 1999).	PFA has long been used in concrete (B.R.E, 1991), as a construction fill, for block manufacture, and as a raw material for the production of lightweight aggregate (e.g. aardelite, lytag) (A.A.S, 1999b). About 50% of PFA is landfilled.	FBA: 1Mt – used in construction. PFA: 5 Mt, 2.3 available (D.C.L.G, 2007).
Sewage Sludge Ash (SSA)	21% of the UK's sewage sludge is incinerated, yielding 300-400kg of ash per tonne of dry sludge (Cyr *et al.*, 2007).	Chemical composition of the ash is highly variable and includes arsenic, cadmium, mercury, nickel, chromium, copper, lead, zinc, iron, aluminium and free cyanide (Lapa *et al.*, 2007).	The ash is landfilled (Cheeseman *et al.*, 2003). Potential as a partial replacement in cement, bricks and ceramics and as sintered lightweight aggregate (Gunn *et al.*, 2004, Cheeseman and Virdi, 2005, Chiou *et al.*, 2006).	100,000 tonnes (Gunn *et al.*, 2004)
Steel Slag Wastewater Sludge	Steel manufacture produces a diverse range of wastes including slags, dusts, fly ashes and wastewater sludges. Manufacture of one tonne of steel produces 2-4 tonnes of waste (Das *et al.*, 2007).	Wastewater sludges may contain lead, chromium, cadmium, zinc, oil and grease (World Bank Group, 1998).	Slags have reuse potential in cement, and as aggregate (Dunster, 2001). Sludges are stabilized and sent to hazardous landfill (Group, 1998)	1,456,000 tonnes (Corus, 2006)

3.3 Methods

3.3.1 X-Ray Diffraction

X-Ray Diffraction (XRD) is a technique for analysing crystalline phases in solid materials. XRD can be used as a tool for measuring carbonation, as material reactivity is influenced its phase composition, and the reaction induces changes in the crystalline minerals.

Pressed powder tablets were prepared from the carbonated and uncarbonated wastes. The wastes were ground to less than 40 microns using an agate mortar and pestle. Powders were pressed into plastic XRD sample holders using a glass slide to ensure a smooth surface finish.

Analysis was performed on a Siemens D500 diffractometer, fitted with a Siemens K710 generator running at 40kV voltage and 40mA current. The tablets were analysed between 5-65° 2θ in 0.02° steps each lasting 2.4 seconds.

Diffraction traces were interpreted using DIFFRAC^{plus} EVA software (Bruker AXS). The X-ray fluorescence data import function in EVA was used to filter the phase database to aid identification. As carbonation results in both the consumption and the growth of new minerals, a shift in peak heights of the phases can be observed. DIFFRAC^{plus} EVA allows one trace to be subtracted from another, hence any differences in peak heights can be readily observed. This was used to assess any changes.

3.3.2 X-Ray Fluorescence

X-Ray Fluorescence (XRF) is used to measure the elemental composition of materials. Material composition is an important indicator of carbonation reactivity, and aids the characterisation of materials using XRD and scanning electron microscopy.

XRF analysis was conducted on fused beads made from the wastes. Three representative samples of waste was obtained by cone and quartering, and were dried at 105°C and calcined at 950°C in a muffle furnace. Loss on ignition (LOI) was then calculated using equation 3.1:

$$LOI(\%) = \frac{Mass_{105°C} - Mass_{950°C}}{Mass_{105°C}} x100 \qquad (3.1)$$

A precision balance was used to weigh 1g of calcined sample and 7g of the flux (to ±0.0001g) into a platinum crucible. A mixed flux containing 34% lithium tetraborate and 66% lithium metaborate was used (XRF Scientific Ltd). Two drops of lithium bromide were added as a non-stick agent. The mixed components were heated to 1050°C for fifteen minutes, swirled periodically to ensure complete melting and homogeneity, and poured into the platinum casting dish preheated by placing in the furnace. The dish was removed from the furnace and the bead rapidly cooled in a stream of hot air. This prevented crystallisation from the melt, but could not be so fast as to cause differential cooling of the bead which resulted in cracking. Metallic-rich materials were fused with the addition of an oxidizer (lithium nitrate). In these instances, the flux content was reduced to account for the dilution caused by adding the oxidiser.

Twelve standards were prepared as fused beads and analysed to create calibration curves for quantitative analysis. These comprised; cement standards (NIST 633, 635, 638, 1881, 1882, 1883), rock standards (NIST 70a; NCS 73301, 73302, 73303), and coal ash standards (NCS FC82012, FC82013).

The wastes analysed contained unusually high concentrations of elements typically present only as traces in the commercial standards, e.g. phosphorus. To achieve the necessary calibration range, in-house standards were prepared from laboratory grade reagents (BDH AnalaR). Sodium and phosphorus standards were prepared from sodium hexametaphosphate, copper and magnesium and zinc from oxide powders, manganese from manganese (IV) oxide, and lead from lead (II) oxide.

A Philips LW1400 X-ray fluorescence spectrometer was used to analyse the fused beads. The x-ray source was a rhodium tube operating at 40kV accelerating voltage and 60mA current. The scintillator and gas-flow detectors were used in tandem to maximise the signal from both heavier and lighter elements respectively. Collimators and beam mask were set to coarse to maximise x-ray transmission between source and detector.

Data collection and interpretation was conducted using XRFWIN software. Qualitative scans were initially performed on the standards to identify the positions of the elements, and the corresponding background positions.

Elemental peak and background 2-theta positions identified from the scans were used as the analysis points to quantify the concentrations in the standards. Detector count times were calculated according to equation 3.2:

$$\frac{S_p}{N_p} = \frac{1}{\sqrt{T}} x \frac{1}{\sqrt{R_g} - \sqrt{R_b}} \qquad (3.2)$$

Where S_p is the standard deviation, N_p is the net peak intensity, R_g is the gross peak count, R_b is the background count, and T is total time. The count times required increase exponentially as the standard deviation becomes equivalent to the peak height. At higher peak intensities (when R_g/R_b equals greater than 10), the effect of the background becomes negligible.

Fundamental parameters correction was applied to the calibration. Calibration drift was corrected for using the software by running the same standard at the beginning of each run. The quality of calibration was then checked by back-analysing the drift standard as an unknown sample, and comparing the result to the certificate.

3.3.3 Particle Size Distribution

Particle size distribution is one of the controlling variables for carbonation, and also has an influence upon the pelletising process employed in later chapters. The particle size distribution of ashes was measured by laser diffraction analysis (Malvern Mastersizer MS2000). Each sample was prepared in triplicate, and analysed twice in each run.

The Mastersizer MS2000 was fitted with a wet sample delivery module (Hydro MU) which transports the material in suspension (in water), and a dry module (Scirocco 2000) which carries the sample in a stream of air. Many of the wastes studied contained lime and other minerals which hydrate in water. These were analysed with the dry module. Wastes which were in the form of pastes or sludges were suited to analysis using the wet delivery module.

Materials analysed using the wet delivery module were soaked in water for 24 hours and occasionally agitated with a glass rod to encourage them to disperse. Immediately before analysis, the dispersed sample was agitated by vigorous stirring, and added drop by drop to the sample holder on the wet delivery module, until the degree of laser obscuration was between 10 and 20%. The default circulating pump speed of 2500rpm was used. Given that the software had no specific settings for the materials analysed, the ‘general purpose’ instrument settings were used. This set the refractive index (RI) of the material to 1.520, and the RI of water to 1.330.

Materials for dry analysis were prepared by oven drying at 40°C. Samples of 200 grams were loaded into the feed hopper on the delivery module. The target laser obscuration was achieved by balancing the vibration rate of the hopper (controlling the feed of material), and the air pressure in the hose connecting the delivery module to the analyser (controlling the speed of transit of particles through the analyser).

3.3.4 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a technique for the study of the microstructural and chemical composition of materials. The structural changes induced by carbonation can be readily identified using SEM analysis.

Fragments of material were cast as vacuum-impregnated resin blocks. The fragments were placed at the base of 30mm moulds coated with release agent. Liquid epoxy resin (Logitech epoxy 301) was poured into the mould to cover half of the fragment. The mould was placed in a desiccator connected to a vacuum pump, and the air was removed. When bubbles ceased to rise from the sample, the vacuum was released. More liquid resin was added to completely cover the fragment, and the vacuum was applied a second time. After releasing the vacuum, the blocks were cured for 24 hours at room temperature and pressure.

The block face was ground to expose the embedded fragment using grit paper (Buehler silicon carbide grit paper 300, 600, 1200). This was followed by successive polishing with 3, 1 and 0.25μm diamond paste (Struers DP Sticks) on silk cloths (Buehler Metcloth), using an alcohol based lubricant (Struers DP Yellow) on an Engis MK2a polishing machine. The polished blocks were coated with carbon using an Edwards Carbon Coater. Coated blocks were stored in sealed plastic chambers containing a silica gel desiccant under a continuous flow of nitrogen to prevent further hydration and carbonation.

Electron microscope analysis was performed on a JEOL JSM-5310LV microscope equipped with an Oxford Instruments Energy Dispersive Spectrometer (EDAX). The electron operated at a voltage of 20kV, and the sample surface was maintained at a working distance of 15mm from the detectors to provide a balance between high resolution and depth of field. Images of the blocks were taken using the backscattered electron (BSE) detector, coupled with chemical analysis using the EDAX. Oxford ISIS software was used for image acquisition and chemical analysis.

3.3.5 Trace metal analysis

Trace metals are a key indicator of the toxicity of waste materials. Total trace metal content is important for comparison to leaching behaviour, as it provides an indication of the mobility of the metals, and the maximum long-term release.

Three samples were obtained by cone and quartering. The metals were extracted by acid digestion according to US EPA 3050B using AnalaR grade nitric and hydrochloric acids (BDH). A certified reference material (contaminated soil, CRM023-050, RTC Ltd) was used to check the degree of metal recovery.

The digests were analysed by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) on a Perkin Elmer Optima 4300DV. The instrument had the ability to analyse the spectroscopic signature using a radial or axial view. During initial setup, the optimum torch viewing position was set by running calibration solutions to align the system. After alignment, a multi-element stab solution was used to check the precision of the system.

Five-point calibration curves were created by analysing standards prepared from single element solutions (BDH SpectrosoL 1000mg/l). Standards were prepared containing 0, 1, 5, 10, and 20ppm of As, Ba, Cd, Cu, Cr, Hg, Mo, Ni, Pb, Sb, Se and Zn. The standards were acidified to achieve a 2% nitric acid solution. The metals analysed were those specified in the UK Landfill Waste Acceptance Criteria (WAC). The calibration range reflected the optimum working range of the instrument.

The wavelengths of peak spectral intensity for the elements were manually adjusted by interpreting scans of the measured signal. The optimum wavelengths are shown in table 3.2.

Detection limits for the elements were measured by repeatedly running a blank solution through the system to determine precision (see table 3.3)

Three certified reference solutions (Perkin Elmer Pure Optima Family multielement standard, Perkin Elmer Pure Instrument Calibration Standard 4, SPEX Certiprep ICP Test Mix CALMIX3-500CA) were analysed to check the accuracy of the initial ICP calibration and after every 10 samples to monitor drift.

Digests were diluted if necessary to ensure that the concentrations of metals in solution fell within the calibration range. Each digest solution was analysed twice; once using an axial spectral view to accurately measure elements in lower concentrations, and again using a radial view for those in higher concentrations. Due to the high concentrations of metals in the digests, the ICP system was flushed with a 2% nitric acid solution for 60 seconds between each sample.

Table 3.2: Element analysis wavelengths

Element	Peak Analysis Range
As	188.979
Ba	455.403
Cd	228.802
Cr	267.716
Cu	324.752
Hg	253.650
Mo	202.031
Ni	231.604
Pb	220.353
Sb	217.582
Se	196.026
Zn	213.857

Table 3.3: Element detection limits

Element	Detection Limit (ppm)
As	0.018
Ba	0.03
Cd	0.007
Cr	0.006
Cu	0.003
Hg	0.020
Mo	0.018
Ni	0.01
Pb	0.024
Sb	0.008
Se	0.016
Zn	0.003

3.3.6 Leaching

Levels of cations and anions in the leachates from wastes are regulated in the landfill Waste Acceptance Criteria (WAC), and ultimately determine the disposal or re-use method.

Materials were leached in triplicate according to BS EN 12457-3. BS EN 12457-3 is a water leaching method for granular materials, which is stipulated as the method required for WAC assessment.

Samples must be of known moisture content and reduced to pass a 4mm sieve. These samples were obtained by cone and quartering, and oven dried at 105°C to remove all moisture. The material was placed in a clean nitric acid washed plastic bottle, along with two times its dry solid weight of water (minus any water present in the sample), achieving a liquid to solid ratio of 2 or l/s2. In each batch, three blanks were prepared by placing deionised water in bottles, to measure any contamination introduced during the method. For six hours the bottles were continuously rotated on an end-over-end shaker. Once allowed to stand and solid had settled, the liquid was filtered using Puradisc 0.2µm syringe filters into acid washed vials. The remaining sludge in the bottle was recombined with eight times the dry solid weight in water (liquid to solid ratio of 8 or l/s8), and rotated for 18 hours. The solution was then filtered. The two samples were each split into two portions. One was acidified to 2% nitric acid and the other used for pH measurement and ion chromatography analysis. Both samples were refrigerated until analysed.

The leachates were analysed by ICP-OES according to 3.3.5. The resulting concentrations of the l/s2 and 8 solution (in mg/l) were added together and converted to mg/kg for direct comparison to the WAC regulations.

The leachates were also analysed for chloride and sulfate content salts using a Dionex 4000i ion chromatography analyser. A four-point calibration using 0, 1, 10, and 15ppm standards was used. Standards were prepared from 1000mg/l stock made with analytical grade sodium sulfate and sodium chloride. The highest standard was run as an unknown to check the calibration and to re-calibrate after every 10 samples.

3.3.7 Optical Microscopy

Optical microscopy provides information on the structure and mineralogy of materials. The optical properties of minerals can be used to give positive identification when analysis by SEM, for example, can only yield morphological and bulk chemical information.

Thin sections were prepared by Keele University. Sections were ground to 30µm, and polished to a surface finesse of 0.25µm.

The thin sections were analysed using a Nikon petrological microscope (Model Optiphot-Pol), fitted with a transmitted light-box. Images were taken using a 12 megapixel digital scanning camera (Kontron ProgRes 3012, manufactured by Kontron Electronik GmbH, Munich, Germany) with the ProgRes software plugin for Adobe Photoshop.

3.3.8 pH

pH of solid materials was measured according to BS 1377-2. Samples of material were air dried and crushed to pass a 2mm sieve. Three samples of thirty grams were each mixed with 75 grams of water (l/s 2.5) and allowed to stand for a minimum of eight hours. The solution was analysed using an electronic pH meter (Hanna HL4521). Four pre-prepared standards at pH 4, 7, 10, and 13 (VWR Ltd), were used to calibrate the meter. Each sample was analysed at least three times until a consistent reading within 0.05 was achieved.

3.3.9 Thermogravimetry

Thermogravimetric analysis (TGA) is used to measure changes in the mass of a material as a result of heating or cooling.

The samples were obtained by cone and quartering, dried at 105°C, and crushed to pass a 40µm sieve. Samples of 40mg were compacted into platinum crucibles, and loaded onto the TGA microbalance. Analysis was conducted using a Stanton-Redcroft STA-780 Series analyser fitted with a Picolog data logging system running Picolog for Windows software.

The furnace temperature was raised from 20 to 1000°C at a rate of 20°C/min. An inert atmosphere was preserved in the furnace chamber by passing 50cc/min of nitrogen. A logging interval of 20 seconds was used. Accuracy was checked by weighing the crucible before and after heating, and comparing the mass change to that measured by the TGA.

Analysis for the purposes of measuring carbonation was primarily concerned with quantifying the amount of Portlandite and calcium carbonate. Portlandite decomposes between 430 and 590°C (Liodakis, 2005), whilst calcite decomposes between 670°C and 850°C (Moropoulou, 1995). The thermogravimetric events were quantified according to the following decomposition reactions:

$$CaCO_3 \xrightarrow{Heat} CaO_{(solid)} + CO_{2(gas)} \qquad \text{(Calcium Carbonate)} \qquad (3.3)$$

$$Ca(OH)_2 \xrightarrow{Heat} CaO_{(solid)} + H_2O_{(gas)} \qquad \text{(Portlandite)} \qquad (3.4)$$

Mass lost during the thermal event can be translated into a weight percentage for the particular phase using equation 3.5:

$$\%Weight = RMMx \frac{LOI}{RMM_{reactant} - RMM_{product}} \qquad (3.5)$$

Where *%Weight* is the percentage of the material composed of the phase concerned, $RMM_{product}$ is the relative molar mass of the product of the thermal event, $RMM_{reactant}$ is the molar mass of the phase prior to the thermal event, and LOI is the changes in weight in % as a result of the thermal event.

Thermal decomposition does not differentiate between the Portlandite or calcium carbonate formed as a result of hydration or carbonation from that naturally present in the material (Sweeney, 2001). The natural Portlandite and carbonate content of the untreated material was measured and subtracted from that in the treated material, according to equation 3.6:

$$\%Weight_{phase} = \%Weight_{after} - \%Weight_{before} \tag{3.6}$$

Where $\%Weight_{phase}$ is the percentage by weight of a phase present in the material as a result of hydration or carbonation, $\%Weight_{after}$ is the percentage by weight of a phase present in the material after treatment, and $\%Weight_{before}$ is the percentage by weight of a phase present in the material before treatment.

3.4 Variability and Experimental Error

Wastes are by definition variable materials since they are not produced to any set standards or specifications. In an attempt to account for the heterogeneity of the materials, representative samples of material were taken by cone and quartering. This process was performed in triplicate, to provide three samples for analysis.

The analytical results were combined to calculate the mean value, which is presented in the figures and tables. The error margin was calculated as the interquartile range. The lower limit was calculated as the 25th percentile of the spread of data as the lower limit, and as the 75th percentile as the upper limit.

3.5 Conclusion

This chapter outlined the analytical methods used in this research.

The degree of reactivity of a material with carbon dioxide is determined by its chemical composition. X-ray fluorescence was used to measure the elemental composition of materials. Carbonation affects the mineralogy of a material, and this was measured by x-ray diffraction. Minerals participating can be quantified by thermal decomposition, which was conducted using a thermogravimetric analyser. The changes in mineralogy are accompanied by alterations to the microstructure of the material. These were analysed using an optical microscope and a scanning electron microscope.

Both carbonation and pelletising are affected by the particle size distribution of the material. Given that the size of particles were too small for conventional sieves, a laser diffraction system was used.

Wastes are leached, and the results compared to landfill regulation to determine the level of risk associated with them. Accordingly, the specified leaching test was used for the analysis of the wastes and any products derived from them.

Chapter 4: Accelerated Carbonation of Wastes

4.1 Introduction

Waste production and management is tightly regulated through national and international legislation. Hazardous waste is a major issue, and must be treated before either disposal or re-use. The UK is heavily dependent upon landfill as a means of disposal. However, taxation on landfilling is increasing to encourage recycling and re-use of waste, and the development of new technologies.

Accelerated carbonation can be used as a rapid-curing technique for cementitious systems. More recently, the technology has been adapted for the treatment of industrial wastes and contaminated soils. The process also sequesters carbon dioxide gas in solid carbonate, promoting retention of certain contaminants through physical solidification of the material, and chemical stabilization. Studies have focused upon the treatment of individual wastes, but an overarching comparative study of a range of thermal wastes has yet to be carried out. Similarly, whilst carbonation constitutes a potential treatment method for many wastes, a study comparing the properties of the treated wastes against the regulatory criteria has not been carried out in many cases.

This chapter examines the use accelerated carbonation to treat thermal process wastes. The suitability for treatment was assessed by measuring the reactivity of wastes with carbon dioxide. Those reacting with carbon dioxide were examined for the effects of carbonation upon the crystalline phase composition, leaching behaviour and microstructure. The leaching results are compared against European landfill criteria to evaluate the effectiveness of accelerated carbonation to reduce toxicity and facilitate cost-effective disposal and potential re-use.

4.2 Materials and Methods

4.2.1 Materials

The investigation focused upon thermal wastes as these are commonly reactive with carbon dioxide since high temperature processes can lead to the formation of reactive minerals (Li *et al.*, 2007, Fernandez-Bertos *et al.*, 2004). The wastes examined were bauxite, biomass ash, cement kiln dust (CKD), cement bypass dust (CBD), clinical incineration ash, municipal solid waste incinerator bottom ash (MSWI-BA), municipal solid waste incinerator fly ash (MSWI-FA), paper ash (six materials from different producers), pulverised fuel ash, sewage sludge ash (SSA), steel wastewater sludge, and wood ash. Portland Cement (CEM1) was used as a reference material.

4.2.2 Methods

4.2.2.1 Waste Preparation

The wastes were primarily in the form of loose dry powders (see table 4.1 and figure 4.1). MSWI-BA was a mixture of ash along with fragments of metal and glass. These were separated, and the remaining ash used in the experiments. Biomass ash, bauxite and steel wastewater sludge contained hardened lumps, and were dried at 105°C (according to British Standard BS EN 1377-2 (1990)), before crushing to pass a 125μm sieve. The remaining wastes were dried at 105°C without any further preparation.

4.2.2.2 Waste Treatment by Carbonation

A high pressure carbonation method was used to treat the thermal wastes. The wastes were carbonated in stainless steel reaction chamber receiving pressurised gas from a cylinder (see figure 4.2).

Table 4.1: Thermal wastes studied

Waste	Description	Moisture Content (% by weight)
Bauxite	Moist rubble-like materials ranging from dust to angular pieces several centimeters in diameter.	8.6
Biomass Ash	Predominantly fine grey ash with fragments of carbonized matter	4.3
Cement Bypass Dust (CBD)	Fine flour-like dust	0.5
Cement Kiln Dust (CKD)	Fine flour-like dust	0.7
Clinical Incineration Ash	Predominantly glass and metal fragments including sharps and needles, with hardened lumps of ash	6.8
MSWI Bottom Ash	Coarse ash containing glass and metal fragments	5.9
MSWI Fly Ash	Fine flour-like ash	0.3
Paper Ash 1	Dry gritty ash	0.1
Paper Ash 2	Dry gritty ash	0.3
Paper Ash 3	Fine ash comprising a mixture of bottom and fly ash from a fluidised bed incinerator	0.8
Paper Ash 4	Granular/fine bottom ash from a fluidised bed incinerator.	0.2
Paper Ash 5	Regular sized white beads; spent fluidised bed sand.	0.1
Paper Ash 6	Fine flour-like ash; APC residue	0.6
Pulverised Fuel Ash (PFA)	Wet gritty powder	0.6
Sewage Sludge Ash (SSA)	Gritty grey ash	0.6
Steel Sludge	Moist metallic paste	13.4
Wood Ash	Granular organic-rich powder	12.7

Bauxite
Biomass Ash
CBD
CKD
Raw Clinical Ash
Clinical Ash
Raw MSWI-BA
MSWI-BA
MSWI-FA
Paper Ash 1
Paper Ash 2
Paper Ash 3
Paper Ash 4
Paper Ash 5
Paper Ash 6
PFA
SSA
Steel Sludge
Wood Ash

Figure 4.1: Thermal residues tested for accelerated carbonation

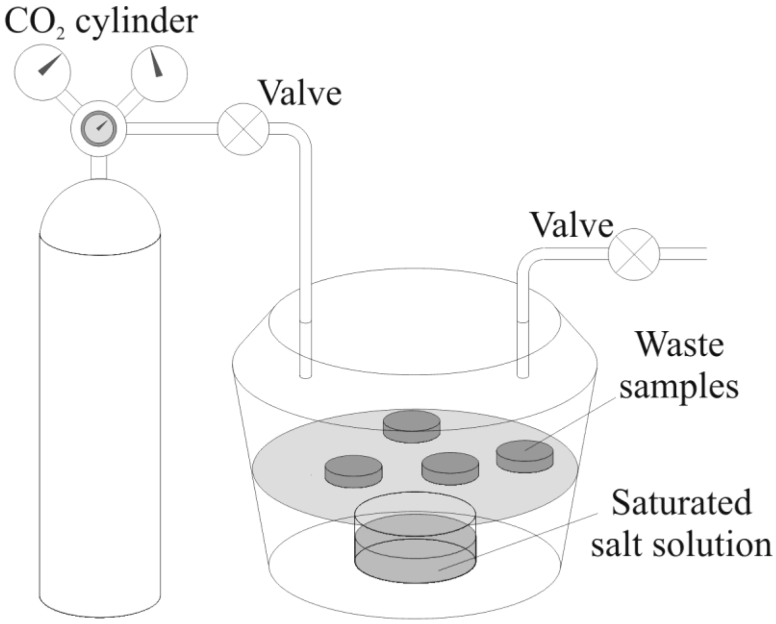


Figure 4.2: Pressurised carbon dioxide reaction chamber

Fifty gram portions of waste were mixed to a water/solid ratio (w/s) of 0.2 in glass beakers. A water/solid ratio of 0.2 has previously been determined as the optimum for the carbonation of thermal wastes (Gunning, 2006). The samples of waste were placed inside the chamber, and the pressure was adjusted and maintained at the optimum of 2 bar (Barnard *et al* 2005). By opening the exhaust valve for 10 seconds, carbon dioxide was allowed to flow through the chamber to purge any air. Humidity inside the chamber was maintained at the optimum for carbonation at 65% using a saturated sodium chloride solution (Russell *et al.*, 2001, Shaffique *et al.*, 1998). After 24 hours, the beakers were removed and placed in a drying oven at 105°C until they reached constant weight. The beakers were cooled in a desiccator, and the contents removed and crushed to pass a 125µm sieve. A ten gram sub-sample was taken to measure the carbonate content. The remaining material was re-weighed and mixed with water to w/s 0.2, and process repeated, until no further increase in carbonate content was measured. All samples were prepared in triplicate.

4.2.2.3 Measuring carbonation

The amount of reaction with carbon dioxide occurring in the wastes was measured by thermogravimetry, as detailed in section 3.3.9.

4.2.2.4 Analysis of materials

The wastes were analysed for crystalline phase composition using x-ray diffraction (section 3.3.1), elemental composition by XRF (section 3.3.2), trace metal content (section 3.3.5), and release of contaminants by leaching (section 3.3.6) before and after carbonation.

4.3 Results

4.3.1 Carbon dioxide uptake

Table 4.2 shows the maximum carbon dioxide attained for each waste after repeated cycles of carbonation and grinding, together with the pH before and after carbonation.

Table 4.2: Carbon dioxide uptake of wastes (error margins expressed as interquartile ranges)

Waste	Maximum CO_2 Uptake (%)	pH	
		Before Carbonation	After Carbonation
CEM1	29.6±0.3	12.8±0.2	9.4±0.3
Bauxite	0±0	9.1±0.2	No change
Biomass Ash	0.6±0.1	10.6±0.4	9.9±0.4
Cement Bypass Dust (CBD)	25.5±0.6	12.8±0.1	11.4±0.5
Cement Kiln Dust (CKD)	9.6±0.4	13.1±0.2	11.1±0.3
Clinical Incineration Ash	0±0	9.9±0.3	No change
MSWI Bottom Ash	4.4±0.5	12.4±0.1	9.0±0.2
MSWI Fly Ash	6.6±0.8	11.0±0.2	8.3±0.4
Paper Ash 1	10.4±0.4	12.7±0.1	9.9±0.2
Paper Ash 2	11.9±0.3	12.6±0.1	12.2±0.3
Paper Ash 3	16.4±0.4	13.1±0.3	11.5±0.5
Paper Ash 4	24.6±0.5	12.9±0.2	11.0±0.2
Paper Ash 5	24.9±0.6	12.9±0.2	10.5±0.3
Paper Ash 6	26.4±0.7	12.9±0.1	9.3±0.2
Pulverised Fuel Ash (PFA)	0±0	9.5±0.1	No change
Sewage Sludge Ash (SSA)	0±0	8.2±0.1	No change
Steel Sludge	0±0	8.9±0.2	No change
Wood Ash	7.5±0.4	13.4±0.3	10.9±0.4

Paper ashes and cement dusts were amongst the most reactive materials identified. Uptake for these materials varied from 9.6 to 26.4% by weight. Many of the wastes had highly alkaline pH, which exceeded the corrosivity threshold of 11.5 according to the Hazardous Wastes Regulations. Carbonation partially neutralised pH, with the result that the majority of the wastes were no longer corrosive. Accordingly, only the wastes reacting with carbon dioxide were studied further for the effect of carbonation treatment upon leaching.

The exothermic reaction resulting from the hydration of lime and carbonation elevated the temperature inside the reaction chamber. This also resulted in the evaporation of water from the samples, which condensed on the walls of the chamber.

4.3.2 Elemental Composition and Mineralogy

The elemental compositions of the wastes are shown in table 4.3, and mineralogies in table 4.4.

Bauxite was composed of nearly 80% aluminium, primarily as the mineral gibbsite ($AlOH_3$). The 13.6% present as iron occurred as a combination of hematite (Fe_2O_3) and goethite (FeO(OH)). Biomass ash was composed of 36% phosphorus, 24% calcium, and 21% potassium, which together formed a mixture of calcium-potassium phosphates ($KCaPO_4$) and the mineral whitlockite ($(Ca_9MgFe)(PO_4)_6PO_3OH$). CKD and CBD shared a similar composition, albeit the latter had a higher proportion of calcium, and a lesser amount of sulfur. The resulting phase composition was of calcite ($CaCO_3$), gehlenite ($Ca_2Al(AlSiO_7)$), portlandite ($Ca(OH)_2$), quartz (SiO_2), and anhydrite ($CaSO_4$), with CKD containing addition sulfur bearing hauynite ($(Na,Ca)6Al_6Si_6O_{24}(SO4)$) and calcium sulfate hydrate ($CaSO_4.0.6H_2O$). Clinical ash contained aluminium, calcium, sodium, titanium and sulfur as anhydrite, calcite, gypsum ($CaSO_4.2H_2O$), halite (NaCl), and perowskite ($CaTiO_3$). MSWI-BA and MSWI-FA were comparable with around 15% aluminium, 32-33% calcium, but MSWI-BA contained 23% more sulfur, whilst MSWI-FA was composed of 27% more silicon. Anhydrite, portlandite, gehlenite, bassanite ($2CaSO_4.(H_2O)$), and quartz were present. The additional sulfur in MSWI-FA was present as anhydrite. Paper ashes were primarily composed of calcium, which was present as varying amounts of calcite, lime, and portlandite. The 10-20% aluminium was present as calcium aluminium oxide ($Ca_3Al_2O_6/3CaO{\cdot}Al_2O_3$), gehlenite, and mayenite ($Ca_{12}Al_{14}O_{33}$). Around 20% silicon was present as quartz, although paper ash 2 also contained calcium silicate (Ca_2SiO_4). PFA was predominantly composed of silicon, aluminium, and iron, as hematite, mullite ($3Al_2O_32SiO_2$), and whitlockite ($(Ca_9MgFe)(PO_4)_6PO_3OH$). Sewage sludge ash (SSA) contained 40% silicon, 21% phosphorus, 11% aluminium, 15% calcium, and 6% iron as whitlockite and hematite. Steel sludge was dominated by 72% iron, along with 8% calcium, which occurred as calcite, hematite, magnetite (Fe_3O_4), and wustite (FeO). Wood ash was 45% calcium, with 17% silicon, 14% potassium, 9% phosphorus, and 7% magnesium. These occurred as calcite, calcium phosphate, calcium silicate, periclase and quartz.

The crystalline phase composition of the waste materials before and after carbonation identified common patterns (see table 4.3). The original X-ray diffractograms are included in the appendices. The reactive wastes contained Portlandite (CaOH) or lime (CaO) in their uncarbonated state, along with calcite ($CaCO_3$). Fully carbonated wastes were dominated by calcite, although paper ash 3, CKD and CBD still contained lime. CBD, MSWI-BA, and paper ashes 1,2, and 3 contained Portlandite after carbonation.

The results also indicate the carbonation of Periclase (MgO) in wood ash and paper ash 5. The participation of calcium bearing phases, including the disappearance of calcium aluminium oxide and mayenite after carbonation in paper ashes 4 and 5. In CKD and MSWI-FA, Gehlenite was apparently consumed by the carbonation reaction, although in other wastes, no change in the peak height was observed.

Peaks heights are affected not only by the amount of a particular phase present, but also the degree of crystallinity of the phase, and if the mineral is particularly susceptible to orientate its crystals in a certain plane (known as preferential orientation). These combined factors can lead to a proportionally larger or smaller peak relative to the true value.

Given the complexity of the diffractograms, positive identification of key phases was not always possible. For example, a peak at 11°2θ in MSWI-BA, played a role in the carbonation reaction, but could not be identified.

Table 4.3: Major oxides composition (expressed as % by weight) (error margins expressed as interquartile ranges)

	Al_2O_3	**CaO**	**Fe_2O_3**	**K_2O**	**MgO**	**MnO**	**Na_2O**	**P_2O_5**	**SiO_2**	**SO_3**	**TiO_2**
Bauxite	79.6±3.4	0.06±0.0	13.6±1.1	0.1±0.0	0	0.01±0.0	0	0.3±0.0	3.4±0.6	0.4±0.1	1.4±0.5
Biomass Ash	0.3±0.1	24.2±2.1	0.7±0.2	21.2±3.1	8.8±0.9	0.1±0.1	0.3±0.0	36.0±2.1	5.1±0.4	3.3±0.2	0
CBD	4.4±0.6	66.3±4.6	2.7±0.7	1.7±0.2	1.1±0.1	0.1±0.0	0.3±0.0	0.2±0.0	17.8±1.9	4.6±0.4	0.2±0.1
CKD	4.6±0.4	46.2±4.6	2.9±0.2	3.9±0.3	1.5±0.1	0.1±0.0	0.5±0.1	0.1±0.05	16.4±2.9	22.3±1.4	0.2±0.1
Clinical Ash	15.7±1.2	28.1±3.1	4.8±1.0	0.5±0.0	1.7±0.1	0.1±0.0	11.2±1.2	1.6±0.2	6.1±0.2	20.5±2.0	7.2±2.1
MSWI-BA	14.5±1.3	33.1±3.1	7.9±1.0	1.1±0.1	2.8±0.2	0.1±0.0	2.2±0.1	1.9±0.1	5.2±0.3	27.9±2.3	2.3±0.8
MSWI-FA	15.8±1.2	32.1±2.8	3.4±0.8	0.8±0.1	3.4±0.4	0.2±0.1	1.8±0.1	2.9±0.3	32.4±1.8	3.6±0.1	2.4±0.6
Paper Ash 1	9.3±1.1	54.9±2.3	4.7±0.3	0.7±0.1	1.6±0.2	0	0.1±0.0	0.2±0.1	20.8±1.0	6.4±0.3	0.3±0.1
Paper Ash 2	8.3±0.6	65.8±1.5	0.8±0.1	0.3±0.0	1.3±0.1	0.1±0.0	2.1±0.1	2.0±0.6	19.7±0.9	0.5±0.0	1.0±0.2
Paper Ash 3	19.0±1.2	45.0±2.3	1.1±0.1	1.0±0.0	5.3±1.0	0	1.2±0.3	0.4±0.0	25.0±1.9	0.8±0.1	0.6±0.1
Paper Ash 4	5.5±0.8	60.0±3.3	1.7±0.1	0.2±0.0	1.4±0.1	0.1±0.0	0.3±0.0	0.7±0.1	23.8±2.1	5.1±0.2	0.7±0.2
Paper Ash 5	6.8±0.9	69.6±3.8	1.0±0.0	0	1.7±0.2	0.1±0.0	0	2.0±0.4	10.0±2.1	7.0±0.2	1.0±0.4
Paper Ash 6	8.8±2.1	67.4±4.8	0.9±0.0	0	2.1±0.1	0	0	1.6±0.4	15.5±0.9	2.0±0.3	0.7±0.2
PFA	23.0±2.2	1.3±0.1	13.8±0.9	2.7±0.5	1.0±0.1	0	0.5±0.0	0.5±0.2	55.6±4.8	0.1±0.0	1.3±0.3
SSA	11.2±1.4	14.8±1.1	5.6±0.6	2.3±0.2	2.9±0.3	0.1±0.0	0.7±0.1	21.2±4.4	39.9±6.8	0.3±0.0	1.2±0.4
Steel Sludge	2.0±0.3	7.9±1.9	71.7±2.4	0.1±0.0	2.6±0.2	1.1±0.1	0.3±0.0	0.7±0.2	0.8±0.1	8.0±0.6	0.1±0.0
Wood Ash	2.6±0.2	45.5±3.4	1.3±0.1	14.0±2.0	6.9±0.9	2.4±0.3	0.9±0.0	9.0±1.2	17.0±1.5	0.6±0.0	0.2±0.2
CEM1	5.2±0.1	64.5±2.1	3.5±0.3	0.2±0.0	2.2±0.4	0.1±0.0	0.1±0.0	0.1±0.0	19.8±1.4	2.9±0.2	0.3±0.1

Table 4.4: Key crystalline phases identified by XRD

	Bauxite	Biomass Ash	CBD	CKD	Clinical ash	MSWI BA	MSWI FA	Paper Ash 1	Paper Ash 2	Paper Ash 3	Paper Ash 4	Paper Ash 5	Paper Ash 6	PFA	SSA	Steel Sludge	Wood Ash
Aluminium, Al							●										
Anhydrite, $CaSO_4$			●	●	○		●	●									
Bassanite, $2CaSO_4.(H_2O)$						●	●	■			□	●					
Bimessite, $Na_{0.55}Mn_2O_4 \cdot 1.5H_2O$	○																
Calcite, $CaCO_3$			▲	▲	○	▲	▲	▲	▲	▲	▲	▲	▲			○	●
Calcite Magnesian, $Mg_{0.1}Ca_{0.9}CO_3$		▲															
Calcium Aluminium Oxide, $Ca_3Al_2O_6/3CaO \cdot Al_2O_3$									●		□	□					
Calcium Phosphate, $Ca_4P_2O_9$																	●
Calcium Silicate, Ca_2SiO_4									▼								●
Calcium Sulfate Hydrate, $CaSO_4 \cdot 0.6H_2O$				■													
Fluorite, CaF_2				●													
Gehlenite, $Ca_2Al(AlSiO_7)$			●	□	○	●	▼			●			●				
Gibbsite, $Al(OH)_3$	○																
Glaucophane, $Na_2(Mg,Fe)_3Al_2Si_8O_{22}(OH)_2$						●											
Goethite, FeO(OH)	○																
Gypsum, $CaSO_4.2H_2O$					○												
Halite, NaCl					○		●										
Hematite, Fe_2O_3	○													○	○	○	
Hauynite, $(Na,Ca)6Al_6Si_6O_{24}(SO4)$				■													
K-Ca- Phosphate, $KCaPO_4$		●															●
Larnite, Ca_2SiO_4				□													
Lime, CaO			▼	▼						▼	□	□	□				
Magnatite, Fe_3O_4																○	
Mayenite, $Ca_{12}Al_{14}O_{33}$											□	□					
Mullite, $3Al_2O_32SiO_2$														○			
Periclase, MgO												□					▼
Perowskite, $CaTiO_3$					○												
Portlandite, $Ca(OH)_2$			▼	□		▼	□	▼	▼	▼	□	□	□				
Quartz, SiO_2		●	●	●		●	●	●	●	●	●		●	○		○	●
Rutile, TiO_2	○																
Sphalerite, ZnS		●															
Talc, $Mg_3Si_4O_{10}(OH)_2$																	
Vaterite, $CaCO_3$							●										
Whitlockite, $Ca_9MgFe)(PO_4)_6PO_3OH$		●													○		
Wustite, FeO																○	
Zinc Iron Oxide, $ZnFe_2O_4$																○	

▲ – increased prominence after carbonation,▼ – decreased prominence after carbonation, ● – no change after carbonation, , □ – disappeared after carbonation, ■ – appeared after carbonation, ○ – phase present in a non-reactive material

4.3.3 Trace Metals

The regulated metals contents of the wastes are shown in table 4.5. Copper, lead and zinc were often present in concentrations greater than 1000mg/kg. Antimony, arsenic, molybdenum, nickel and selenium were found in concentrations typically below 100mg/kg. Cadmium and mercury were not detected in the wastes. The degree of recovery of metals, as measured against the certification for the certified reference material, varied between 67 and 89.5%. Residual elements not released by an aqua regia digestion are mostly bound to silicate minerals (Chen & Ma, 2001). Whilst the degree of recovery from the certified reference material may be used as an indicator, the amount of recovery may vary between materials depending upon their chemistry.

The assessment of wastes for landfill disposal is based upon metal leaching rather than total metal content. However, the total metal content is an indicator of the leaching potential of the material, and the degree of mobility.

4.3.4 Leaching

The results of leaching of the wastes are shown in figures 4.3a-4.3c. These are compared to the regulatory limits for inert, stable non-reactive hazardous wastes, and hazardous wastes, as stipulated in the Landfill Regulations (Europa, 2010).

Carbonation resulted in partial pH neutralisation of the leachates. This has implications for metal leaching through pH dependent solubility. No measurable levels of cadmium or zinc were detected in the eluates. Similarly, arsenic, barium, and copper levels were below the inert landfill limits in most cases. Carbonation reduced barium leaching to below inert levels for paper ashes 2-6. Lead levels in the CKD eluate failed the criteria for hazardous waste, although carbonation reduced leaching to within stable non-reactive hazardous landfill limits. Molybdenum was present at stable non-reactive levels in the majority of wastes, and was largely unaffected by carbonation. Hazardous levels of chromium were leached from MSWI-BA, but were effectively reduced to stable non-reactive by carbonation. Conversely, carbonation elevated chromium leaching in paper ashes 3-6 from inert to stable non-reactive levels.

Table 4.5: Waste acceptance criteria metals (expressed as mg/kg) of the designated hazardous wastes (error margins expressed as interquartile ranges)

	As	**Ba**	**Cr**	**Cu**	**Mo**	**Ni**	**Pb**	**Se**	**Sb**	**Zn**
Biomass Ash	0	32±15	0	71±30	0	0	0	0	0	1044±150
CBD	0	53±18	10±6	0	0	0	158±89	0	0	204±58
CKD	0	106±38	0	10±6	0	196±108	13738±1550	0	0	504±230
MSWI-BA	0	365±146	117±55	6656±620	0	41±19	648±201	0	22±13	10367±2780
MSWI-FA	0	609±332	260±126	4094±1067	2±0	72±28	3003±782	5±2	163±82	7718±2221
Paper Ash 1	0	202±47	0	15±8	0	18±10	0	0	0	17±12
Paper Ash 2	0	120±39	2±0	38±34	0	0	0	0	0	0
Paper Ash 3	0	93±25	39±28	289±111	0	9±3	10±7	0	0	37±16
Paper Ash 4	0	80±22	60±31	899±165	0	55±23	2±0	0	0	415±134
Paper Ash 5	0	87±26	23±21	33±12	0	0	0	0	0	311±147
Paper Ash 6	0	167±69	12±4	281±102	0	0	50±26	0	0	373±155
Wood Ash	0	1003±375	2±0	272±87	0	6±2	212±43	0	0	2±0
% recovery	*79.7*	*76*	*80.6*	*71.9*	*88*	*81.8*	*85.9*	*89*	*78.2*	*89.5*

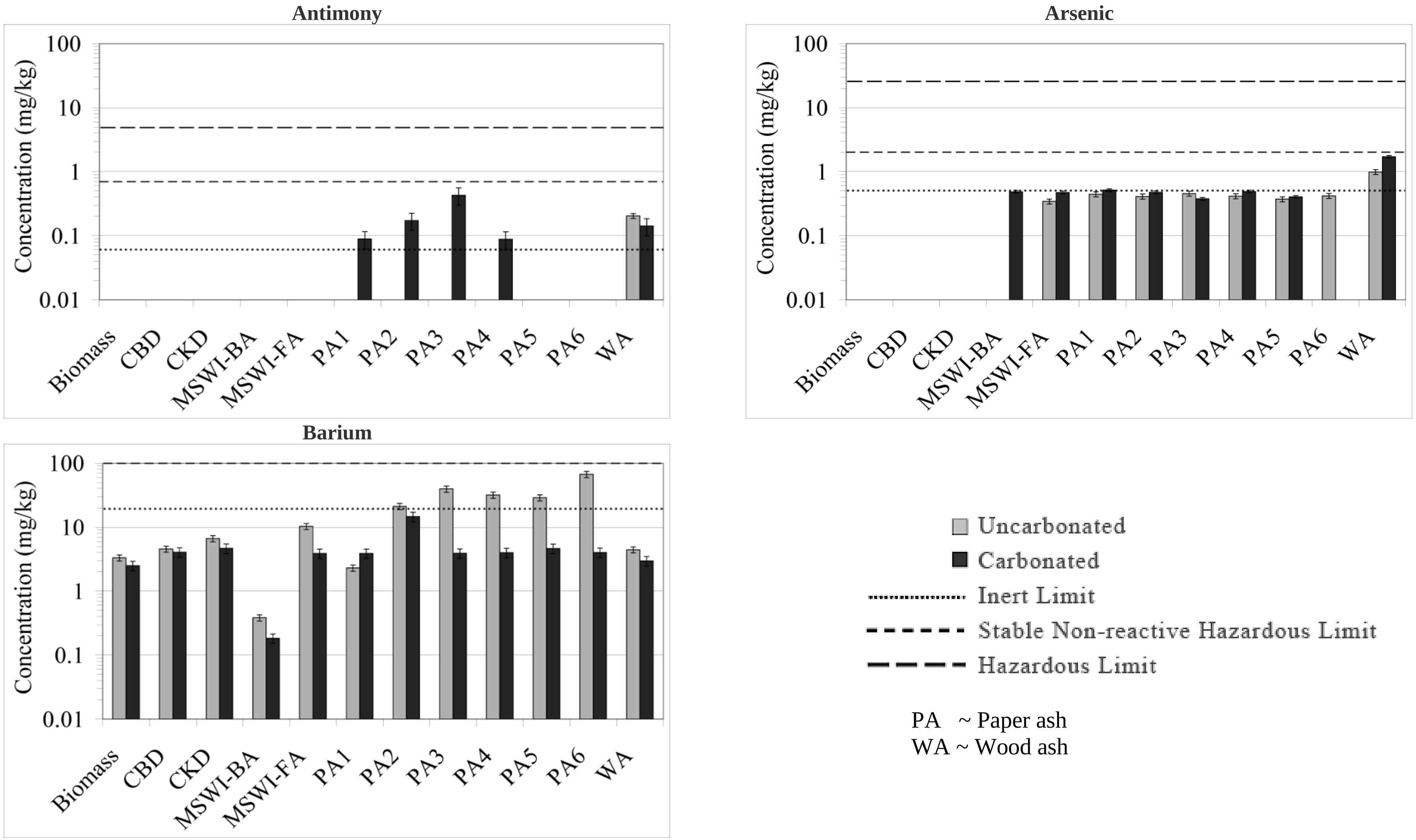


Figure 4.3a: Metal and anion leaching behaviour of wastes (error bars represent the interquartile ranges)

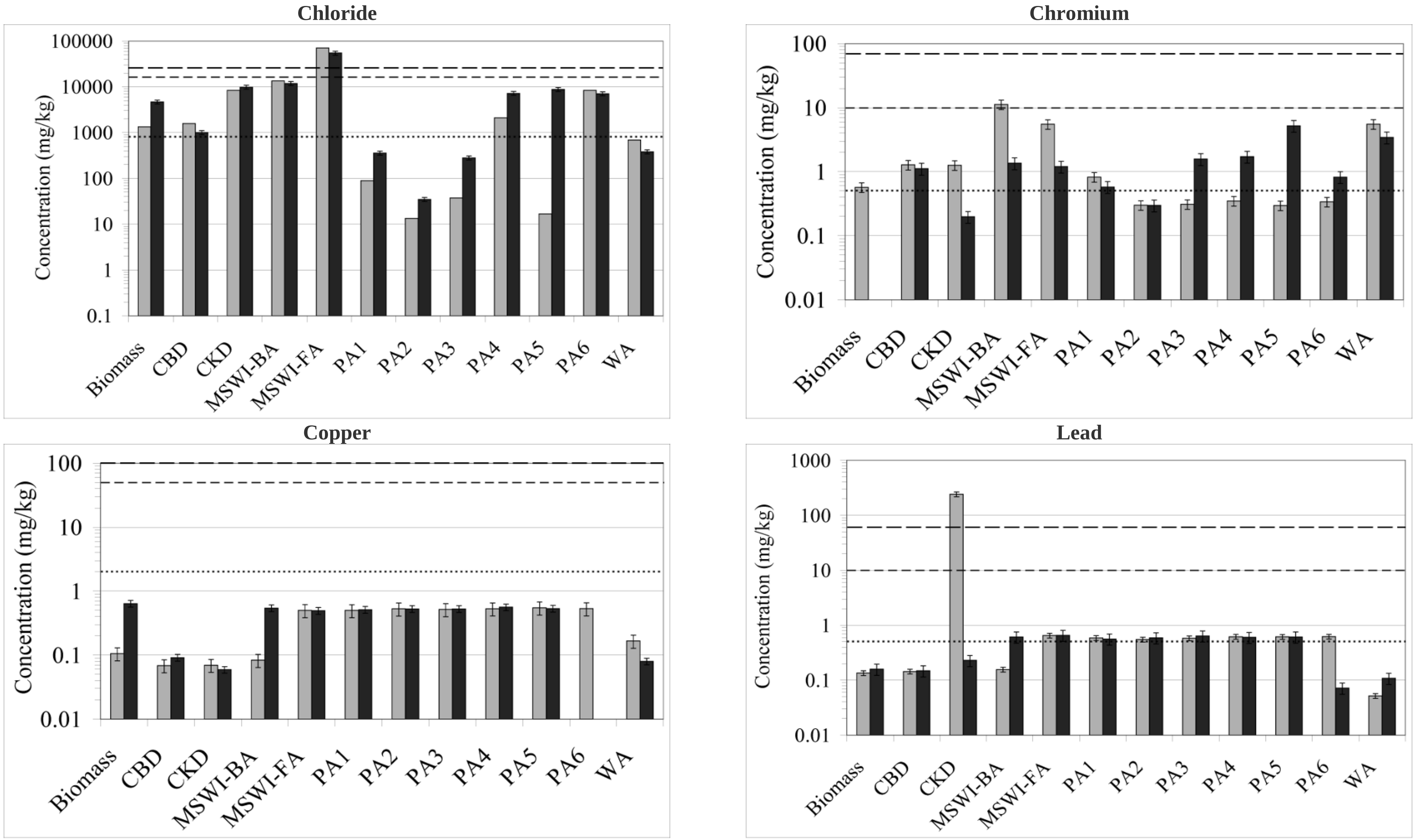
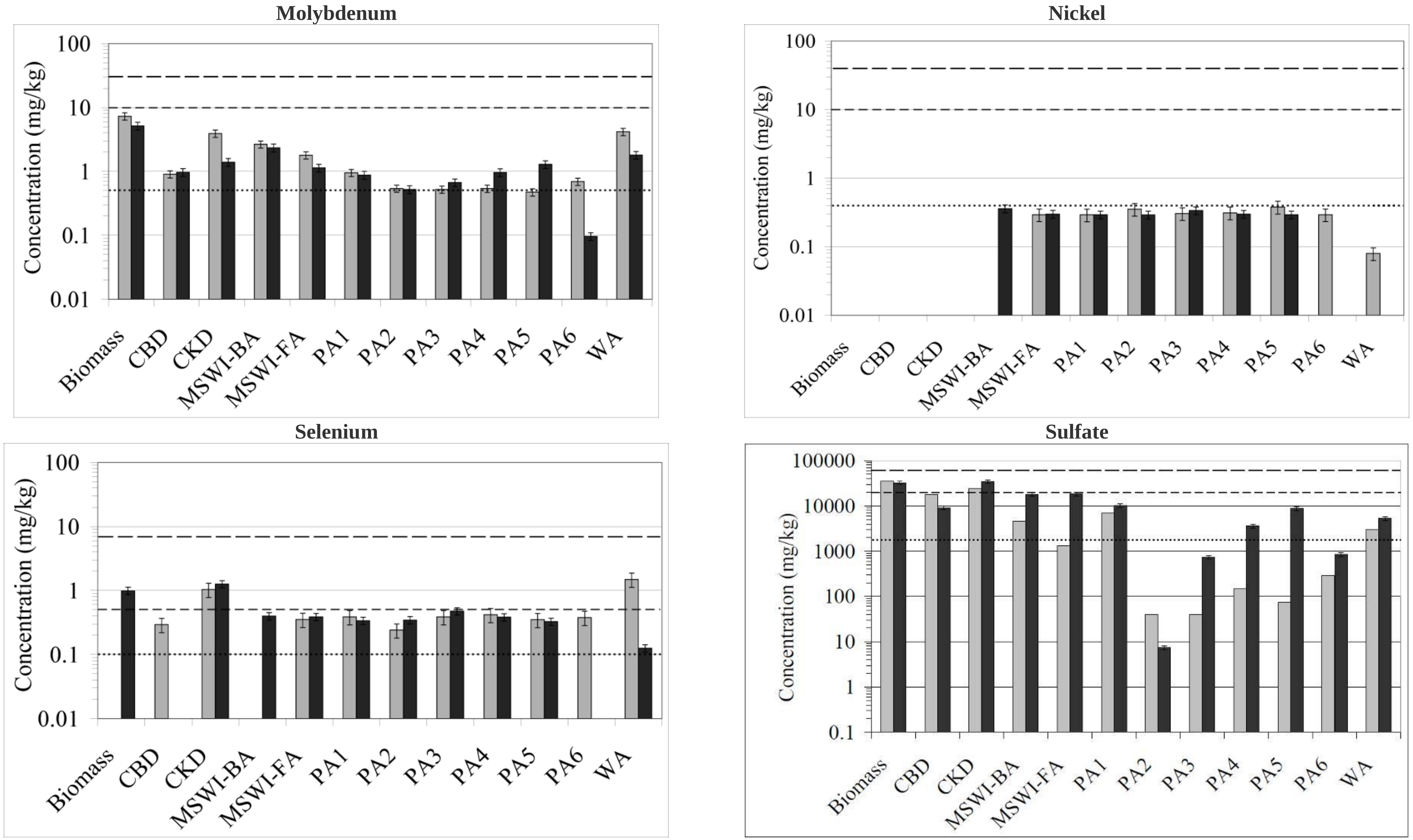


Figure 4.3b: Metal and anion leaching behaviour of wastes (error bars represent the interquartile ranges)



Molybdenum

Nickel

Selenium

Sulfate

Figure 4.3c: Metal and anion leaching behaviour of wastes (error bars represent the interquartile ranges)

Sulfate and chloride leaching were unaffected or increased by carbonation. Fluoride leaching from wood ash reached stable non-reactive levels, and reduced to inert after carbonation. Chloride leaching was often within stable non-reactive limits. Hazardous levels of sulfate were found in the biomass ash and CKD. Leaching of sulfate in MSWI-FA and paper ashes 5 and 6 was increased from inert before treatment, to stable non-reactive after carbonation.

Carbonation had little effect upon anion leaching, and in many cases promoted it. Non-hazardous levels of chloride were measured in MSWI-BA, MSWI-FA, CKD, paper ash 5, and paper ash 6. Similarly, high levels of sulfate were found in biomass ash, MSWI-BA, MSWI-FA, CKD, CBD, and paper ash 1.

4.4 Discussion

4.4.1 Carbonation and chemical composition

Accelerated carbonation as a treatment for waste is only directly applicable to materials that are naturally reactive with carbon dioxide gas. Non-reactive wastes may be treated by mixing with an appropriately reactive binder e.g. cement or lime.

Johnson (2000) noted the relationship between the oxide content of calcium and the carbon dioxide uptake of the material. The uptake versus oxide content of calcium is shown in figure 4.4.

Portland cement provides a benchmark for carbon dioxide reactivity, achieving almost 30% uptake with a calcium content of around 65%. Calcium-rich materials including cement bypass dust and certain paper ashes combine with up to 26% by weight of carbon dioxide. Municipal incineration ashes, cement kiln dusts and wood ash achieve uptakes of between 4 and 9%. Calcium-deficient materials such as bauxite, PFA, steel sludge and SSA showed little or no reactivity. Similarly, biomass ash and clinical incineration ash had no reaction with carbon dioxide, yet contained over 20% calcium. Paper ash 2 exhibited disproportionately low reactivity for a material containing a calcium content of 66%.

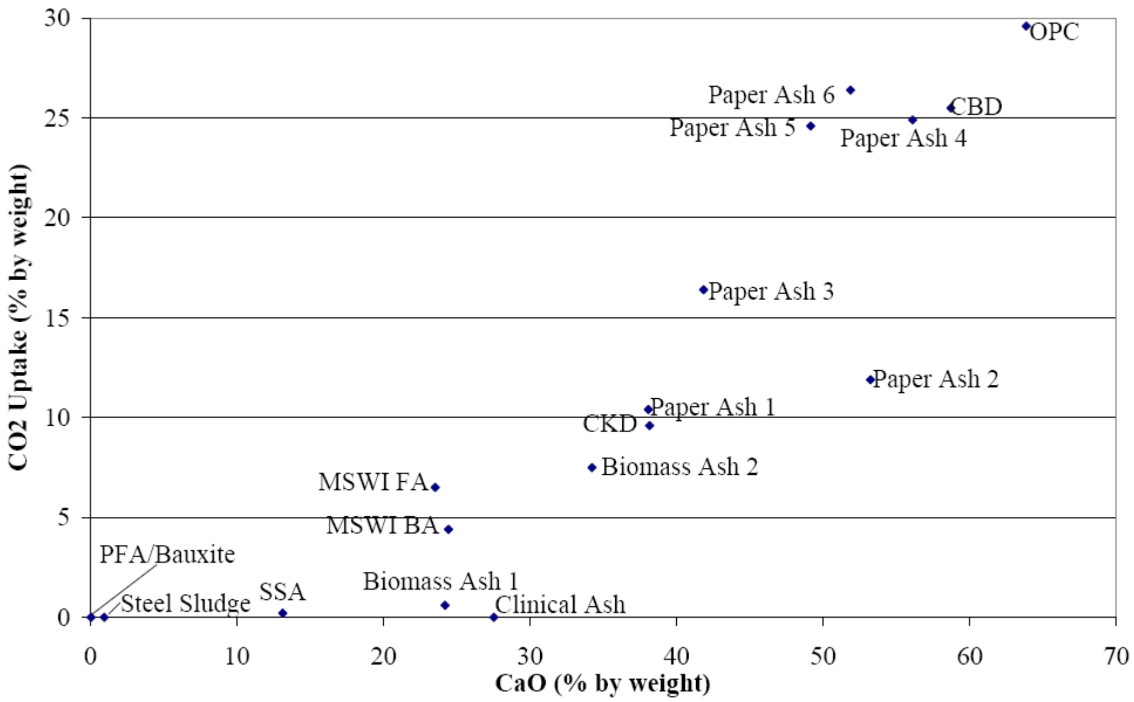


Figure 4.4: Relationship between calcium content and carbon dioxide uptake

Carbon dioxide uptake behaviour can be related to elemental composition using the Steinour formula, which calculates the maximum theoretical uptake based upon the amount of calcium, potassium, sodium and sulfur present in the material (Fernandez-Bertos *et al.*, 2004). Comparing the Steinour uptake against the measured uptake revealed that the measured uptakes were substantially lower than the maximum theoretical uptakes (see figure 4.5).

Carbon dioxide reactivity is controlled not just by the total calcium content, but by the phases in which the calcium is bound. Calcium already in, for example, stable carbonate form will contribute to the total oxide, but will not participate in the carbonation reaction.

Biomass ashes (including wood ash) have compositions varying according to the type of the plant matter being burnt (Pitman, 2006). XRD analysis revealed a complex mineralogy dominated by an indistinguishable mixture of calcium phosphates which may contain magnesium. Calcite was prominent in the uncarbonated material, suggesting carbonation prior to analysis, or that the thermal processes generating the waste operated at temperatures insufficient to induce total calcination of the ash.

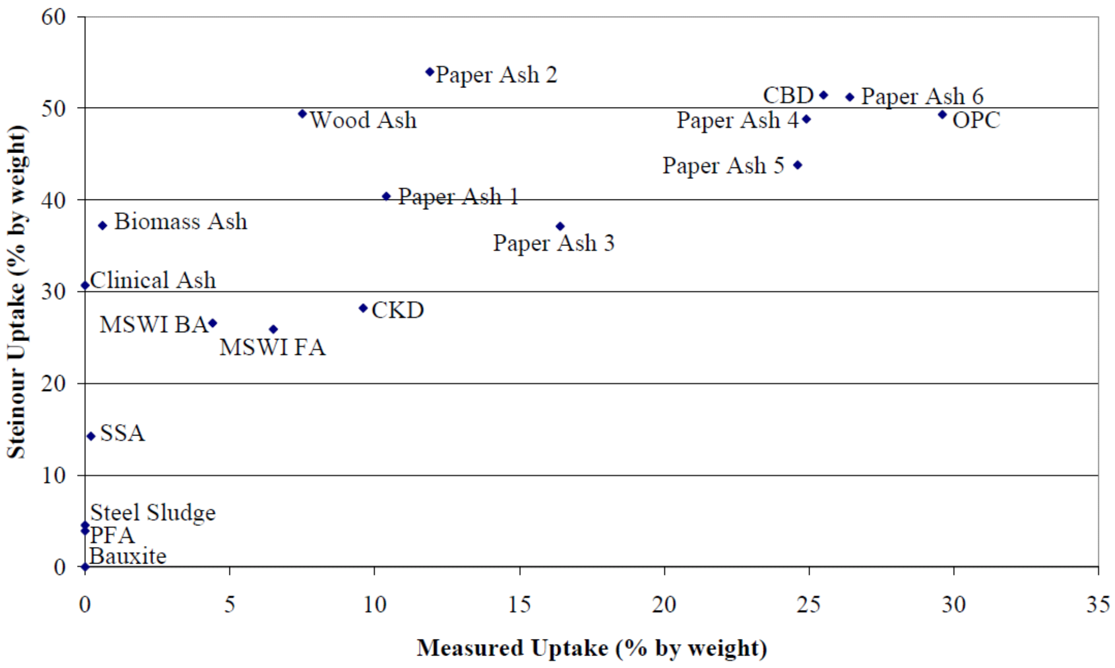


Figure 4.5: Relationship between measured carbon dioxide uptake and theoretical uptake according to Steinour

Paper ashes are among the most reactive materials due to the use of calcium carbonate as an additive during the papermaking process (Boni *et al.*, 2004). Calcination during incineration converts the carbonate to calcium oxide. Depending upon the type and grade of paper product incinerated, the calcium content varies. Accordingly, the oxide content for calcium of the six ashes tested varied from 45 to 69.6%, accounting for the variation in carbon dioxide reactivity. The complexity of the phases present in paper ashes 4-6 is attributed to the practice of co-firing paper sludge mixed with plastic waste at the incinerator. Calcium was also present as gehlenite ($Ca_2Al[AlSiO_7]$) in several of the ashes.

Clinical ash would be expected to be reactive on account of the oxide weight of calcium in clinical ash. Clinical waste is incinerated at temperatures in excess of 1000°C (Blenkharn, 2005), which is sufficient to decompose calcium carbonate into calcium oxide. However, calcite was identified by XRD. This suggests that the sample was already weathered prior to analysis.

Cement by-products have high calcium contents akin to that of the cement clinker. Cement kiln dusts are separated during the preheating stage of the cement production process. At this point, the temperature is not sufficient to induce total calcination, whereas the bypass dusts are removed at the kiln firing stage (Sreekrishnavilasam *et al.*, 2006, Singh *et al.*, 1995). However, CBD already contained calcite before carbonation, suggesting the sample had already partially weathered. Cement dusts are rejected based upon the high levels of alkalis and sulfates (Konsta-Gdoutos and Shah, 2003). High levels of sulfur were present as anhydrous calcium sulfate (anhydrite).

The composition of MSWI is highly variable, depending upon the feed to the incinerator, which includes calcium deficient materials; metal, plastic and putrescible waste (Arickx *et al.*, 2006, Bethanis *et al.*, 2002). The calcium was bound in calcite or as phosphate, but detectable levels of Portlandite account for the moderate reactivity of the ashes.

Pulverised fuel ash showed no reaction with carbon dioxide. The coals mined in the UK are high purity superior forms such as anthracite. These high purity coals are deficient in calcium, which result in low reactivity class F ash (D.O.E, 1995a).

SSA is primarily composed of the calcium-bearing mineral Whitlockite ($Ca_7Mg_2P_6O_{24}$). Whitlockite is sparingly soluble at high pH, and is unlikely to contribute to carbonation (Cyr *et al.*, 2007).

4.4.2 Effect of carbonation upon leaching

The behaviour of cationic and anionic species with respect to carbonation is complex and conflicting results have been obtained by various authors (Van Gerven *et al.*, 2004b). The generalised behaviour is summarised in table 4.6.

The regulated metals detected in the leachates, including arsenic, barium, copper, and nickel, were not identified in the phases detected by XRD. These may be bound in poorly crystalline or phases occurring in too smaller amounts to be detected. Therefore, the interpretation of metal leaching can only be related to the change in eluate pH as a result of carbonation.

The pH of CBD, CKD, and paper ashes 2-4 remained above 12 after repeated cycles of carbonation, as a result of the reactive phases including Portlandite and lime being present. However, these wastes showed no measurable increase using TGA in their calcium carbonate content upon further carbonation. This indicated that the rate of mass increase was below the procedural error margin.

Table 4.6: Leaching behaviour of anions and cations with respect to carbonation

Element	**Behaviour**
Antimony	Carbonation increases leaching due to pH moderation, which also facilitates the breakdown of portlandite and Ettringite, with which Sb has a strong affinity (Cornelis *et al.*, 2006, Paoletti *et al.*, 2001, Meima and Comans, 1998).
Arsenic	As leaching is controlled through S/S treatment by reduced solubility at high pH (Dutré and Vandecasteele, 1995). Carbonation induced pH reduction promotes As release (Camacho *et al.*, 2009). Arsenic is commonly incorporated into ettringite (Venhuis and Reardon, 2001).
Barium	Leaching is reduced at neutral pH (Van Gerven *et al.*, 2004b), and through the formation of insoluble barium carbonate and also barium sulfate derived from ettringite decomposition (Valls and Vazquez, 2001).
Cadmium	Has a strong affinity for both portlandite and calcite, thus unaffected by carbonation. Cadmium hydroxide and carbonate are low solubility (Shaffique *et al.*, 1998).
Chromium	Chromium (III) binds with calcium hydrates, and may be mobilised by carbonation (Macias *et al.*, 1997). pH neutralisation may reduce leaching, as does physical contaminant through calcite formation (Lange *et al.*, 1997, Johnson *et al.*, 2003).
Copper	Copper exhibits amphoteric behaviour, with minimum solubility around 9.5. Calcite formation may also be an important retention mechanism (Arickx *et al.*, 2006).
Lead	Lead is amphoteric with minimum solubility around 9.5, but leaching may be reduced over the entire pH range through precipitation as lead carbonate (Van Gerven *et al.*, 2004).
Mercury	Hg compounds are unaffected by carbonation, but leaching is increased at neutral pH (Bonen and Sarkar, 1995).
Molybdenum	Molybdenum leaching was found to be largely unaffected by carbonation (Meima *et al.*, 2002).
Nickel	pH reduction increases leaching, but this may be reduced by the conversion of Nickel hydroxide to carbonate (Van Gerven *et al.*, 2004).
Selenium	Se leaching is significantly reduced above pH 5.5, thus carbonation induced neutralisation is inconsequential. However, calcium selenates may form a solid solution with calcite (Cornelis *et al.*, 2008).
Zinc	Zinc may be increased by the decomposition of ettringite, decalcification of C-S-H, and pH neutralisation (Valls and Vazquez, 2001, Fernández-Bertos *et al.*, 2004b). May form hydroxyl-carbonates or carbonates (Bonen and Sarkar, 1995).
Sulfate	Sulfate leaching is increased by ettringite decomposition (Fernández-Bertos *et al.*, 2004a, Valls and Vazquez, 2001).
Chloride	Increased by Friedel's salt decomposition (Valls and Vazquez, 2001, Yuan *et al.*, 2009)

Carbonation was ineffective against arsenic, molybdenum and nickel, which is in accordance with previous research (Camacho *et al.*, 2009, Van Gerven *et al.*, 2004b, Meima *et al.*, 2002, Dutré and Vandecasteele, 1995). Leaching of copper was unaffected, despite the neutralisation of leachate pH, which assists in stabilisation (Arickx *et al.*, 2006). Selenium leaching was unaffected above a pH of 7, but can be immobilised in solid solution, although no evidence for this was observed (Cornelis *et al.*, 2008). The reduction in barium and lead levels can be related to the measured pH (Van Gerven *et al.*, 2004). Similarly, increased antimony leaching for paper ashes 2 and 3, may be attributed to the reduced pH of the leachate and conversion of portlandite to calcite (Cornelis *et al.*, 2006, Paoletti *et al.*, 2001, Meima and Comans, 1998). Changes in chromium mobility varied for different wastes, and this could result from its speciation or the efficacy of retention in the as-received wastes, being subsequently altered by carbonation (Johnson *et al.*, 2003; Lange *et al.*, 1997; Macias *et al.*, 1997).

4.4.3 Waste Variability

The condition of the as-received waste materials was found to vary significantly between samples taken over time. Repeat batches of the same materials exhibited different physical and reactive properties.

Wood ash was a granular powder, which increased in weight by 7.5% after carbonation. Samples of wood ash obtained later in the project were virtually unreactive and contained large unburnt wood fragments. The ash was also wetter, containing 21% water compared to 12.7% in the original sample. Paper ash 3 initially had an increase in weight upon carbonation of 16.4%, whilst a second sample achieved 24.1%. Similarly, MSWI-FA showed variations in reactivity between 6.6 and 9.6%.

This variability represents the dynamics of waste management practices and sampling methods. Waste producers rarely provide full details of their on-site management practices or the raw materials that are being fed into the thermal process. Changes in contractual arrangements alter the availability of the feed materials that go into the thermal process, with a consequence that the chemistry, and therefore reactivity of the resulting thermal waste varies. Similarly, changes in handling methods, separation or treatment methods, storage, and seasonal variations in weather, all have a significant influence upon the chemical and physical properties of the waste. Sampling is very often undertaken by different personnel on site, and different stockpiles or materials of different ages may be selected.

Many of the wastes showed signs of natural carbonation and hydration prior to analysis. Consequently, the age of the material before sampling will have a direct effect upon the extent to which this processes have progressed.

This variability needs to be considered, especially if these materials are to be treated in a full scale process. The chemical composition plays an important role in the properties of the products.

4.5 Conclusions

This chapter examined thermal residues for their potential to be treated by accelerated carbonation.

Cement dusts and paper incineration ashes were the most reactive materials, although the latter did vary considerably. Biomass ashes and municipal incineration ash were moderately reactive, whilst bauxite, PFA, clinical ash, SSA, and steel sludge were unreactive. Carbon dioxide reactivity was partially related to total calcium content, although the mineral phases also had an influence. The presence of calcium in unreactive crystalline phases accounted for the low reactivity of some thermal residues. The persistence of reactive phases in the carbonated wastes showed that carbonation had not gone to completion, but that the reaction had slowed sufficiently to be undetectable.

Based upon leaching, all of the reactive wastes were classified as hazardous prior to carbonation. Carbonation reduced the alkalinity of the wastes, in many cases to below the Hazardous Waste Regulation threshold for corrosivity, although pH is not a regulated property for disposal of waste to landfill.

Carbonation proved effective in reducing the leaching of lead and barium, but increased antimony and chromium. Arsenic, copper, molybdenum, nickel and most anions were largely unchanged. CKD was reclassified from failing the hazardous WAC criteria to a hazardous WAC conforming waste, whilst MSWI-BA and wood ash were reclassified from hazardous to stable non-reactive hazardous wastes. Increased selenium leaching as a result of carbonation reclassified biomass ash as a hazardous waste, whereas the MSWI-FA continued to fail hazardous WAC on account of chloride leaching. The other wastes remained as stable non-reactive.

Hazardous wastes treated by carbonation can be reclassified, and potentially disposed of more readily at a lower cost. However, in the longer term, the recycling of wastes is favoured instead of disposal. The following chapter will consider the application of accelerated carbonation to convert these wastes into pelletised form for re-use as aggregate.

Chapter 5 : Production of Aggregate from Waste

5.1 Introduction

The previous chapter examined the use of accelerated carbonation for treating a variety of thermal process waste materials. Thermal residues derived from cement and paper making processes were found to be highly reactive with carbon dioxide. Carbonation was effective in reducing the alkalinity of the wastes which had implications for the retention of regulated contaminants. Therefore, accelerated carbonation may be a suitable treatment method for certain hazardous wastes to allow disposal to a stable non-reactive landfill.

The treatment of waste for landfill disposal is a short term solution. The recycling of wastes into new products is a potentially important route for the diversion of wastes from landfill. This chapter investigates the basis for the re-use of thermal-process residues blended with wastes from a quarrying process as new aggregate materials.

A pelletising process is used to bind the fine grained wastes into granular products, and carbonation is employed to cement the granules together. The effect of the pelletising conditions upon the rate of the carbonation reaction is considered. These include the type of mixer used, the mixer speed, the processing time, and the moisture content of the material. Thermal residues reactive with carbon dioxide are investigated as binders for solidifying other non-reactive wastes. The pelletised products are examined for strength, density, and chemical and microstructural changes attributed to carbonation.

5.2 Materials and Methods

5.2.1 Materials

Quarry wastes comprise 29% of the waste produced in the UK (D.E.F.R.A, 2007). Gallagher (Aggregates) Ltd is quarrying company located near Maidstone in Kent, UK, who provided funding for this project.

Gallagher (Aggregates) extracts Kentish Ragstone, a durable limestone interbedded with Hassock, a soft calcareous sandstone rich in silt. The process of rock extraction and processing is shown in figure 5.1. Hassock and Ragstone are separated in a rotary Trommel screen (see figure 5.2a). Ragstone is crushed and screened into various grades including sharp sand, which must be washed to remove fines. Hassock was originally sold as a low-grade fill, but became overpriced with the introduction of the aggregate levy (KCC, 2003). Washing the Hassock to remove the silt fraction produces marketable higher-grade sand. A large amount of silt-laden waste water is generated by washing the Ragstone and Hassock. The silts are separated using chemical flocculant in settlement cone thickeners (see figure 5.2b). Thickened underflow from the cones is dewatered by the addition of further flocculant and passing through belt presses. The result is a gelatinous sludge containing around 45% water (see figure 5.3). No use exists for the sludges, which are backfilled into the quarry void. Similarly, the Hassock and Ragstone sand products are produced in excess due to the demand for the other graded products, and can be considered as waste (see figure 5.3).

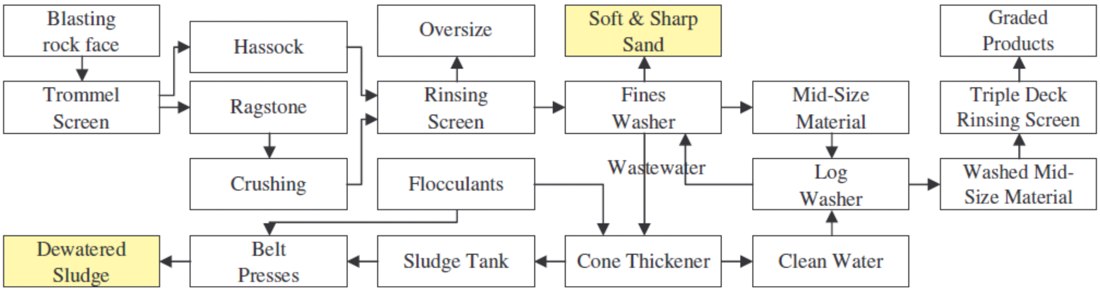


Figure 5.1: Flowchart of Gallagher Aggregates Ltd quarrying process (waste products coloured yellow)

All materials were oven dried at 105°C in accordance with BS EN 1097-5: 1999. Since the fines harden into a solid mass on drying, they were crushed to pass a 2mm aperture sieve.

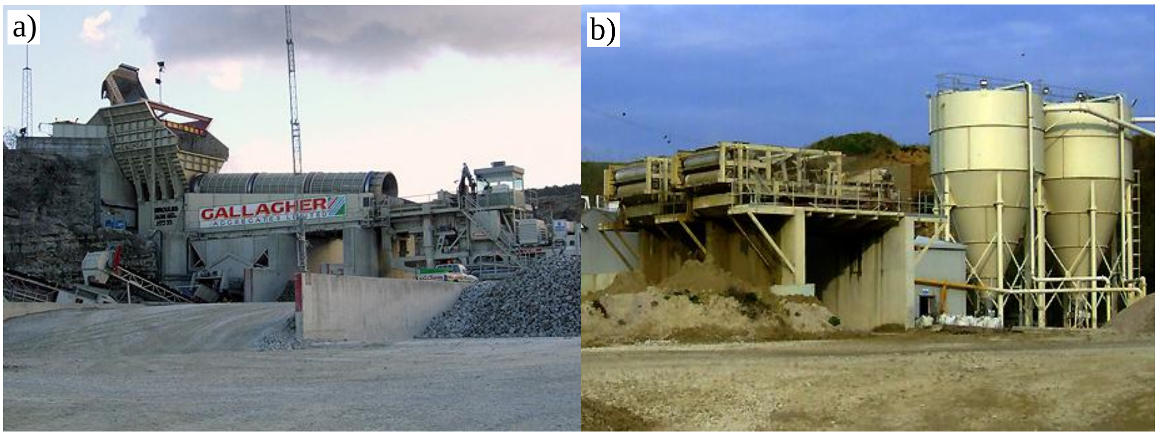


Figure 5.2: Quarry processes at Gallagher Aggregates Ltd; a: Rotary Trommel screen (left) and primary crusher (right), b: washing plant showing the cone thickeners (right) and belt presses (left)

Figure 5.3: Quarry fines studied

5.2.2 Characterising Materials

The new materials were analysed for elemental composition by XRF (3.3.2). These and the wastes studied in the previous chapter were tested for particle size distribution (3.3.4), which has been shown to affect pelletising behaviour (Keleb, 2004, Iveson, 2002).

5.2.3 Pelletising Process

The method of producing pellets from waste is shown as a flowchart in figure 5.4. First the dried waste materials and binders were weighed and premixed together in small bucket manually using a spatula. The appropriate amount of water was added, and again mixed using a spatula to form a cohesive granular material. The granular material was pelletised in a drum, whilst a stream of carbon dioxide was applied. After pelletising, the pellets were subjected to controlled curing as described later.

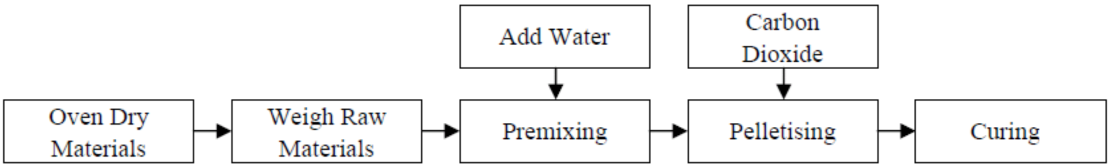


Figure 5.4: Laboratory scale pelletising process

The pelletising process is controlled by a series of variables, which include equipment and mix variables. This was discussed in Chapter 2. These variables must be optimised to achieve a satisfactory product, and are investigated in this chapter (see figure 5.5).

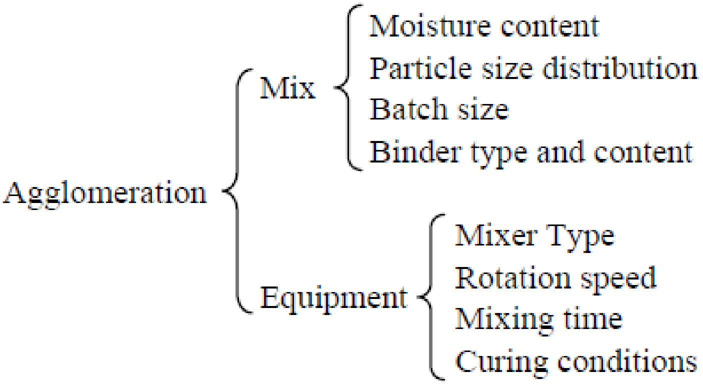


Figure 5.5: Pelletising variables investigated

5.2.3.1 Materials

To investigate the pelletising variables, a material that would readily pelletise was required. Considering the aim to broaden the scope for producing carbonated aggregate by mixing waste that is reactive with CO_2 with wastes that are not, three examples were selected. Hassock sand and silt were used as examples of non-reactive wastes, and CEM1 was used as a substitute for a reactive waste.

Table 5.1 shows the variables investigated, and the common link between each. Thus when rotation speed was considered, mixing time was maintained at 10 minutes, moisture content at 23%, the batch size at 200g, and the particle size distribution was maintained at a 3:2 ratio of sand:silt. These factors are considered in section 5.3.2, 5.3.

Table 5.1: Pelletising variables investigated

Variable	Increments						Section
Rotation Speed (rpm) [linear velocity m/s]	10 [0.11]	20 [0.21]	**30** **[0.31]**	40 [0.42]	50 [0.52]		5.3.2
Mixing Time (mins)	2	5	**10**	20	30		5.3.2
Moisture Content (%)	21	22	**23**	24	25		5.3.3.1
Particle Size Distribution (sand:silt)	1:0	4:1	**3:2**	2:3	1:4	0:1	5.3.3.2
Batch Size (g)	100	**200**	300	400	500		5.3.3.3

*Increments in **bold type** indicates the common factor*

5.2.3.2 Mix Variables

The particle size of the raw materials have a significant effect upon the pelletising process (Palzer, 2005, Pietsch, 2003). To investigate this, materials with different particle size distributions were produced by blending different proportions of silts and sands with CEM1. Hassock silt and Hassock sand were used as examples. Blends of sand and silt were prepared in the following ratios: 1:0, 1:4, 3:2. 2:3, 1:4, 0:1. These were mixed with 10% by weight of CEM1 and pelletised.

The moisture of the material influences the growth of agglomerates (Zed, 2001). The silt, sand and 10% CEM1 mix, pelletised effectively at a moisture content of 23%. Accordingly, the influence of moisture was assessed by altering the water content between 21 and 25% in 1% increments.

The level of drum fill also influences agglomerate growth patterns (Mellman, 2001). Batch sizes were varied in 100g increments from up to the maximum drum capacity of 500g.

After pelletising, the pellets were cured in an oven set to 40°C. Exposing cementitious materials to temperatures above the boiling point of water can lead to differential heating and the build up of pressure in the saturated pores as water boils (Ichikawa and England, 2001).

5.2.3.3 Equipment Variables

Low shear pelletisers induce agglomeration by gentle tumbling of the material in a revolving drum or disc. High shear mixers impart high energy to the particles through a high speed impeller or blade. Low shear mixers are generally employed for bulk processing of voluminous materials as in the mining and heavy industries, and can be effectively scaled-up (Ennis, 1996). High shear mixers are suited to small-scale processing of lighter materials as in the pharmaceutical and detergent industries.

A 5 litre grinding mill (Pascall Engineering Ltd) minus the grinding media was used as a low shear drum pelletiser (see figure 5.6). Rotation speed was regulated by a variable speed controller. Carbon dioxide was feed into the drum at a rate of 5 litres per minute through a pipe connected via a pivoting elbow. The drum measured 20cm in diameter, 20 centimeters in length, and had a total volume of 6.3 litres.

The influence of the drum pelletiser rotation speed and mixing time were investigated. In accordance with the past studies discussed in chapter 2, rotation speed was varied from 10-50rpm in 10rpm increments, and mixing times of 2, 5, 10, 20 and 30 minutes were studied.

The effect of introducing CO_2 into the drum was evaluated by making identical batches of pellets under a flow of CO_2 and in a normal atmosphere. The curing of materials in a CO_2 atmosphere to promote the desired chemical and physical properties is a long established method. The effect of curing upon the pellets carbonated in the drum was considered by subjecting pellets to curing for three days. As a control, sub-samples of the pellets were cured in air at 100% relative humidity for three days. A non-pressurised plastic chamber was used for dynamic carbonation of samples (see figure 5.7). Gas from a pressurised cylinder was passed through a rotameter to regulate flow, and through a flask containing deionised water before entering the chamber. The flow of gas was set to 100cc/min, as this was the lowest graduation on the rotameter. An outlet hole in the lid of the chamber allowed the incoming gas to escape, preventing pressure build-up. After carbonation, the pellets were dried in an oven set to 40°C. These results are described in section 5.3.3.4.

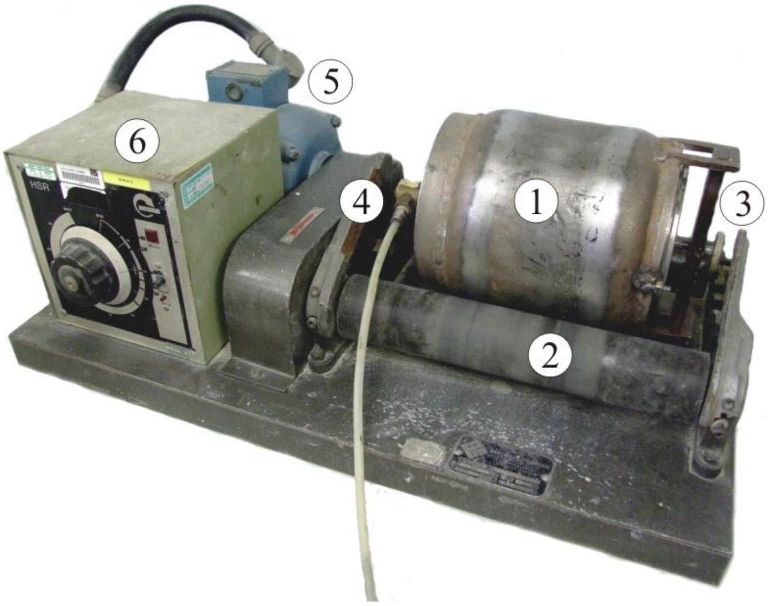


Figure 5.6: Laboratory drum pelletiser, (1) – pelletising drum, (2) – drive roller, (3) – door lock (4) –,gas pipe (5) – motor, (6) – speed control

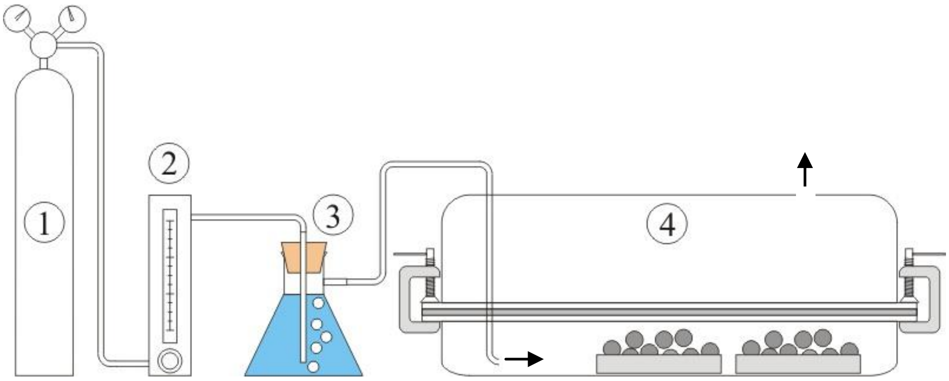


Figure 5.7: Dynamic flow carbonation chamber, (1) – CO_2 cylinder, (2) – Flow regulator, (3) – Gas humidifier, (4) Curing chamber containing samples

5.2.4 Mix Formulations

Wastes from thermal processes can be used as cement replacements (Wang and Baxter, 2007, Bai *et al.*, 2003, Taha *et al.*, 2002, Shoaib *et al.*, 2000). In accordance with the results of Chapter 4, wastes reacting with at least 5% by weight of carbon dioxide, were deemed to be sufficiently reactive to be trialed as CEM1 replacement binders (as listed in table 5.2). These wastes were used to bind the blended quarry wastes into pellets. Pellets were made using binder contents from 10% to 50% by weight.

Non-reactive wastes were blended with reactive wastes in an attempt to produce cemented products entirely from waste (see table 5.2). The pellets were dried in an oven set to 40°C. This is explored in section 5.3.4.

Table 5.2: Wastes used in the pelletising trials

Non-reactive	**Reactive**
Bauxite	Cement Kiln dust
Biomass Ash	Cement Bypass Dust
Clinical Ash	MSWI-FA
MSWI Bottom Ash	Paper ash 1[†]
PFA	Paper ash 2[†]
Hassock Sand	Paper ash 3
Hassock Silt	Paper ash 4
Ragstone Sand	Paper ash 5
Ragstone Silt	Paper ash 6
Sewage Sludge Ash	Wood Ash
Steel Sludge	CEM1

[†] *wastes not examined due to availability*

5.2.5 Testing Pellets

5.2.5.1 Compressive Strength

British Standards provides a limited specification for lightweight aggregate. Similarly, there is limited information in the literature describing LWA requirements, the majority pertaining to specification for lightweight concrete. A single pellet compressive strength test is specified in the American Standard ASTM D4179-01 for use with formed catalyst shapes. This method has been modified for use with single aggregate particles (Arslan and Baykal, 2006a, Cheeseman *et al.*, 2005, Li *et al.*, 2000). The strength is measured by crushing the pellet between two flat platens. According to Arslan and Baykal (2006) and Li (2000), the pellet strength can be calculated according to eq (1).

$$\sigma_c = \frac{2.8Fc}{\pi dm^2} \tag{5.1}$$

where σ_c is the compressive strength in megapascals, F_c is the fracture load in kilonewtons, A_m is the mean area of the pellet, and d_m is the mean diameter of the pellet. For each sample, ten pellets of varying size were crushed, and the average strength calculated. The three axis of each pellet were measured using digital callipers, and crushed with a hand-held force meter (Mecmesin MFG250). The pellets were also soaked for 24 hours and crushed to obtain the wet strength.

5.2.5.2 Particle Size Distribution

The particle size distribution of the pelletised products were measured using a dry sieving technique according to British Standard BS 812-103.1 (1985). A sample of pellets was dried to constant weight at 105°C according to British Standard BS EN 1377-2 (1990). This was passed through a nest of sieves; 28mm, 20mm, 14mm, 10mm, 6.3mm, 5mm, 3.35mm, 2.36mm, 1.18mm, and 850µm, and the fraction retained was weighed.

The mean diameter of the pellet batches was calculated by multiplying the mid point of the class interval (MP) by the frequency (F) in % by weight in that class (see table 5.3). The sum of the F*MP column is divided by the sum of the frequency column to give the mean particle size in mm.

Table 5.3: Calculation of mean particle size

Class Interval	Mid Point (MP)	Frequency (F)	F*MP
28-20mm	24.00	0.00	0
20-14mm	17.00	0.00	0
14-10mm	12.00	0.00	0
10-6.5mm	8.25	7.67	63.26199
6.5-5mm	5.75	5.43	31.23356
5-3.35mm	4.18	13.59	56.71976
3.35-2.36mm	2.86	12.77	36.46129
2.36-1.18mm	2.03	15.62	31.70135
1.18mm-850µm	0.85	44.93	38.18789
		$\sum(F)=100$	$\sum(F*MP)=257.5658$

$\sum(F*MP) \div \sum(F)=$**2.5757**

5.2.5.3 Carbon Dioxide Uptake

The degree of carbonation in the pellets was measured by thermogravimetric analysis. A ten gram sample of pellets dried at 105°C was crushed to pass a 40μm sieve. The powder was then analysed according to section 3.3.9.

5.2.5.4 XRD

The crystalline phase compositions of the pellets were measured by XRD. A ten gram sample of pellets dried at 105°C was crushed to pass a 40μm sieve. The powder was analysed according to section 3.3.1.

5.2.5.5 SEM

SEM analysis was performed upon resin blocks containing embedded pellet fragments. The pellets were split in half by placing pressure on a knife edge positioned on the equatorial plane. These halves were then placed at the bottom of a resin mould, and vacuum impregnated with resin according to section 3.3.4. Analysis of the resin blocks was performed with the backscattered electron detector and the energy dispersive spectrometer.

5.2.5.6 Optical Microscopy

Pellets were prepared as thin sections by an external specialist laboratory. The thin sections were prepared to 30μm thickness, according to section 3.3.8.

5.3 Results

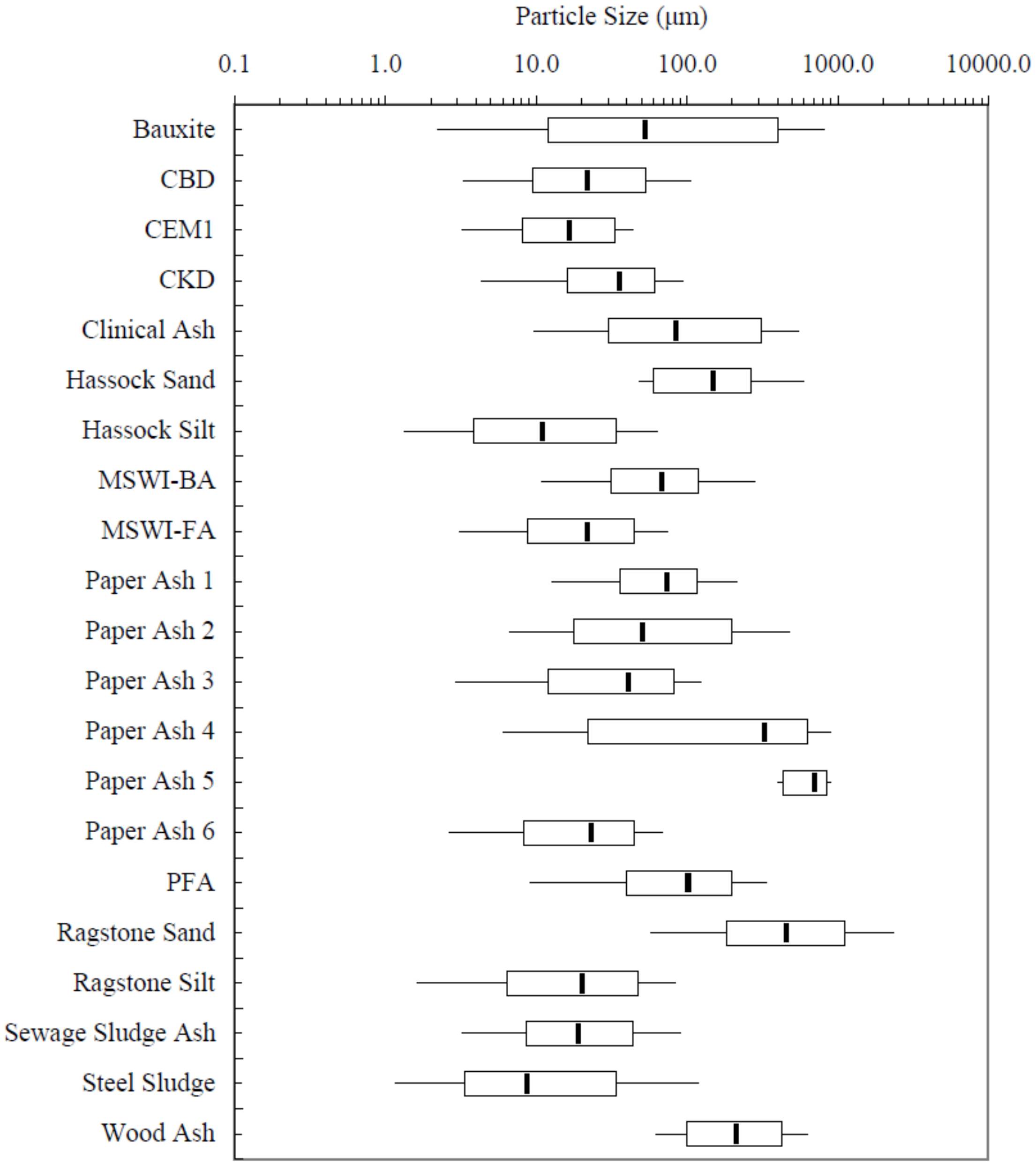
5.3.1 Materials

The elemental compositions of quarry wastes are shown in table 5.4. Silicon and calcium were the largest components, and iron was present up 3.9%, aluminium up to 5.6%, and magnesium up to 1.9%.

Table 5.4: Elemental compositions of the wastes examined (values in % by weight, errors are the interquartile ranges)

	Al_2O_3	**CaO**	**Fe_2O_3**	**K_2O**	**MgO**	**MnO**	**Na_2O**	**P_2O_5**	**SiO_2**	**SO_3**	**TiO_2**
Hassock Sand	3.9±0.2	50.5±2.0	3.6±0.3	1.0±0.2	0.9±0.1	0.1±0.1	0.1±0.0	0.3±0.2	39.2±2.9	0.2±0.0	0.2±0.1
Hassock Silt	4.3±0.3	38.5±2.4	3.9±0.1	1.3±0	0.7±0.0	0.2±0.1	0.1±0.0	0.3±0.1	50.2±3.4	0.2±0.0	0.1±0.1
Ragstone Sand	2.1±0.1	57.1±3.7	3.0±0.1	0.9±0.1	1.3±0.2	0.1±0.1	0.1±0.0	0.2±0.2	34.3±3.6	0.3±0.0	0
Ragstone Silt	2.7±0.1	54.5±3.9	3.1±0.2	0.8±0.1	0.9±0.1	0	0.1±0.0	0.1±0.1	36.1±3.2	0.2±0.0	0.2±0.2
CEM1	5.2±0.1	64.5±2.1	3.5±0.3	0.2±0.0	2.2±0.4	0.1±0.0	0.1±0.0	0.1±0.0	19.8±1.4	2.9±0.2	0.3±0.1

Particle size distributions for the wastes are shown in figure 5.8. Particles are classified by size as clay below 2µm, as silt between 2 and 65µm, and as sand between 65µm and 2mm. The wastes can be broadly described as silty-sands. CBD, CKD, MSWI-FA, paper ashes 3 and 6, hassock silt, ragstone silt, sewage sludge ash, and steel sludge were predominantly composed of silt-sized particles. Clinical ash, Hassock sand, paper ashes 1, 4 and 5, PFA, Ragstone sand, and wood ash, were largely composed of sand-sized particles.



Vertical black lines designate the means, boxes represent the interquartile ranges, whiskers extend to 10th and 90th percentiles

Figure 5.8: Particle size range of as-received wastes

5.3.2 Pelletising Equipment Variables

5.3.2.1 Rotation Speed

The effects of the drum pelletising variables, including rotation speed upon the physical appearance of the pelletised product can be seen in figure 5.9.

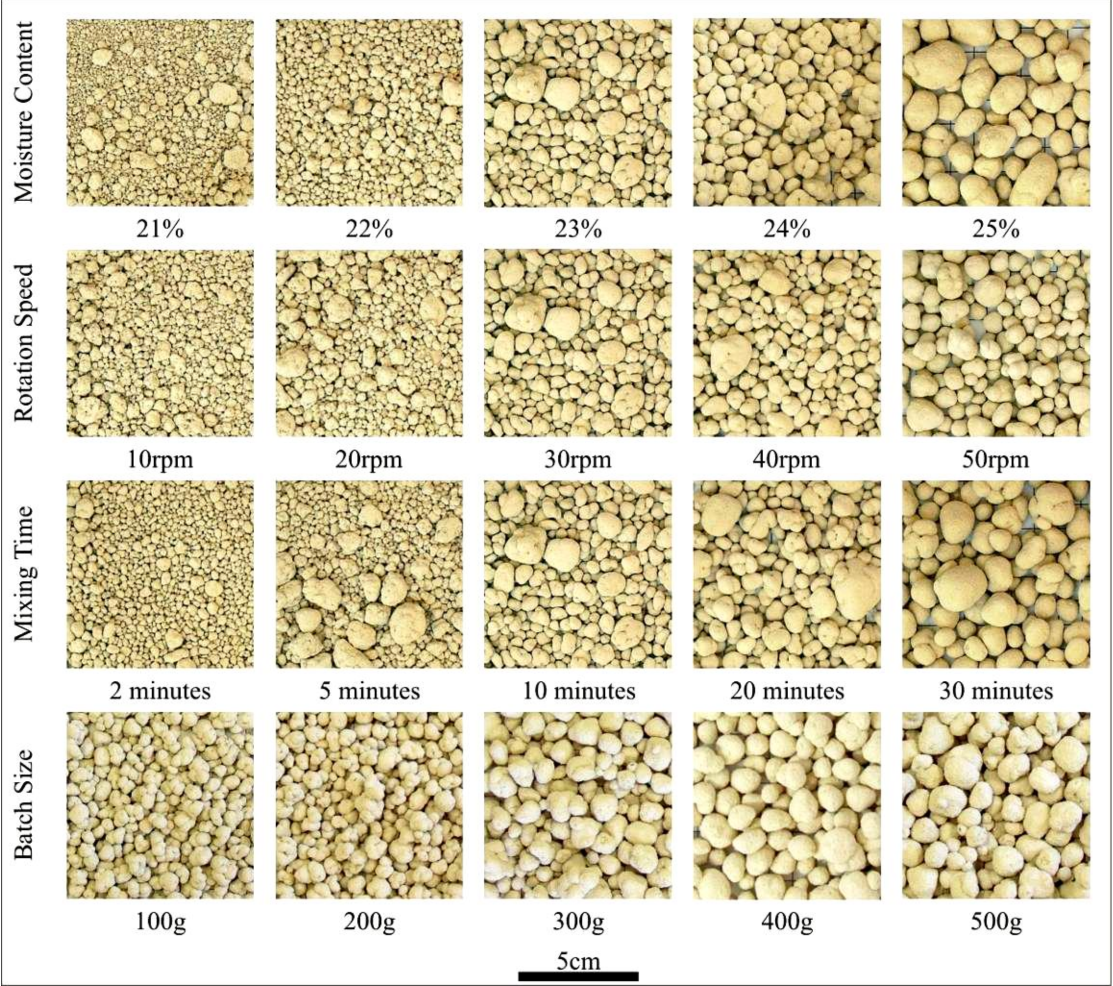


Figure 5.9: Effect of operating variables on the morphology of pellets

The particle size distribution was affected by the rotation speed (see figure 5.10). Agglomerates became enlarged by increasing the speed of the drum. Conversely, reducing the drum speed limited growth. At 10rpm, the mean pellet size was 4.2mm. Given that the graph shows almost a straight line, pellet growth is apparently directly related to the speed of the drum. At 50rpm, the mean size was 13.5mm, but variability was significantly greater.

Rotation speed also affected pellet strength (see figure 5.11). At 10rpm, mean pellet strength was between 0.04 and 0.08MPa if the pellet was in a wet or dry state respectively. Dry strength increased to 0.18MPa at 40rpm, and fell to 0.13MPa, when the speed was raised to 50rpm. Whilst wet strength increased to 0.08MPa at 40rpm, and did not show a significant increase as rotation speed was raised further.

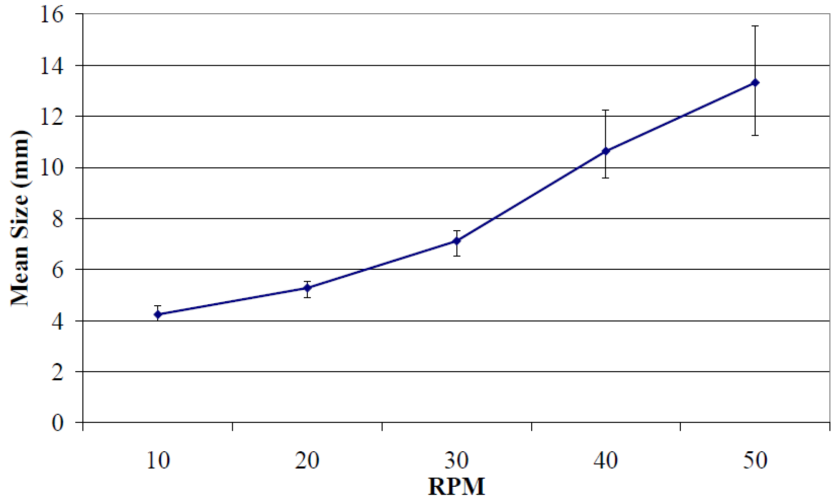


Figure 5.10: Effect of rotation speed upon mean pellet size

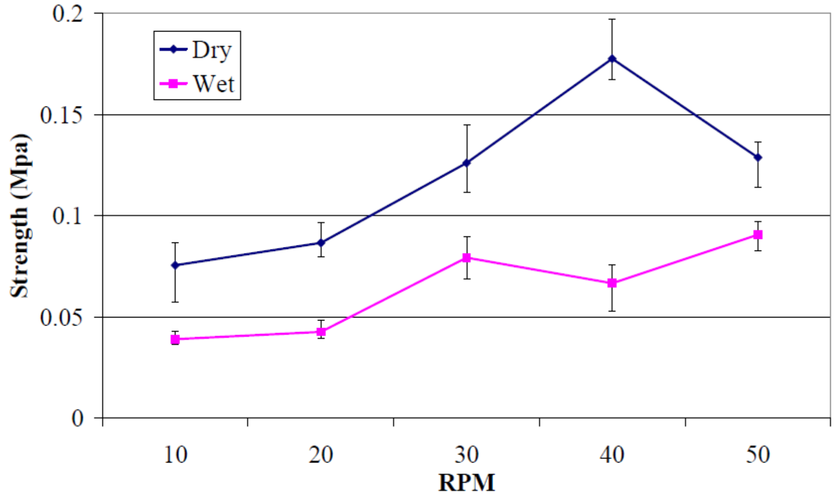


Figure 5.11: Effect of rotation speed upon pellet strength

Carbon dioxide uptake reached a maximum of 1.2% by weight of binder at 10rpm (see figure 5.12). Given that CEM1 can achieve a maximum uptake of 29.6%, the uptake achieved was around 4% of the total (see table 4.2). As the rotation speed was increased, and hence the growth rate of the pellets increased, carbon dioxide fell to 0.5% by weight of binder at 40rpm.

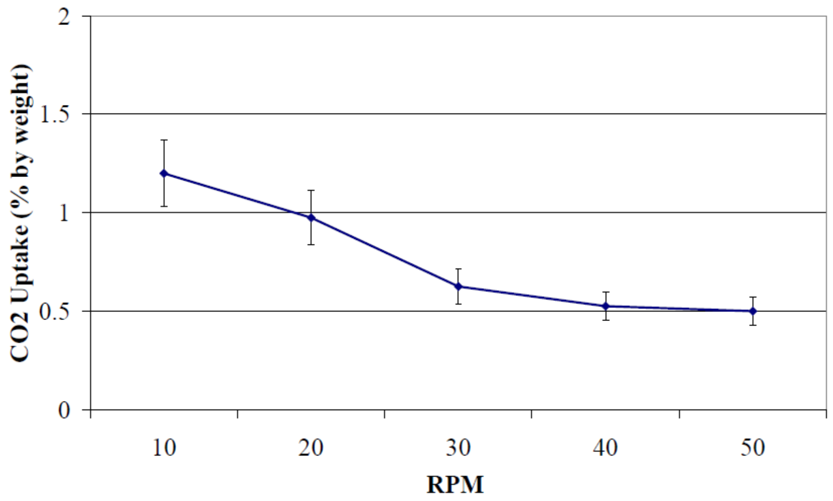


Figure 5.12: Effect of rotation speed upon pellet carbon dioxide uptake by weight of binder

5.3.2.2 Mixing Time

Extending the mixing time promoted continued growth of the pellets (see figure 5.13). Between 2 and 5 minutes mixing, the mean pellet size remained constant at 5.5mm. This indicates an induction phase, during which the pellets consolidate and the surfaces become wet.

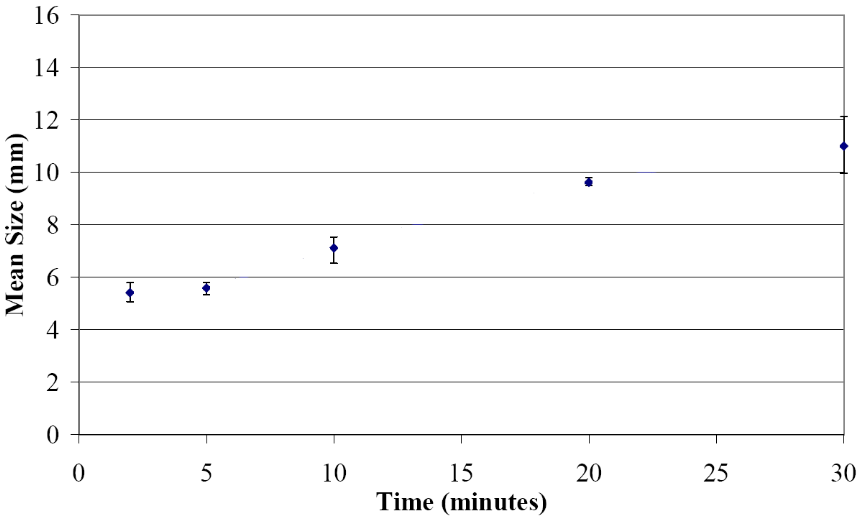


Figure 5.13: Effect of mixing time upon mean pellet size

Growth in the first five minutes was slow, indicating an induction phase before steady-growth commenced. Between five and thirty minutes, pellet growth was steady, ultimately increasing to 11mm. The curvature of the graph suggests that the rate of growth was slowing with time, and that with further mixing, growth would ultimately cease, when further consolidation was no longer possible.

Pellet strength followed a similar pattern to that of the particle size distribution (see figure 5.14). In the first five minutes, dry strength development was not significant. After ten minutes, dry strength increased from 0.08MPa to 0.12MPa. Prolonged pelletising did not increase dry strength, but did continue to improve wet strength.

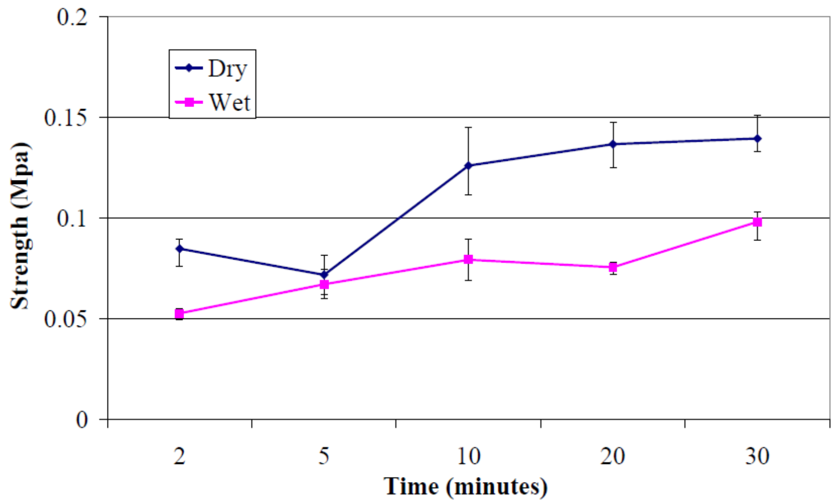


Figure 5.14: Effect of mixing time upon pellet strength

Although exposure to carbon dioxide for a longer period of time should promote uptake, no significant increase was observed (see figure 5.15).

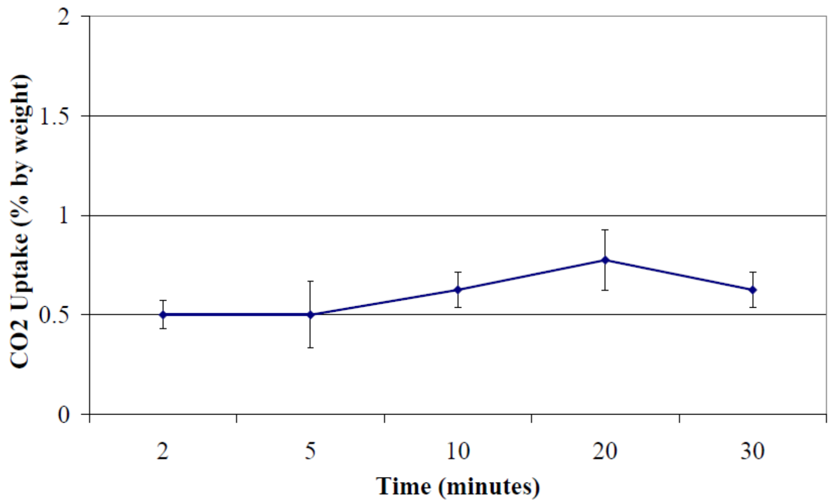


Figure 5.15: Effect of mixing time upon pellet carbon dioxide uptake by weight of binder

5.3.3 Pelletising Mix Variables

5.3.3.1 Moisture Content

Moisture content had a significant effect upon the mean particle size of the pellets (see figure 5.16). At 21% moisture, pellets of 3mm were formed, and increased to 13.3mm at 25% moisture. Over the range tested, the size increase was steady, with minimal variation between batches.

Strength of the pellets also increased with moisture content (see figure 5.17). At 21% moisture, dry strength was 0.8MPa and wet strength was 0.05MPa. Dry strength peaked at 0.17MPa at 24% moisture, whilst wet strength continued to increase up to 0.09MPa at 25% moisture. Strength is reduced in concretes with a higher water/cement ratio (w/c), due to a decrease in the quantity of cement paste and reduced porosity from excess water (Concrete Society, 2005, C.I.R.I.A, 2001).

The maximum carbon dioxide uptake achieved was 1.5% by weight of CEM1, which represents 5% of the total potential for CEM1 (see figure 5.18). Between moisture contents of 21% and 23%, carbon dioxide uptake fell from 1.5% to 0.6%. Carbon dioxide remained constant above 23% moisture content.

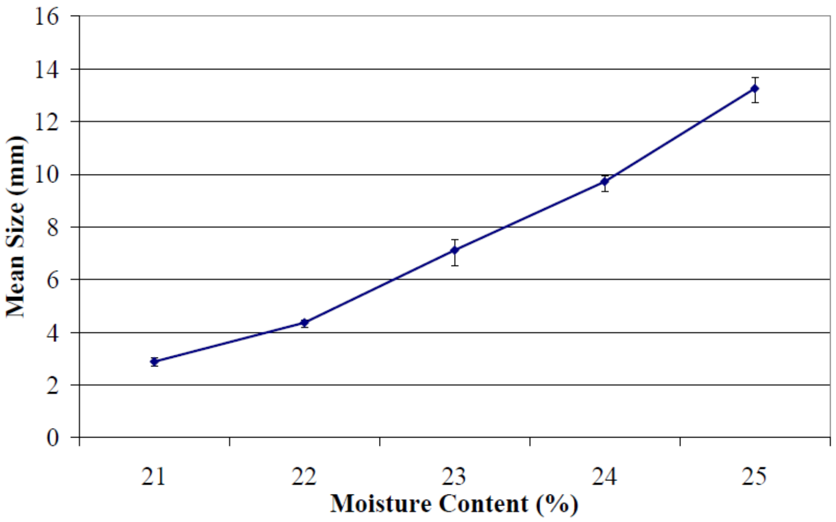


Figure 5.16: Effect of moisture content upon mean pellet size

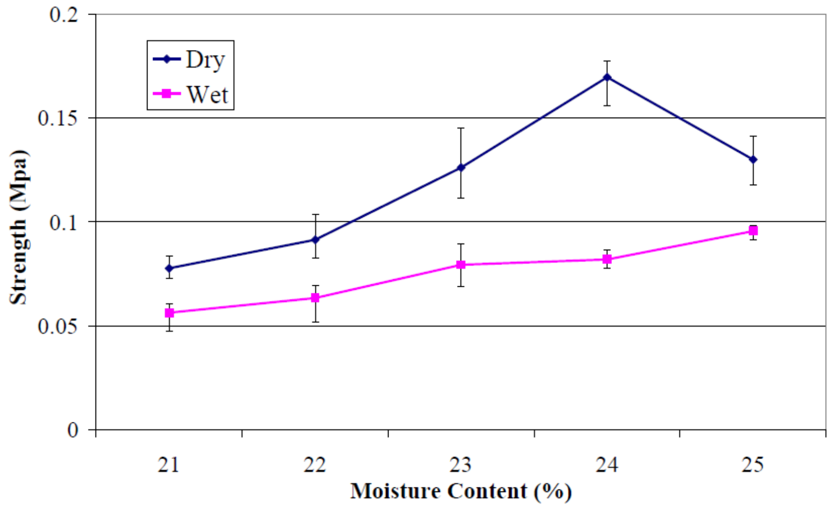


Figure 5.17: Effect of moisture content upon pellet strength

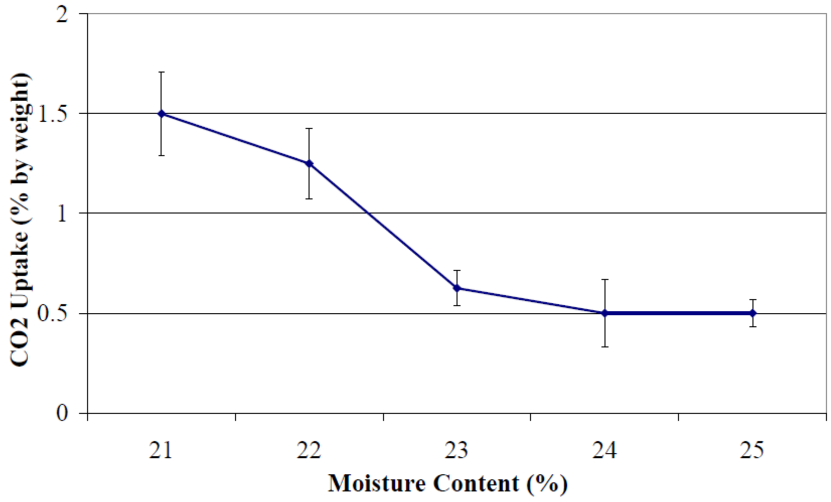


Figure 5.18: Effect of moisture content upon pellet carbon dioxide uptake by weight of binder

The relationship between carbonation and agglomeration over a broad moisture range and reaction time was examined. Pellets made from a quarry fines and CEM1 according to section 5.2.3.1, were produced at a series of different moisture contents and cured for 24 hours in the dynamic carbonation chamber. The pellets were tested for particle size distribution and carbon dioxide uptake (see figure 5.19).

Carbon dioxide uptake peaked at 11.2% by weight of CEM1 at a moisture content of 14%. Between 5% and 18% carbon dioxide uptake was above 10%, but rapidly fell to less than 2% at 26% moisture. Carbon dioxide uptake remained steady at around

1.5% up to the limit of the test at 36% moisture. Agglomeration began to occur significantly above 16% moisture, coinciding with the sudden drop off in carbon dioxide uptake. Above 22% moisture, agglomerate growth rapidly increased, peaking at 10.9mm at 32% moisture. Above 35% moisture, the material became a slurry upon pelletising.

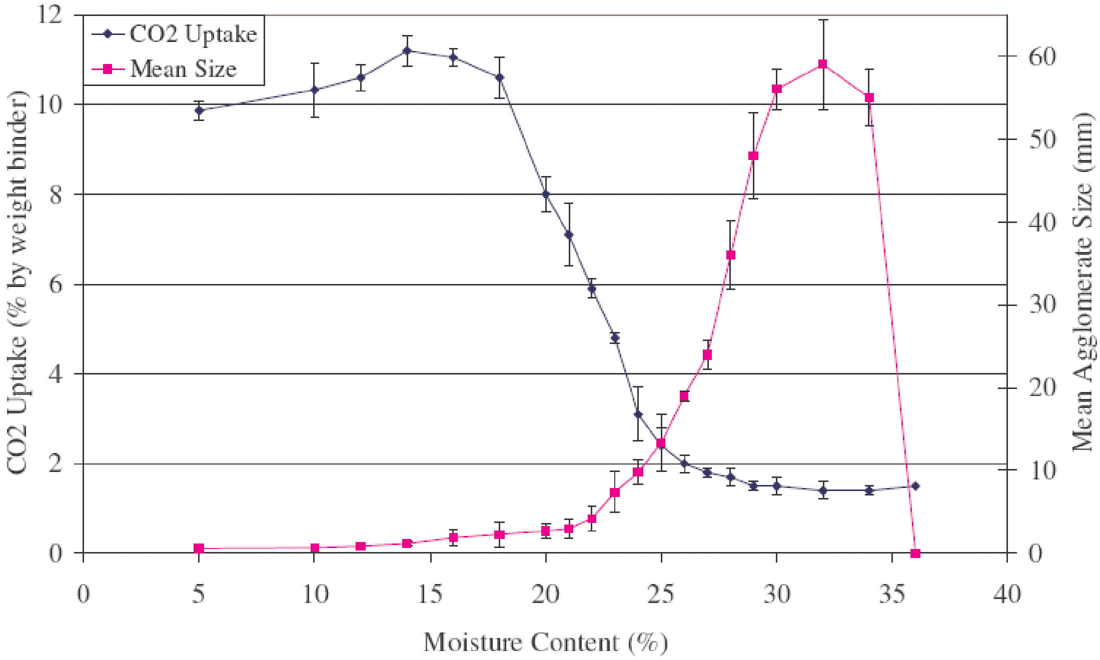


Figure 5.19: Relationship between carbon dioxide uptake and agglomerate growth (error bars represent the interquartile ranges)

5.3.3.2 Particle Size Distribution

The dominance of either silt or sand, made the mixture difficult or impossible to pelletise. Whilst mixes containing only silt could be pelletised, mixes containing only sand could not, suggesting that the fines content was needed for agglomeration to occur. However, excess fines resulted in uncontrollable growth and a soft product. If either the fines or coarse content was dominant, the pelletising speed and mixing time must be carefully controlled to achieve agglomeration. Given that the particle size distribution of the feed affected the wetting behaviour of the material, different amounts of water had to be added to achieve agglomeration. Therefore, presentation of the mean pellet size data would not be a fair comparison.

Pellet strength was affected by the particle size distribution of the material (see figure 5.20). It was found that pellets could not be made entirely from sand sized grains. An approximately equal mix of sand and silt sized particles produced pellets with the greatest strength. As either the sand or silt sized fraction became more dominant, the strength decreased. Carbon dioxide uptake of the material was not significantly affected by the particle size distribution, and remained between 0.5 and 1% by weight of binder (see figure 5.21).

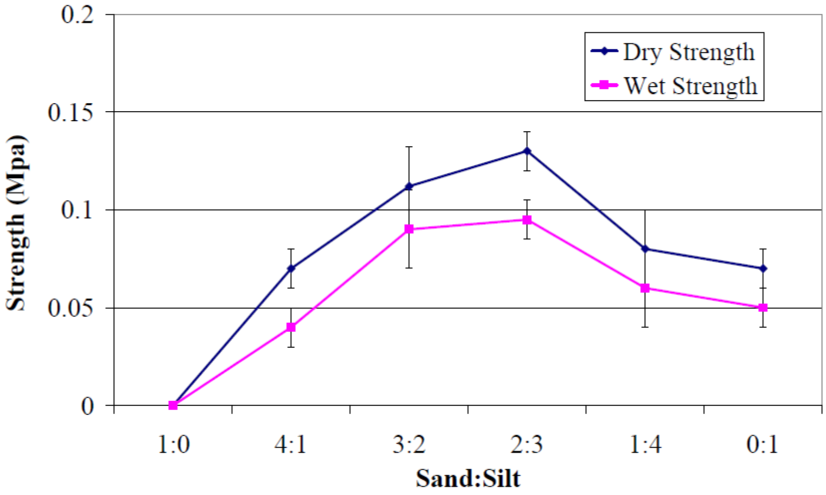


Figure 5.20: Effect of particle size distribution upon pellet strength

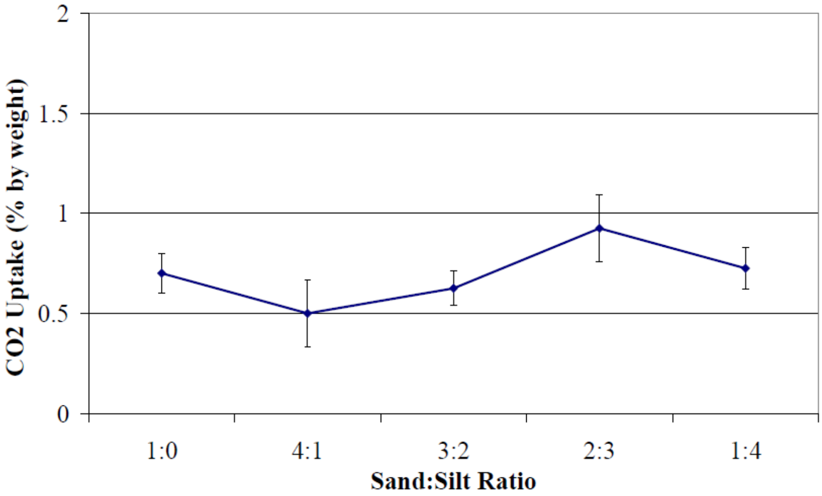


Figure 5.21: Effect of particle size distribution upon pellet carbon dioxide uptake by weight of binder

5.3.3.3 Batch Size

Increasing the batch size also promoted pellet growth (see figure 5.22). Below a batch size of 100g, the volume of material was insufficient to induce tumbling in the drum, the pellets only grew to 6mm in size. The drum was operating at full capacity at 500g, and produced pellets 10.5mm in size. As the batch size increased, the variation in the mean particle size became greater. This may in part have been due to the difficulties of premixing larger amounts of material to the same consistency. The strength of the pellets was unaffected by the batch size, despite the effect upon growth rate (see figure 5.23). Carbon dioxide uptake reached a maximum of 0.7% at 100g drum fill. Uptake decreased steadily to 0.4% at a 500g batch size (see figure 5.24) .

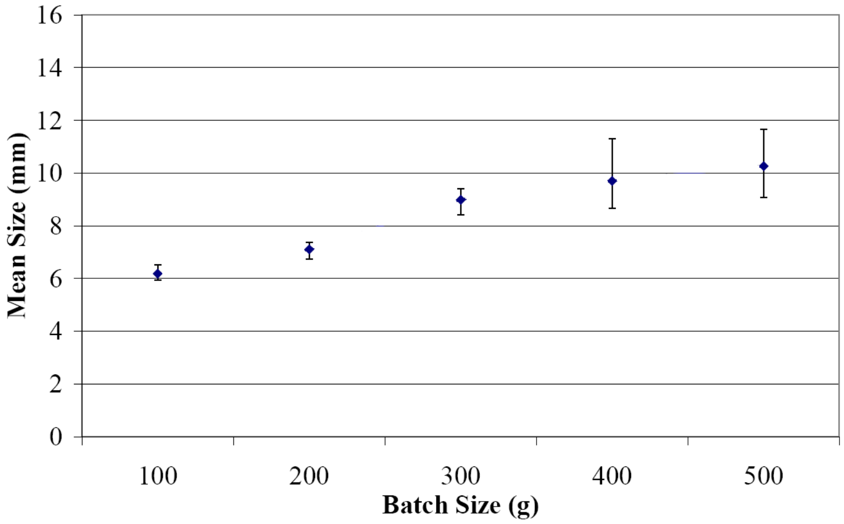


Figure 5.22: Effect of batch size upon mean pellet size

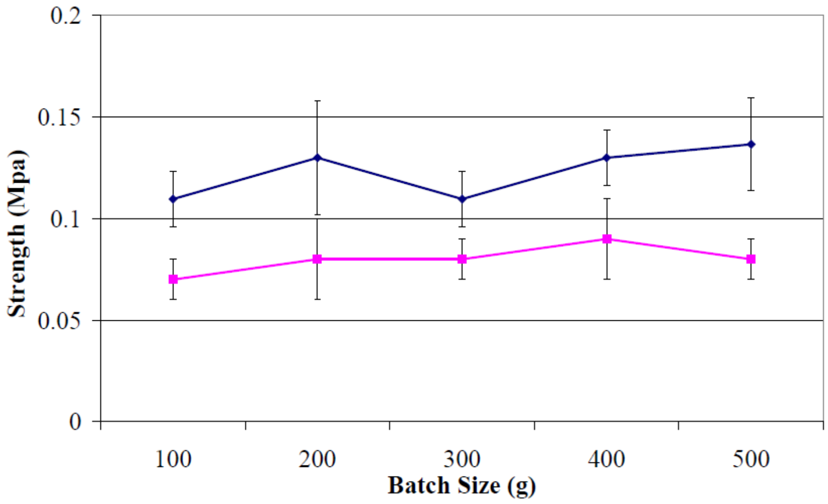


Figure 5.23: Effect of batch size upon pellet strength

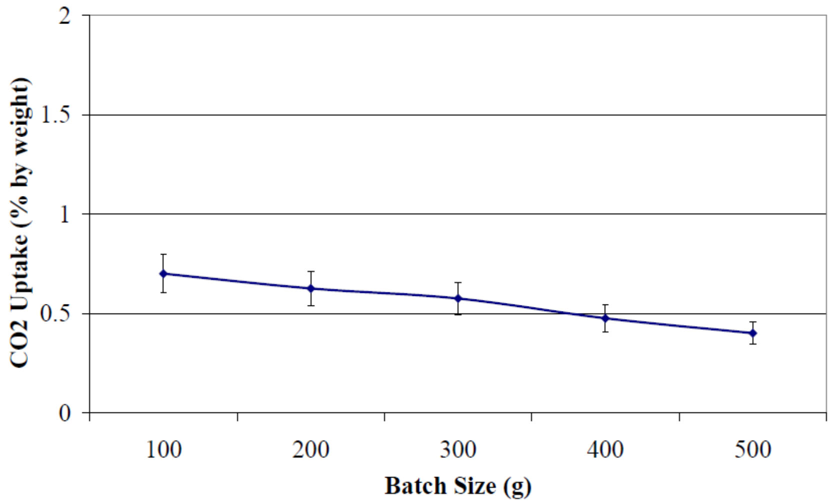


Figure 5.24: Effect of batch size upon pellet carbon dioxide uptake by weight of binder

5.3.3.4 Binder Content

Figures 5.25, 5.26 and 5.27 show the dry strength, pH and carbon dioxide uptake of pellets made using the same 1:1 ratio of sand and silt with different waste binders and with CEM1, and the affects of further curing upon the pellets.

Irrespective of the binder type or content, no significant difference in strength was observed between those pelletised in air (oven dried), and those pelletised in a carbon dioxide atmosphere. The strength of drum carbonated and drum pelletised materials was lower than that recorded for LECA, and comparable or stronger materials could only be produced by further curing.

CEM1-based pellets without further curing achieved strengths of 0.02MPa at 10% binder content, increasing to 0.7MPa at 50% binder content. Pellets containing 30% CEM1 which were hydrated for 72 hours reached 0.39MPa, but only attained 0.33MPa when carbonated for the same amount of time.

Pellets bound with MSWI-FA and paper ashes 4, 5, and 6, did not achieve strengths greater than 0.03MPa, even at 50% binder content. These pellets disintegrated through attrition and normal handling. MSWI-FA and paper ash 4 showed a slight increase in strength as the binder content was increased. However, paper ashes 4 and

5 only produced pellets with measurable strength, when cured either by hydration or carbonation, although the difference between the two was indistinguishable. MSWI-FA showed no significant increase in strength upon further curing.

As a binder, CBD did not have a measurable strength until cured, with carbonated pellets realising 0.05MPa at with a 50% binder, dosage, compared to 0.02MPa through hydration. At 40% content, CKD pellets cured for 72 hours in carbon dioxide achieved a strength comparable to LECA (0.09MPa). For comparison, the same pellets allowed to hydrate reached 0.05MPa.

Paper ash 3-bound pellets obtained a equivalent strenngth to the LECA aggregate with 40% binder content after curing. In this product, hydration had a more beneficial effect upon strength development than carbonation. Conversely, wood ash strength was promoted by carbonation, and at a40% binder content, carbon dioxide-cured pellets achieved a strength of 0.12MPa.

As a general observation, increasing the binder content resulted in an increase in the carbon dioxide uptake and the pH of the final pelletised product. Curing in carbon dioxide promoted uptake above that achieved by drum carbonation. Drum carbonation alone achieved a maximum uptake of 2% by weight of binder. Considering that MSWI-FA was the least reactive binder, achieving 6.6% maximum carbon dioxide uptake, this level of reaction in the pellets amounted to less than 8% of the total potential.

Curing CEM1 pellets in carbon dioxide increased carbon dioxide uptake by a factor of 20. With the exception of MSWI-FA, the drum carbonated materials had pHs above 11. After 72 hours carbonation, the pHs decreased for CKD, MSWI-FA, paper ashes 3 and 6, wood ash, and CEM1. This decrease in pH was more marked at below 30% binder content. The remaining materials showed negligible decrease in pH after 72 hours of carbonation.

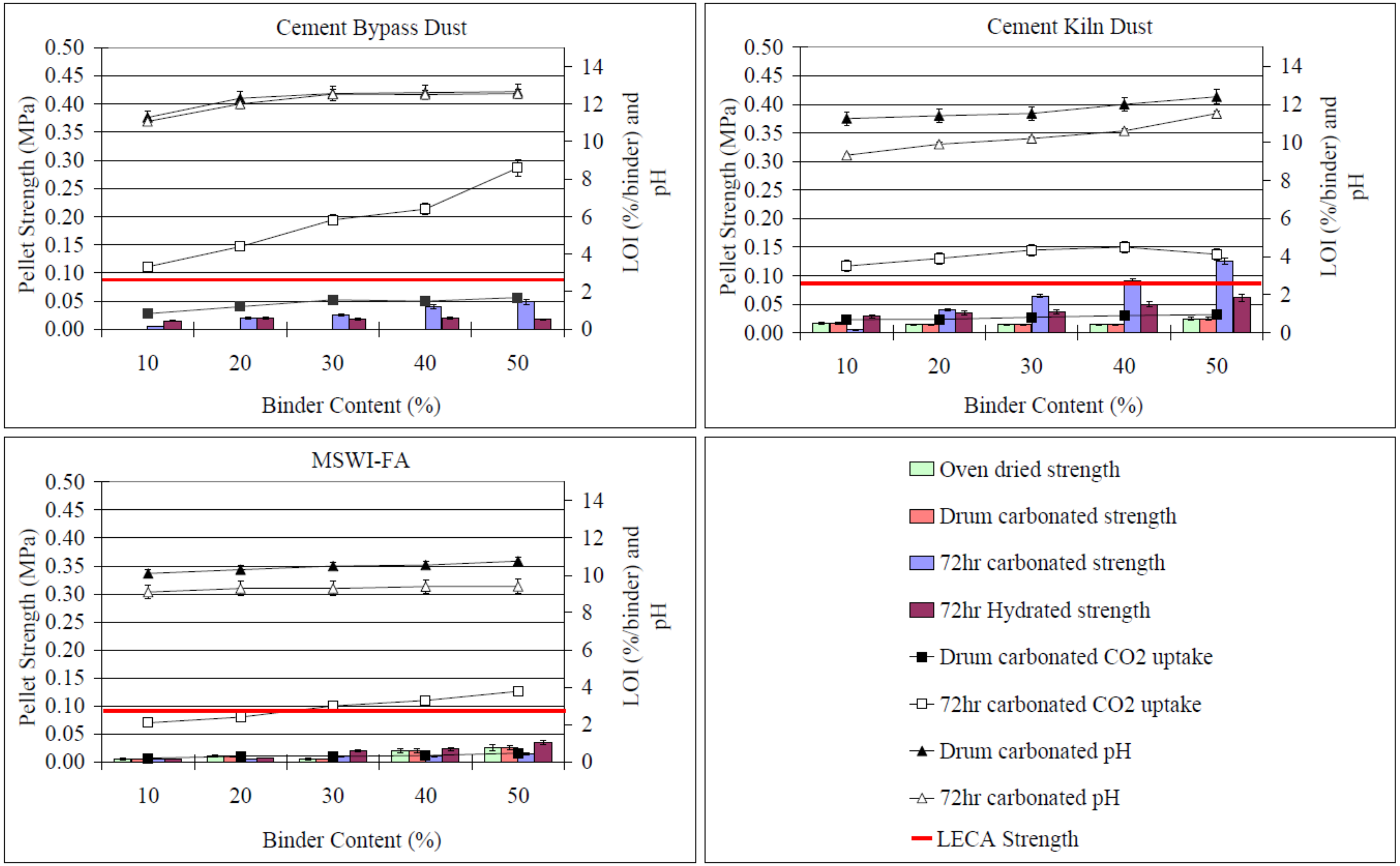


Figure 5.25: Strength, pH and LOI of quarry fines pellets with different binders (error bars represent the interquartile ranges)

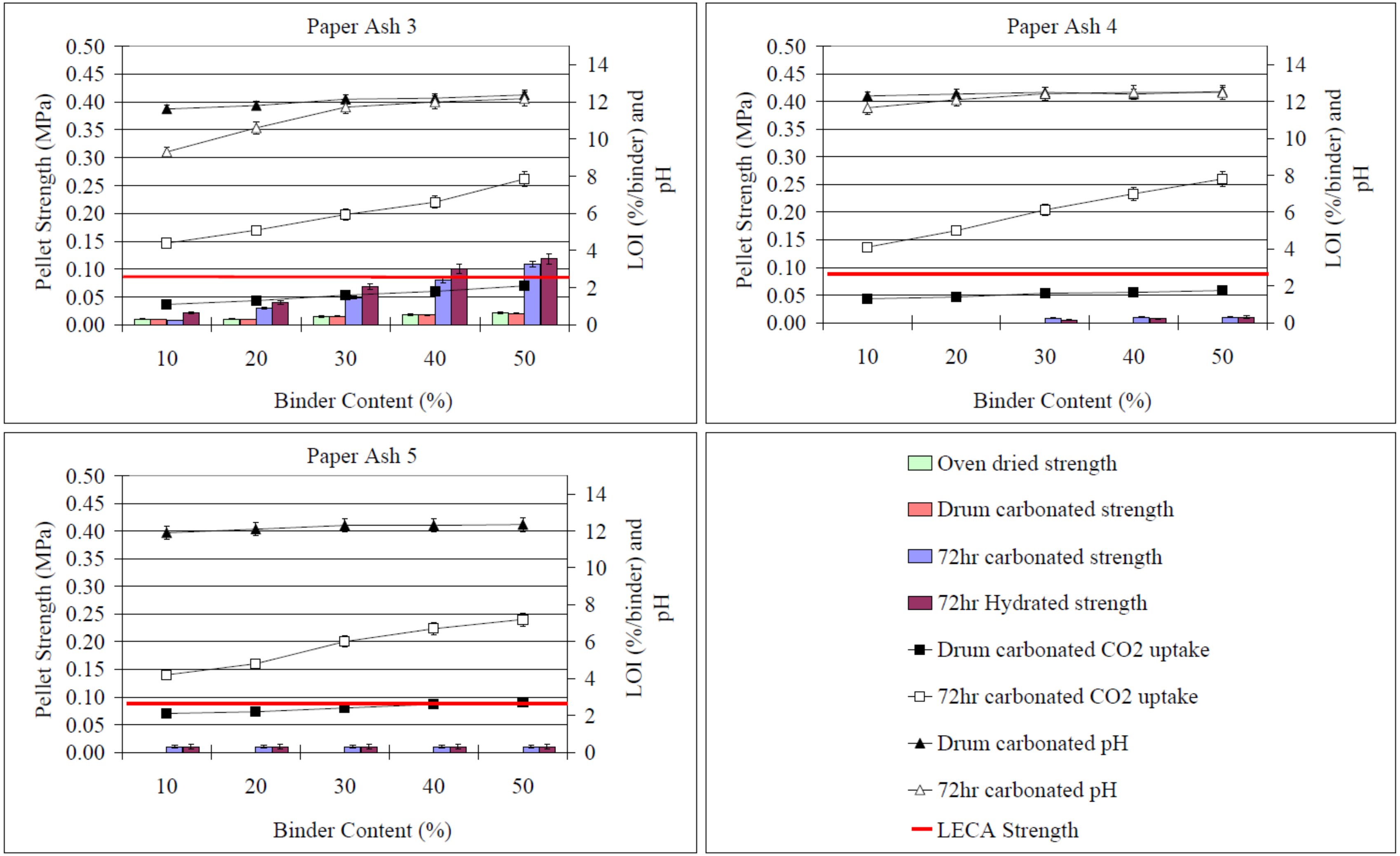


Figure 5.26: Strength, pH and LOI of quarry fines pellets with different binders (error bars represent the interquartile ranges)

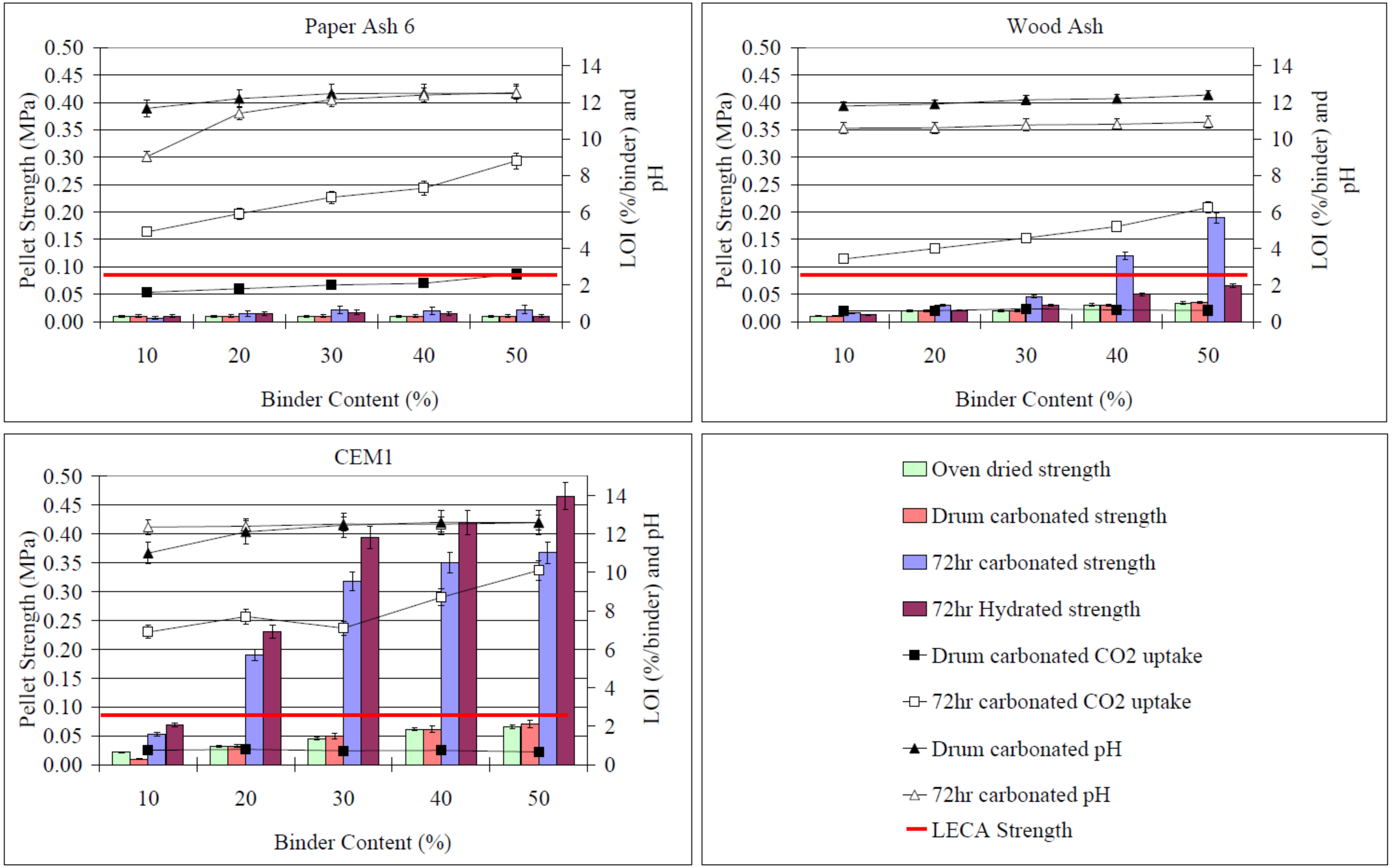


Figure 5.27: Strength, pH and LOI of quarry fines pellets with different binders (error bars represent the interquartile ranges)

5.3.3.5 Other Pelletising Factors

The premixing of material was an important step in the pelletising process. The variation in the particle size distribution of the pelletised products was found in the process of preparing triplicate batches (see figure 5.28). Occasionally, one or more oversized pellets would form in a batch of ‘normal’ sized agglomerates. The significantly greater mass of these pellets resulted in uncontrolled coalescence with smaller agglomerates. It has been recognized that in a wet agglomeration process, poor mixing of the dry powder and the liquid binder results in a wide range of pellet sizes (Gluba, 2003).

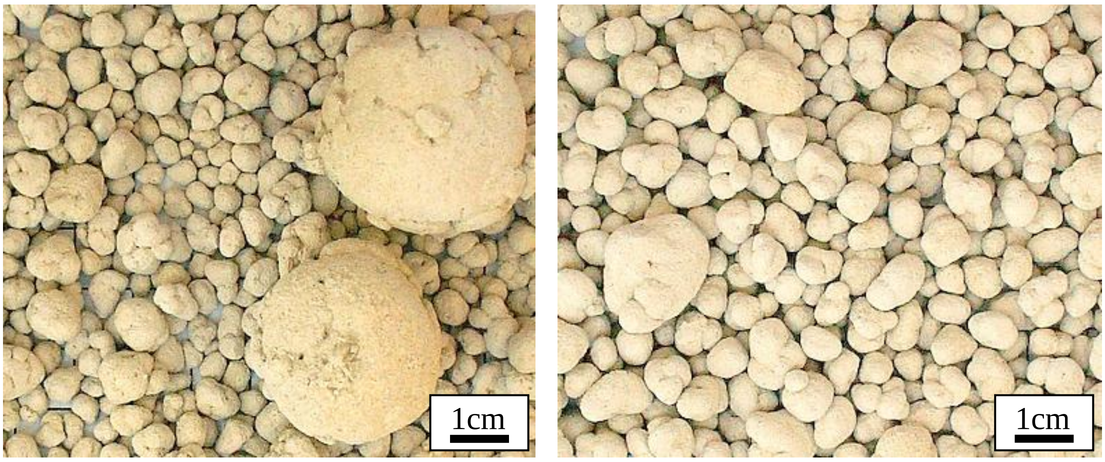


Figure 5.28: Pellets prepared with identical mix designs

5.3.4 Pelletising Wastes

Pelletising trials were conducted for the full range of wastes. Based upon the observations of the pelletising variables, including the binder type and content, and particle size distribution of the material, mixes of wastes were trialled systematically until a pelletised product was obtained.

Each waste displayed a unique behaviour, requiring a great deal of trial-and-error to design a material that could be pelletised, and produce a product with the required strength. The optimized mix formulations for each of the wastes are shown in table 5.5. Given that some of the wastes could be used as binders, there is potential for the binders listed to be substituted for others. According to the respective strength of the binders, the proportions would have to be adjusted to produce comparable pellets e.g 30% CKD would have to be used instead of 10% CEM1 to attain the same strength. It was noted that certain wastes, e.g bauxite, biomass ash and clinical ash, produced pellets of measurable strength with minimal binder, or using other wastes as cement substitutes. Other wastes, e.g. MSWI-BA, MSWI-FA, and SSA could only be produced by mixing with at least 20% of CEM1. Paper ashes 4-6 cracked after curing, suggesting problems of unsoundness.

Aside from binding the material together, blending wastes with complimentary physical properties, e.g. particle size, was necessary. The particle size of the wastes influenced agglomeration and the strength of the pellets. Figure 5.29 shows the particle size of the raw wastes classified as clay (below 2µm), as silt (between 2µm and 65µm), and as sand (between 65µm and 2mm). Whilst the wastes were deficient in clay-sized particles, the importance of a balance of sand and silt-sized particles was apparent. Materials with less than 30% and greater than 60% sand particles could not be pelletised without blending with other materials.

Particle size distributions of the optimized mixes listed in table 5.5 are shown in figure 5.30. The formulations are limited to the region between 20 and 60% sand, with the remainder composed of silt and clay sized particles.

Table 5.5: Mix formulations to produce pellets from waste

Waste	Mix Formulation
Bauxite	+ 30% paper ash
Biomass ash	+ 20% sand + 30% paper ash 3
Cement bypass dust	+ 40% Hassock sand
Cement kiln dust	+ 60% Hassock sand
Clinical ash	+ 10% CEM1
MSWI-BA	+ 40% Hassock sand + 20% CEM1
MSWI-FA	+ 25% Hassock sand + 8% CEM1
Paper ash 1	+ 10% CEM1
Paper ash 2	+ 10% CEM1
Paper ash 3	No addition required
Paper ash 4	+ 20% Hassock silt + 20% CEM1
Paper ash 5	+ 20% Hassock silt + 20% CEM1
Paper ash 6	+ 25% Hassock sand + 20% CEM1
PFA	+ 30% Hassock sand + 20% paper ash 3
Hassock Sand	+ 25% Hassock Silt + 50% paper ash 3
Hassock Silt	+ 25% Hassock sand + 50% paper ash 3
Ragstone Sand	+ 25% Ragstone silt + 50% paper ash 3
Ragstone Silt	+ 25% Ragstone sand + 50% paper ash 3
Sewage sludge ash	+ 25% Hassock sand + 20% CEM1
Steel sludge	+ 20% Hassock sand + 20%CEM1
Wood ash	+ 20% finely ground wood ash

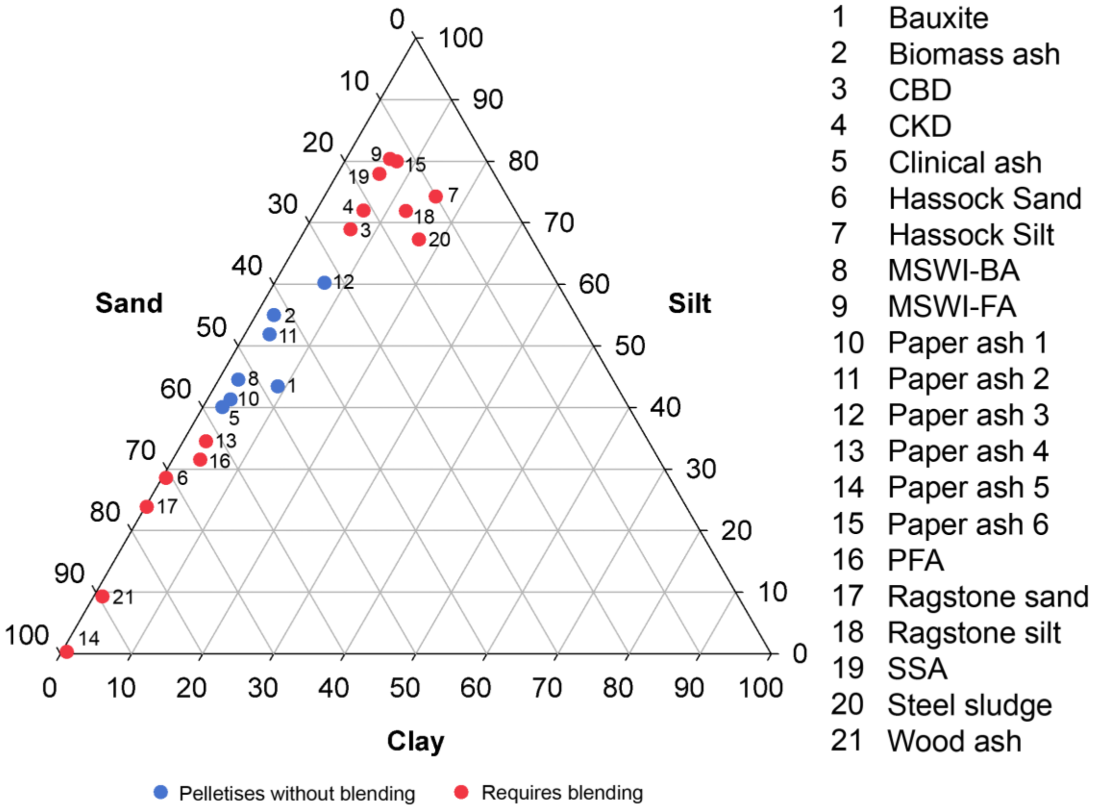


Figure 5.29: Particle size distribution of wastes

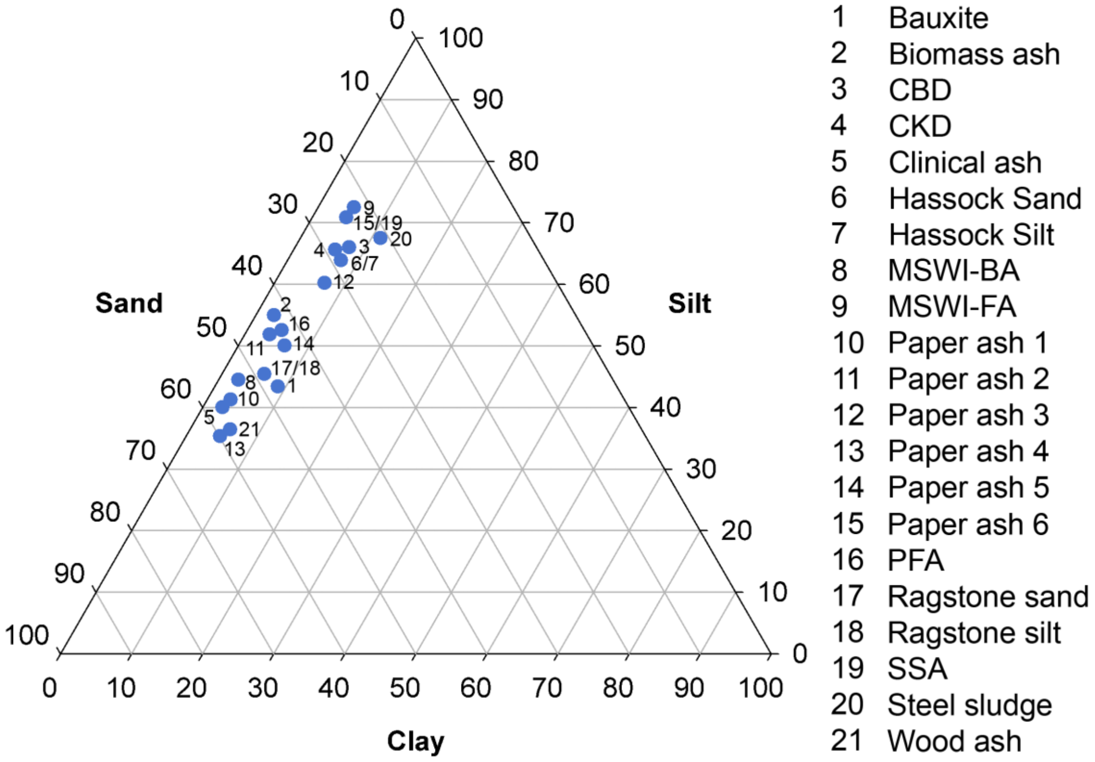


Figure 5.30: Particle size distribution of pellet mixes

Wastes composed of coarser sand-sized particles, including paper ash 5, wood ash, and Ragstone sand required mixing with a silt-sized materials to bind together into agglomerates. Conversely, very fine materials including MSWI-FA and paper ash 6 had to be mixed with coarser grained material. Where the grain size balance was not optimised, agglomeration became very difficult as the moisture content and machinery variables had to be precisely controlled, or could not be achieved at all.

5.3.5 Mineralogy and Microscopy

5.3.5.1 Binding Mechanisms of Waste

The use of wastes as binders, was discussed in section 5.3.3.4. Waste binders producing pellets with strengths greater than LECA after exposure to carbon dioxide, achieved equivalent strengths by hydration in air, suggesting the importance of hydration processes (and low levels of carbonation).

The binding mechanisms of the wastes were investigated by XRD, SEM and optical microscopy. XRD and SEM analyses carried out on the pellets did not give meaningful results, as the calcium carbonate content of the Hassock wastes masked any phase or microstructural changes. Optical microscopy was not suitable, as the maximum level of magnification achievable with an optical lens was not sufficient to discern individual grains and their petrographic characteristics. Hence, XRD and SEM analyses were conducted on the waste binders alone which were mixed with excess water to form a slurry and allowed to hydrate in sealed plastic bags filled with nitrogen for seven days. The amount of water required varied depending upon the chemistry of the wastes. A second set of waste slurries were carbonated in the dynamic chamber for seven days.

Backscattered electron and EDAX analysis of the microstructure and chemistry of the phases revealed that carbonation resulted in the infilling of the pore spaces with calcium carbonate (see figures 5.31-5.34). The key features identified are summarised in table 5.6. Cracks and voids were frequently observed in the hydrated pastes, and were clearly absent in the carbonated pastes.

Table 5.6: Key features indentified from SEM analysis of wastes

Waste	**Key Features**
CBD	Predominantly calcium silicate grains and occasional iron rich particles. Carbonation promoted calcite crystal growth, infilling the pores.
CKD	Predominantly calcium silicates with calcite. Patches of the matrix rich in sulfur. Carbonation produced a solid mass replacing discrete grains.
MSWI-FA	Composed of individual grains rich in calcium, silicon, iron, chromium and phosphorus. Some densification evident as a result of carbonation.
Paper Ash 3	Hydrated sample consisted of large grains (250µm) of calcium alumino silicates set in a fine calcite matrix. Carbonation resulted in the formation of a solid mass, with less distinct boundaries between grains and the matrix.
Paper Ash 4	Hydrated ash was composed of discrete grains of calcium carbonate and quartz with little or no matrix and extensive cracking. Carbonation produced a densified structure incorporating grains into the matrix.
Paper Ash 5	Composed of calcium carbonate, with some quartz and iron. A infilled structure resulted from carbonation.
Paper Ash 6	Hydrated sample rich in calcium carbonate, with some quartz. Dense mass of calcite formed due to carbonation.
Wood Ash	Hydrated grains were predominantly composed of calcite, with varying amounts of Si, Mn, Fe, P and Mg. Carbonation produced an infilled structure.

XRD analyses of the hydrated wastes are summarized in table 5.7, which can be compared to the results for the carbonated wastes shown in chapter 4, table 4.3. The change in peak heights respective to one another are used as an indicator of a change in phase composition. All of the wastes formed Portlandite ($Ca(OH)_2$) as a result of the hydration of lime (CaO). Cement kiln and bypass dusts formed ettringite ($(CaO)_3(Al_2O_3)(CaSO_4)_3 \cdot 32H_2O$) and gypsum ($CaSO_4.2H_2O$) as a result of anhydrite ($CaSO_4$) hydration. Hydrocalumite ($Ca_2Al(OH)_7 \cdot 2H_2O$) was also formed in the paper ashes . Wood ashes and MSWI-FA showed little or no change after hydration, but the complex mineralogy of the materials may have masked any changes.

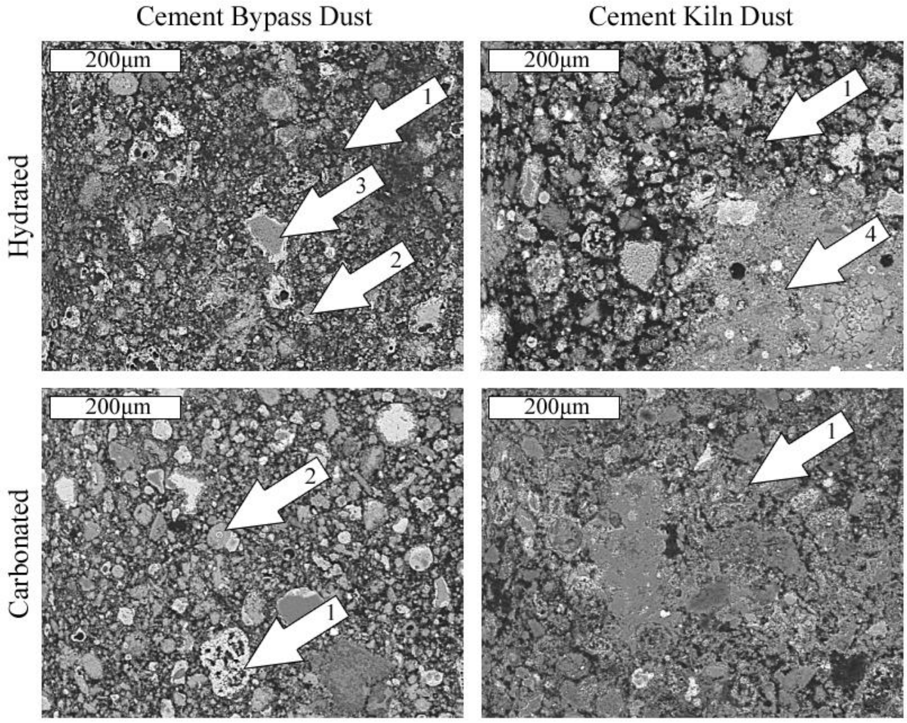


Figure 5.31: SEM micrographs of hydrated and carbonated pastes, (1) – Calcium carbonate, (2) - Quartz, (3) - Calcium silicate, (4) – Sulfur-rich calcium carbonate

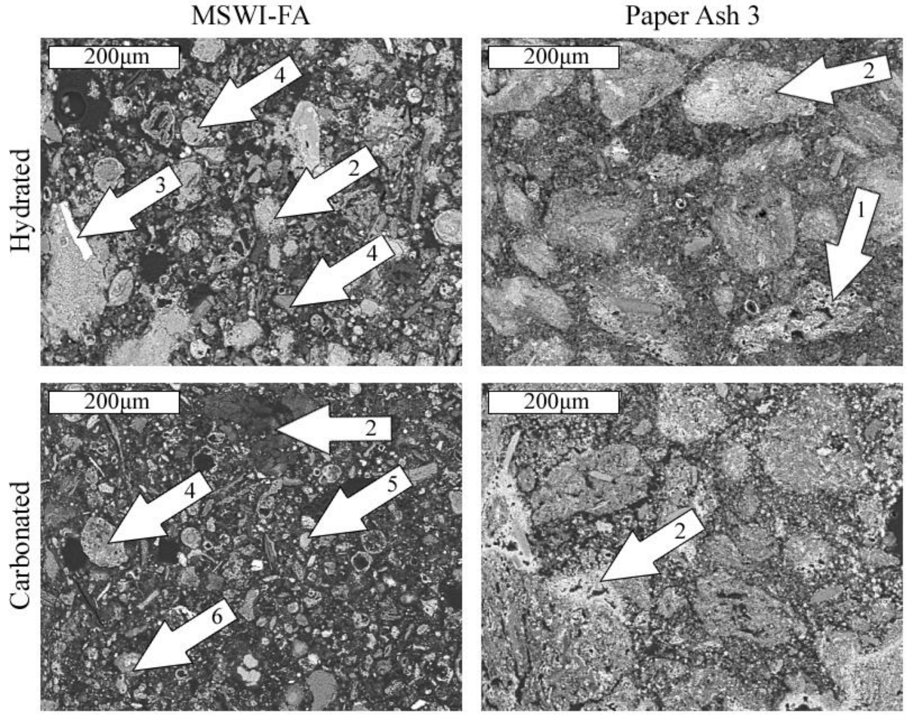


Figure 5.32: SEM micrographs of hydrated and carbonated pastes, (1) – Gehlenite, (2) – Calcium carbonate, (3) – Iron, (4) – Quartz, (5) – Calcium phosphate, (6) – Calcium silicate

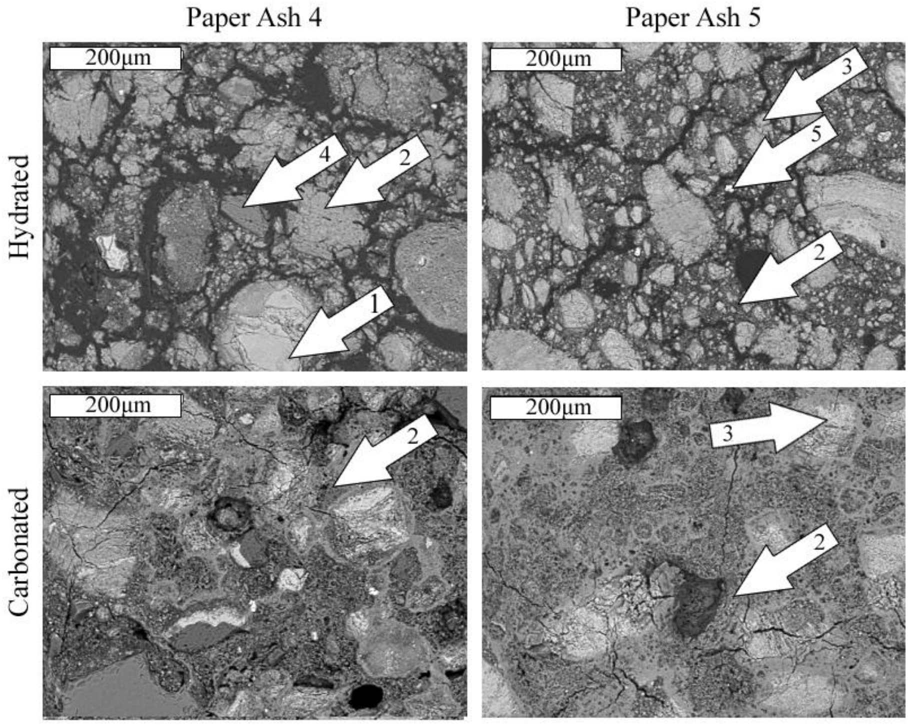


Figure 5.33: SEM micrographs of hydrated and carbonated pastes, (1) – Calcium silicate, (2) – Calcium carbonate, (3) – Gehlenite, (4) – Quartz, (5) - Iron

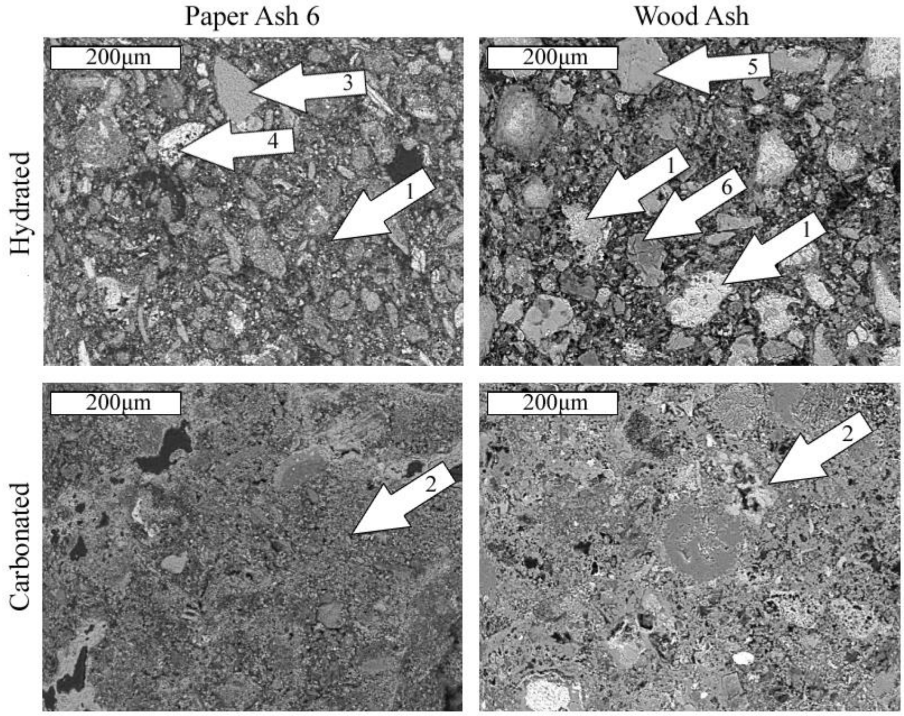


Figure 5.34: SEM micrographs of hydrated and carbonated pastes, (1) – Calcium carbonate, (2) - Quartz, (3) – Calcium carbonate mixed with titanium, (4) – Calcium phosphate, (5) – Calcium/magnesium/aluminium silicate

Table 5.7: Key phases participating in the hydration process identified by XRD

	CBD	CKD	MSWI FA	Paper Ash 3	Paper Ash 4	Paper Ash 5	Paper Ash 6	Wood Ash
Anhydrite, $CaSO_4$	▼	▼						
Gypsum, $CaSO_4.2H_2O$	●	●						
Ettringite, $(CaO)_3(Al_2O_3)(CaSO_4)_3 \cdot 32\ H_2O$	●	●						
Hydrocalumite, $Ca_2Al(OH)_7 \cdot 2H_2O$					●	●	●	
Lime, CaO	▼	▼		▼	▼	▼	▼	
Portlandite, $Ca(OH)_2$	▲	▲		▲	▲	▲	▲	

▼ – Decreased peak height, ▲ – Increased peak height, ● – Appearance.

5.3.5.2 Carbonation of pellets

Considering the difficulties of identifying carbonation in the pelletised materials, aggregates were prepared for SEM and XRD analysis to study carbonation of the pellet structure. Paper ash 3 was selected for study as it readily formed pellets of appreciable strength, was amongst the most reactive wastes, and exhibited a microstructural change upon carbonation. This material could be readily sectioned and polished, and would provide a clear indication of the extent of the reaction.

The evolution of the carbonation reaction was studied by analyzing paper ash 3 pellets which were pelletised under normal atmosphere. Paper ash 3 was also pelletised under a stream of carbon dioxide, and then subjected to further curing in the dynamic carbon dioxide chamber for 24, 72, and 144 hours. X-ray diffractograms of these pellets are shown in figure 5.35 along with the raw uncarbonated ash, together with corresponding backscattered electron micrographs in figure 5.36.

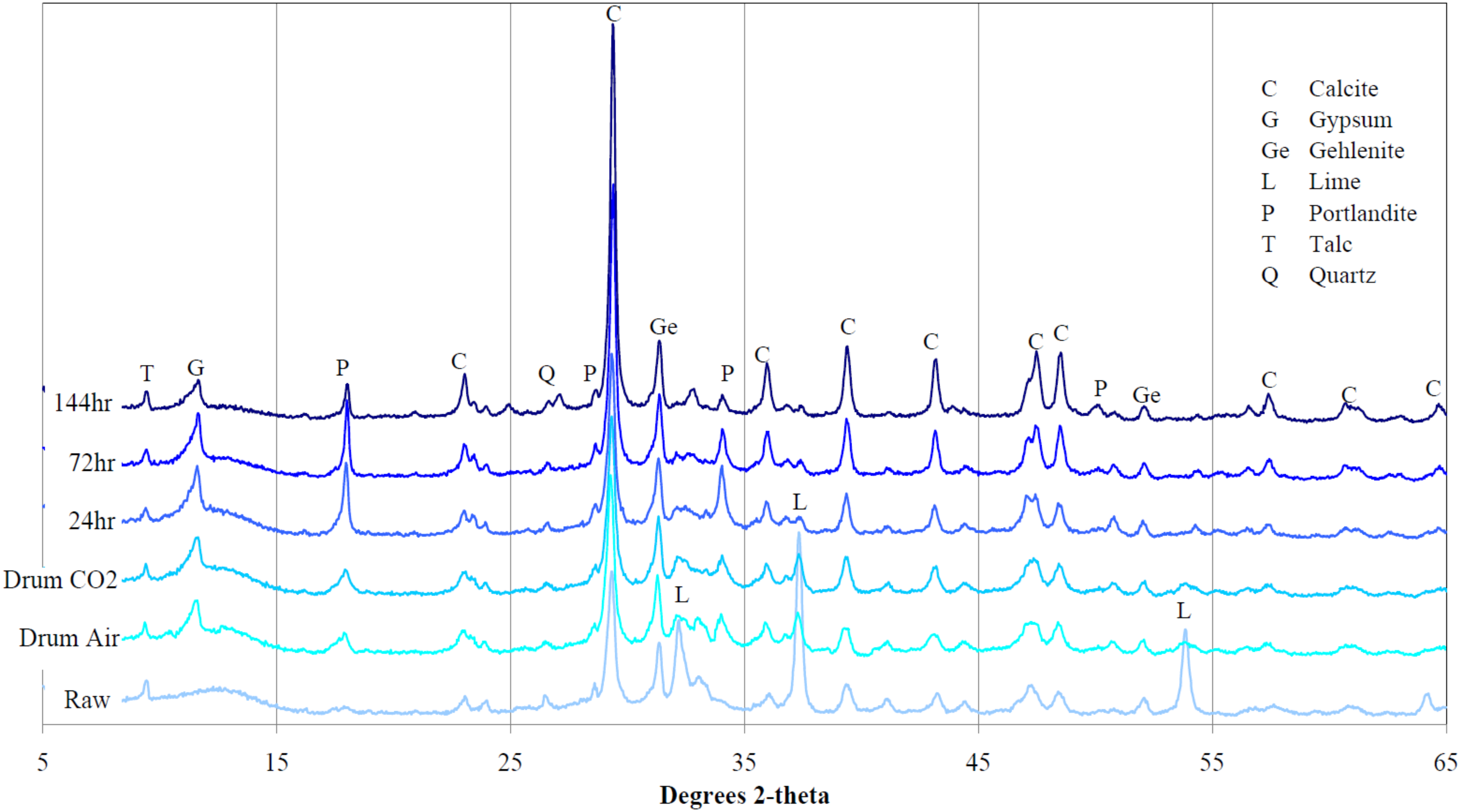
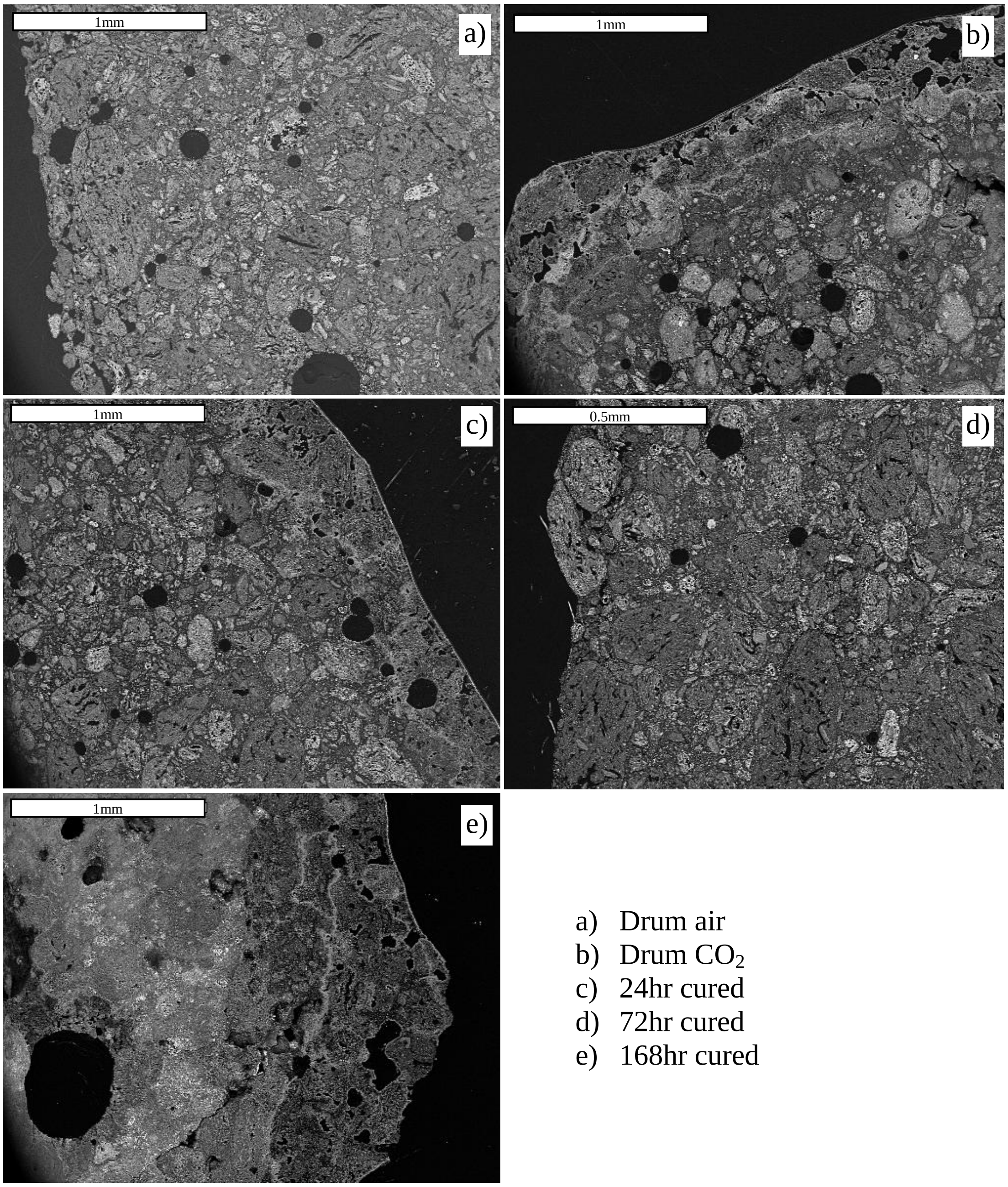


Figure 5.35: Diffractograms of carbonated paper ash 3 pellets



a) Drum air
b) Drum CO_2
c) 24hr cured
d) 72hr cured
e) 168hr cured

Figure 5.36: Electron micrographs of carbonated paper ash 3 pellets

The drum carbonated pellets showed a slight increase in the peak height of calcite compared to the pellets formed in air (figure 5.35). This indicated that the extent of carbonation occurring during the agglomeration process was negligible, although reaction rims had begun to develop around the pellets (figure 5.36b). However, mixing the ash with water in order to pelletise, led to the disappearance of lime and the formation of gypsum and Portlandite. Exposure to carbon dioxide for 24 hours resulted in an increase in the intensity of calcite and Portlandite (figure 5.35). This may be explained by hydration in the saturated pellet until carbon dioxide is able to diffuse into the structure. Portlandite began to diminish by 72 hours, as calcite intensity increased (figure 5.35), accompanied by densification of the structure (figure 5.36d). By 144 hours, calcite predominated and the structure contained a mass of calcium carbonate (figure 5.36e).

5.4 Discussion

5.4.1 Pelletising process

The results suggest that a balance between rotation speed, moisture content and mixing time is important to manufacture a strong pellet. The pelletising process must be carefully tailored for each waste. Pellet growth is enhanced by increasing the energy input through higher rotation speed and duration promotes a greater degree of aggregate compaction, and further growth (Harikrishnan and Ramamurthy, 2006, Mehta *et al.*, 1996).

The importance of fines in the mix suggested that high inter-particle friction was essential for agglomerates to form. The difficulties associated with agglomerating fines or coarse mixtures have previously been noted by Keleb (2004). Larger grains have fewer contacts, resulting in low interparticle friction. Larger particles are associated with greater pore spaces, requiring more moisture to form liquid bridges. The excess of water lubricates grain contacts, reducing friction, and may cause the mixture to disintegrate into slurry (Iveson and Litster, 1998b, Hjemsted and Schneider, 1996). A broad particle size distribution improves interparticle friction, and reduces the liquid bridge distance. A model such as that shown in figure 5.37, illustrates these observations. The arrangement of the points in figure 5.30 prohibits defining exact boundaries. Furthermore, the absence of clay in the materials prevented an assessment of its role in the agglomeration process.

Particle size distribution contributed to strength, as was shown by the lower strength of materials predominantly composed of fine silt-sized or coarse sand-sized particles. However, this alone was not responsible for strength. Agglomerates made from blended material with a broad particle size distribution, but still having poor strength suggested the influence of other material properties. Examples included SSA, PFA and MSWI-BA, which had to be blended with 20% CEM1 to achieve the desired strength. Pietsch (2003) highlighted the importance of particle shape, wettability, and reactivity of the raw materials upon the strength of the agglomerates. PFA particles are typically characterised as glassy cenospheres (Mehta and Monteiro, 2006), whilst SSA is composed of glassy phases (Cyr *et al.,* 2007; Cheeseman *et al.,* 2003). Glassy materials are typically hydrophobic, which would result in weak capillary bonds between the liquid and solid (Holuszko and Laskowski, 2004).

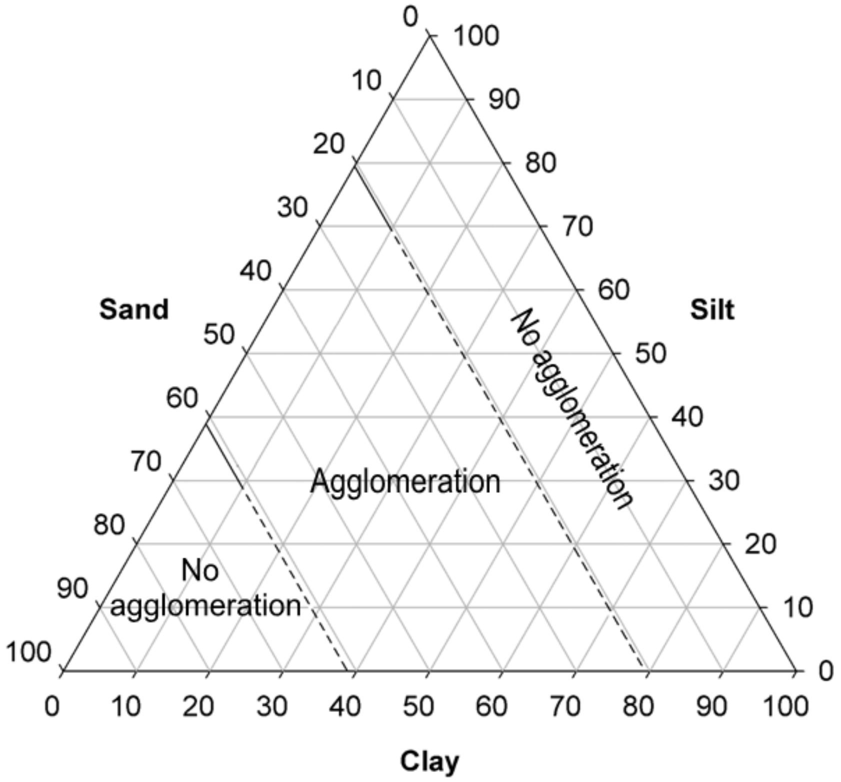


Figure 5.37: Ternary plot of agglomeration potential

The moisture content had a significant effect upon agglomerate formation. Agglomeration proceeds when pore saturation of a material reaches the funicular or capillary state (Iveson and Litster, 1998b). In reality, the funicular and capillary states spanned a narrow moisture content window of 2-4%. The breadth of this window was affected by the particle size distribution. Strength development of the pellets was also moisture dependent, and was promoted by increasing the moisture content to enhance plasticity and consolidation (Iveson and Litster, 1998a). However, excess moisture causes suspension of the particles, resulting in poor cementation upon drying (Concrete Society, 2005, Gluba *et al.*, 2001, Teramura *et al.*, 2000).

Agglomeration is further complicated by minor variables, including the heat generated by the hydration of lime-bearing wastes inducing drying. Conversely, this water is liberated upon carbonation, promoting further agglomerate growth. The moisture content was indirectly influenced by the dryness and cleanliness of the drum, as any residual dirt or water dried or wetted the mix respectively. Ambient temperature and humidity had a similar, albeit minor effect. These factors required changes to the moisture content of the mixture in order to maintain a consistent product.

A flowchart for producing pellets according to this methodology is presented in figure 5.38. An unknown waste material is first prepared by drying, screening or sieving as required. Next the carbon dioxide reactivity of the waste is measured to determine if it has binding potential, or must be blended with cement or another reactive waste. It may be possible to skip this step and assess the potential for carbonation by identifying the mineralogy. However, the findings suggest that the presence of reactive phases alone does not ensure that the waste will cement together. Calcium silicates appear to be key phases in the development of strength in the carbonated wastes, although other phases may be important. The proportion of these phases can be addressed by blending with cement or another reactive waste. The particle size distribution of the waste is then measured, and compared against the ternary plot shown in figure 5.37. Wastes falling outside the agglomeration zone are blended with other materials predominantly composed of silt and clay sized particles (fines), or predominantly sand sized particles as required. The mixture is pelletised, and if necessary, the moisture content of the mix adjusted accordingly if the pellets are too large or too small, and the process repeated. Pellets of the correct size are cured and tested for strength. Mixes with insufficient strength require a greater binder content, or the use of an alternative binder. This change will require the particle size distribution of the mixture to be reassessed.

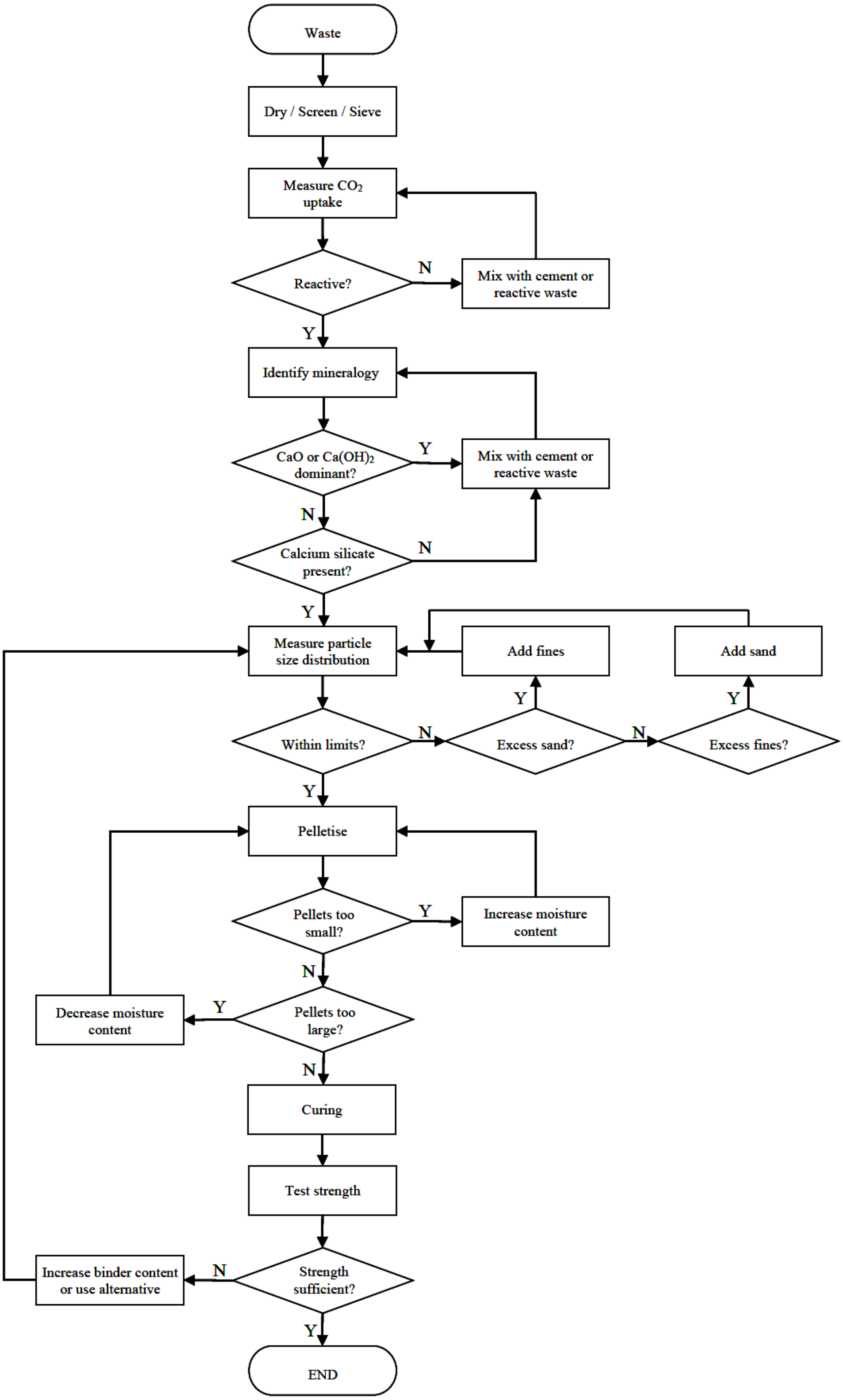


Figure 5.38: Flowchart for the production of carbonated pellets from waste

5.4.2 Carbonation of pellets

Carbonation effectively ceases in a state of near-total saturation and as a result of decreased surface area. This occurs as agglomerates grow in size, and porosity is reduced by consolidation. As a result only the exterior rinds of agglomerates exposed to carbon dioxide during the pelletising process were carbonated (Arandigoyen *et al.*, 2006, Cultrone *et al.*, 2005, Zhang *et al.*, 2004, Venhuis and Reardon, 2003, Johnson *et al.*, 2003, Russell *et al.*, 2001, Klimesch and Ray, 1997). The formation of these reaction rims was observed by SEM analysis.

Carbonation is promoted by a large reaction surface, as in fine grained materials (Klimesch and Ray, 1997, Arandigoyen *et al.*, 2006). However, in very fine grained materials, tighter particle packing restricts carbon dioxide permeation (Johnson, 2000, Zhang *et al.*, 2004). It has been established that the fines content is essential for agglomeration. Therefore, this may also be restricting the extent of carbonation.

Exposure of pellets to carbon dioxide during the pelletising process resulted in the formation of hydrated minerals, rather than carbonates. Further exposure to carbon dioxide by storing the pellets in carbon dioxide for several days was necessary to form carbonate minerals, and allow strength development. Hydration processes predominantly in the pellet structure indicate that carbonation was not occurring. The progressive growth of the carbonated zone observed by SEM indicates that carbonation was occurring according to the growing rind model, shown in figure 2.2.

Reducing the moisture content of the material promoted carbonation, but the degree of agglomeration was also limited. Hence, a process combining agglomeration and carbonation must compromise the efficiency of either process. The production of granular materials rather than pellets, would provide a balance between the degree of reactivity, and an improvement in the physical properties of the raw material.

5.4.3 Binding Mechanisms

The use of wastes as cement replacements is economically and environmentally beneficial. However, the cementitious properties of the wastes were not directly related to their reactivity with carbon dioxide, suggesting that simultaneous reactions including hydration, contributed to strength development.

The microstructure of treated wastes was altered by carbonation. The extent of alteration experienced was not necessarily influenced by the apparent reactivity of the material being treated. The changes observed upon carbonation can be related to the calcium-bearing phases present in the waste. Wastes containing calcium silicate or alumino-silicate appeared largely unaltered, whereas wastes predominantly composed of lime exhibited substantial change due to the formation of calcite. Lime is entirely converted upon carbonation to calcium carbonate, resulting in a significant microstructure change. In this respect, the microstructural alteration of a lime-rich waste would be expected to be more significant than a calcium silicate-based material such as cement bypass dust or paper ashes 1-3. However, the degree of microstructural alteration was not linked to the pellet strength. Both wood ashes and paper ashes 4-6 exhibited microstructural change, yet wood ash pellets were stronger. This suggests the importance of the mineral phases involved. Wood ash in particular showed no change in mineralogy measured by XRD after carbonation, so the mechanism may be attributed to a poorly crystalline or amorphous phase.

Hydration of waste binders was noted as an important process for strength development. In the case of CEM1, CKD, CBD, and paper ash 3, the hydrated material attained a greater strength than a carbonated one. This suggested the formation of a mineral phase with a greater binding capacity than calcium carbonate. Previous work has demonstrated that CKDs and CBDs form ettringite and portlandite as primary hydration products (Peethamparan *et al.*, 2008, Pitman, 2006, Heikal *et al.*, 2002). In the case of Portland cement, the strength contribution of Portlandite and ettringite is largely inconsequential, and it may be assumed to be the same in this instance (Mehta and Monteiro, 2006). Conversely, CKDs may benefit from the presence of calcium silicates (Buchwald and Schulz, 2005, Demeyer *et al.*, 2001). The greater strength of CKDs compared to CBDs may be attributed to a lesser amount of free lime in CKD, which is associated with expansion caused by the hydration of lime (Konsta-Gdoutos and Shah, 2003). MSWI fly ash initially forms ettringite (Piantone *et al.*, 2004, Polettini and Pomi, 2004), with longer term strength development through the formation of calcium hydrates and silicates (Piantone *et al.*, 2004). The lower strength of MSWI pellets observed may be due to unsoundness arising from expansive chemical reactions (Pera *et al.*, 1997). Paper ash forms calcium silicates and hydrates, but unsoundness may arise from free lime hydration (Mozaffari *et al.*, 2006, Bai *et al.*, 2003). Variations in the relative proportions of calcium silicates and free lime, and therefore strength of the formed agglomerates, may be expected considering the different types and grades of paper produced.

5.4.4 Variability

As already established in the previous chapter, wastes are variable materials, which have implications for an effective treatment process. Equally, the manufacture of a pelletised material has been shown to be affected by slight changes in the properties of the material, including particle size distribution and moisture content. Similarly, variations in the chemistry of the waste will have implications for the quality of the pelletised product if it is used as a cement replacement. Ensuring a consistent supply of material will be essential for the efficient running of the process, or a mix has to be designed to tolerate these variations.

5.5 Conclusion

This chapter considered carbonating industrial wastes to recycle them as aggregate. A method for manufacturing aggregates using a drum pelletiser was explored. This included examining the effects of the machinery and mix formulation variables upon the growth of pellets and the degree of carbonation.

The machine parameters and properties of the mixture had an effect upon the particle size distribution and shape of the pellets. Optimising the mix and machine variables was important for agglomerate strength development. Sources of variability, particularly the premixing, had to be carefully controlled to obtain a consistent product. The physio-mechanical properties of the wastes also had an influence upon agglomeration and particle strength development. The fines content of the material was critical for successful agglomeration.

Carbonation and pelletising were found to be affected by the degree of saturation and degree of compaction, as well as the surface area of the reacting material. Carbonation was more efficient in fine grained material with low moisture content and low consolidation. Agglomeration required near total saturation of the material, and led to consolidation and a decrease in surface area. Consequently, the extent of carbonation attained was rarely more than 5%. Further curing was necessary to achieve strength development in the pelletised materials. To maximize both carbonation and pelletising, a compromise between the degree of size enlargement of the material, and the extent of reaction has to be struck.

In the next chapter, methods of promoting the carbon reaction as part of a pelletising process are investigated.

Chapter 6 : Carbonation in a Pelletising Process

6.1 Introduction

The development of a laboratory scale pelletising and carbonation process was explored in the previous chapter. The process variables including moisture content, rotation speed, mixing time and batch size had an effect upon the particle size distribution and strength of the pelletised product. Increasing the moisture content of the material, or the energy input by increasing the rotation speed or the mass of material in the drum, promoted pellet growth. The particle size distribution of the material was determined whether a material could be pelletised. Optimum pellet growth required a balance of coarse sized particles and finer silt and clay sized particles.

The rate of carbonation slowed dramatically in saturated materials, which was due to the reaction being diffusion controlled. A carbonated rim developed upon the surface of the growing pellets, but did not penetrate into the core. Effective agglomeration required near-total pore saturation in order to form liquid bridges between particles and initiate growth of nucleates. Upon compaction, a pellet forms a denser structure and its pores become totally saturated. However, accelerated carbonation proceeds rapidly in a porous material containing a small amount of water to dissolve carbon dioxide and calcium ions.

An efficient process combining carbonation and pelletising must reconcile these different moisture demands. This is considered in this chapter by investigating alternative methods of agglomeration and carbonation, and the introduction of admixtures that alter the chemical and physical properties of carbonating materials.

6.2 Methods

To enhance the efficiency of carbonation and agglomeration in a combined process, carbonation must be promoted in a saturated material, or the water demand for agglomeration reduced. Several methods were examined:

- Carbonating the material prior to agglomeration.
- Superplasticisers and surfactants incorporated into the mix to modify rheology and reduce the water requirement for agglomeration.
- The use of chemical rate enhancers to promote the hydration of carbon dioxide in water in saturated pore systems.
- Modification of particle size distribution to achieve ideal packing to present maximum surface area for reaction and reduce porosity, and reduce the water demand.
- Alternative pelletising techniques to change water delivery and pellet growth.
- A curing stage after pelletising by partially drying the pellets prior to carbonation, or by allowing natural carbonation to take place.

6.2.1 Raw Materials

A 1:1 mixture of Hassock sand and Hassock silt was found to readily pelletise in Chapter 5. These were selected as examples of non-reactive wastes, and were mixed with paper ash 3 as an example of reactive waste or with CEM1. For some experiments the use of other materials was more appropriate, and these are discussed along with the relevant method.

6.2.2 Pelletising

Mixes were pelletised in the laboratory drum, at a rotation speed of 30rpm, for ten minutes.

6.2.3 Preconditioning

Mixes of quarry fines blended with 30% paper ash 3 or 10% CEM1, were premixed in 500g batches with 50g of water to moisten the mixture, in a Hobart planetary mixer under a steady stream of carbon dioxide. Samples of premixed material were taken after 1, 2, 3, 4 and 5 minutes. These samples were mixed with the required amount of water to pelletise. The exact amount of water required varied depending upon the amount of premixing time. The formed pellets were dried at 40°C and tested for their carbon dioxide uptake, strength and pH.

6.2.4 Rate of hydration of carbon dioxide

The speed of the carbonation reaction is controlled by the rate of hydration of carbon dioxide in the pore solution (Jiang *et al.*, 2000). This comparatively slow step in the reaction sequence may be catalysed by a variety of agents. Several authors have investigated the catalysis of carbon dioxide hydration (Medeiros *et al.*, 2008, Garcia-Carmona *et al.*, 2003, Wanninkhof and Knox, 1996, Maries, 1992, Dennard and Williams, 1966, Ho and Sturtevant, 1963, Sharma and Danckwerts, 1963, Kiese and Hastings, 1939). Sharma and Danckwerts (1963) measured the relative catalytic power of various compounds. Many compounds were eliminated on account of their cost and toxicity. Sodium sulfite, sodium hypochlorite, and sucrose were selected for investigation.

A eudiometric technique was used to investigate the effect of these compounds upon the carbonation of mortars and pellets. A eudiometer measures gaseous exchange during a chemical reaction. The apparatus used was based upon a design conceived by Maries (1992) and developed by Johnson *et al.* (2003) (see figure 6.1).

The reaction chamber is connected to a gas bag inflated with carbon dioxide within a sealed water tank. Inflation of the bag displaces water into the measurement column. Gas is consumed as the reaction progresses, causing the bag to shrink and the water level in the column to drop. A graduated scale attached to a float in the column breaks the path of a light sensor connected to a computer. The signal is recorded against the time elapsed and converted into carbon dioxide uptake by weight of cement. The software allows correction for ambient pressure and humidity which affect gas density.

Gas syringes were added to the system to allow the chamber to be purged with an equal volume of gas prior to each run. Preliminary trials had shown this to have a major effect upon the rate in the early stages of the reaction. Care during operation including equal filling of the gas bag and firm tightening of the reaction chamber lid were critical for achieving consistent results.

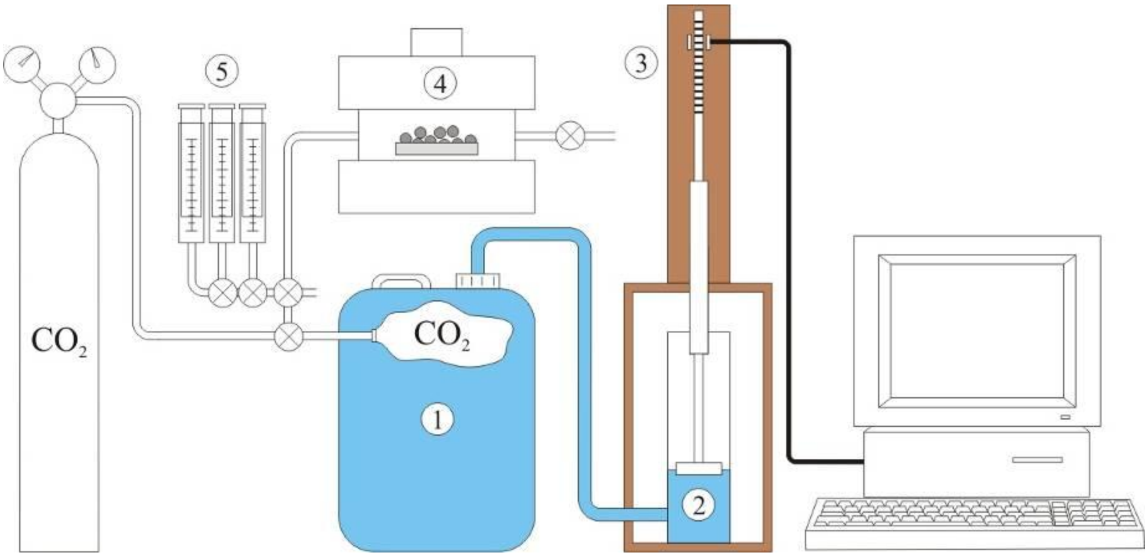


Figure 6.1: Eudiometer apparatus, (1) Water tank containing CO_2 gas bag, (2) Water column and float, (3) Graduated gauge and sensor, (4) Reaction chamber containing sample, (5) Gas syringes for purging chamber

Rate enhancer solutions were prepared at 1, 10 and 20% concentrations by dissolving the compounds in powder form in deionised water. These solutions were used to mix mortar pastes from sub-1mm quartz sand and 20% cement. Mortar pastes were prepared to water/solid ratios between 0.05 and 0.5 in 0.05 increments, and cured in the pressurised carbonation chambers at 2 bar pressure for 30 minutes. The effect of these compounds upon the carbonation of pellets was investigated by pelletising these mortar mixes and cured them in the eudiometer for 24 hours.

6.2.5 Cement Additives

The formation of liquid bridges is critical for agglomeration to proceed, and which requires near total pore saturation. Assuming that a 1:1 mixture of Hassock sand and silt and 10% CEM1 is analogous to that of a normal concrete, a range of cement additives were trialled to observe the effects upon the water demand needed for pelletising. These included commercially available cement additives, and additional chemicals identified in consultation with GPC Associates Ltd, a company specialising in chemicals for industrial water systems (see table 6.1). The additives investigated had varied effects upon materials. Flocculants and coagulents induce the clumping together of powders. Plasticisers and superplasticisers have the reverse effect, reducing flocculation and evenly distributing the mix water. Other additives affected the rheology of the mix and encouraged adhesion between particles. Wetting agents assist in distributing water over the grain surfaces, reducing the tendency to form localized over-wetted patches.

Table 6.1: Cement additives trialled as agglomeration aids

Product	**Manufacturer**	**Properties**
Culminal	Hercules	Thickener/adhesion
Conplast	Fosroc	Superplasticiser
Elotex 1212	Elotex	Adhesion
Flopam AN 943*	SNF	Flocculant - anionic
Floquat FL2949*	SNF	Coagulant - cationic
Floset C88*	SNF	Wetting agent
Floset C99*	SNF	Detergent/cleaning agent
Flosperse 3000*	SNF	Dispersant
Polyox DLP 210	Dow	Rheology/adhesion
Ultrazine	Borregaard Lignotech	Superplasticiser
WRDA 22	Grace Construction	Plasticiser
WRDA P4	Grace Construction	Plasticiser

*recommended by GPC Associates Ltd

The additives were prepared as 0.1, 0.5, 1 and 5% solutions in deionised water. Repeat mixes of 1:1 Hassock sand:silt and CEM1 were premixed manually with the solutions in a plastic container using a spatula and then pelletised. A control mix was prepared using deionised water at a water solid ratio of 0.23. The water/solid ratio of the mix was increased in increments of 0.01 until pellets of comparable size to the control were formed.

6.2.6 Particle Size Distribution

Particle size distribution has been shown previously to have a significant influence upon carbonation. The ideal material for carbonation will have high porosity and a large surface area (Cultrone *et al.*, 2005, O’Connor *et al.*, 2005, Khan and Lynsdale, 2002). However, very fine particles inhibit the reaction due to tighter particle packing which restricts carbon dioxide permeation (Johnson, 2000, Zhang *et al.*, 2004). Similarly, the agglomeration behaviour is influenced by particle size distribution

(Keleb, 2004). This was affirmed by the findings of Chapter 5, which identified that the presence of silt-sized particles was critical for agglomeration, which may reduce effective porosity and the amount of carbonation achieved.

Andreasen (1930) calculated the particle size distribution required for optimum particle packing. The equation and its subsequent directives, are applied to bulk solids handling applications, and more relevantly to the production of self-compacting concrete (Brouwers and Radix, 2005). Optimum particle packing may be calculated according to equation (6.1).

$$\frac{\%<}{100} = \left(\frac{d}{d_{\max}}\right)^{Q} \tag{6.1}$$

In equation (1), %< is the percentage passing the sieve size, d is the particle diameter (or sieve size), d_{max} is the largest particle size in the material, and Q is the Fuller constant. An increase and decrease in the Fuller constant value results in an greater volume fraction of coarser and finer particles, respectively (Suzuki *et al.*, 2001).

An Andreasen-graded material has theoretically zero porosity, maximum dimensional stability in its green state (due to interparticle friction), and a minimised water demand to achieve workability. Carbonation should benefit from the large surface area, and from the reduced water demand to achieve agglomeration. Conversely, the low porosity will reduce carbonation. This may be overcome by ‘gap-grading’ through the omission of grains in a particular size window, whilst closely preserving the ideal packing distribution (Maries, 2007). For example, by removing particles between 63 and 150µm a highly compactable material with an engineered porosity in this size range is created. The material should readily agglomerate with minimal water content, whilst preserving the porosity necessary to promote carbonation (Maries, 2007).

Andreasen graded sand was prepared using washed sharp sand. Fractions were separated at 2.36mm, 1.18mm, 850µm, 600µm, 300µm, 150µm, and 63µm, by wet sieving, and dried at 105°C. Graded sands with different Q values between 0.1 and

0.5 were prepared to ascertain the maximum particle packing (see figure 6.2). The sand was mixed with 20% Portland cement, which was included in the sub-63µm fraction. Maximum packing was achieved at Q=0.3 (see 6.3.5), and this was used for the gap-grading experiments. Separate portions of Q=0.3 sand were prepared with particle size gaps between 63-150µm, 300-600µm and 850-1180µm (see figure 6.2 and 6.3).

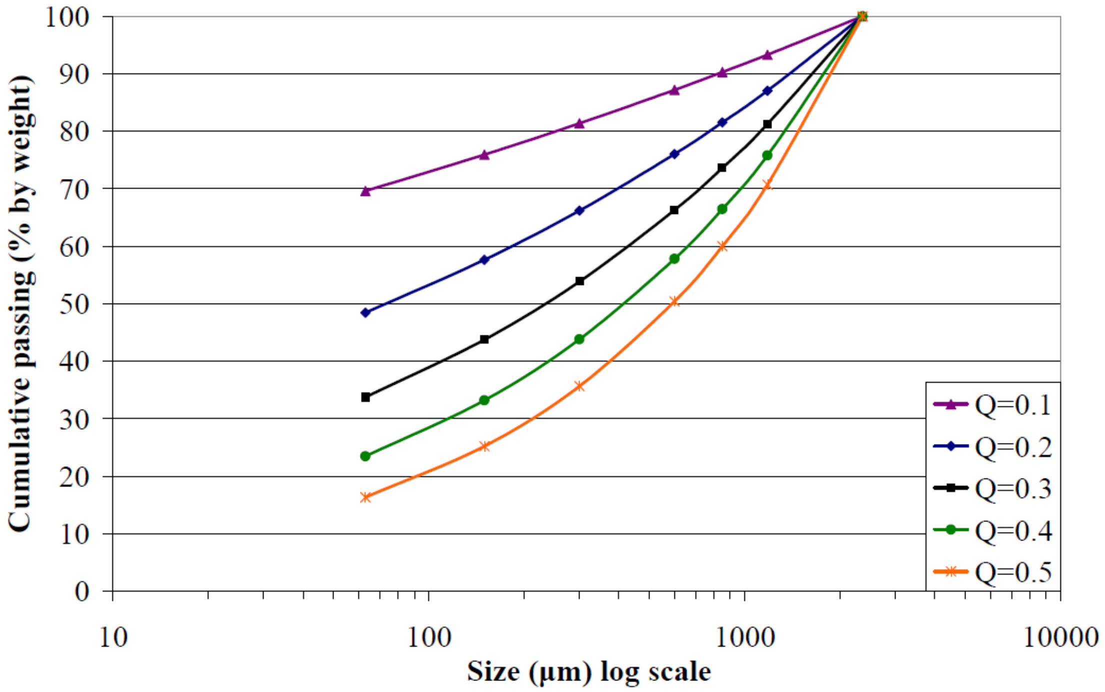


Figure 6.2: Andreasen particle size gradings

Mortars were mixed with water/solid ratios between 0.02 and 0.16 in 0.02 increments and carbonated in the static chamber at 2 bar pressure for ten minutes. At a water/solid ratio of 0.16, the mortar mixture had a distinct layer of water upon the surface. Mortar samples were also mixed with water, pelletised in the laboratory drum pelletiser and cured in the eudiometer for 24 hours.

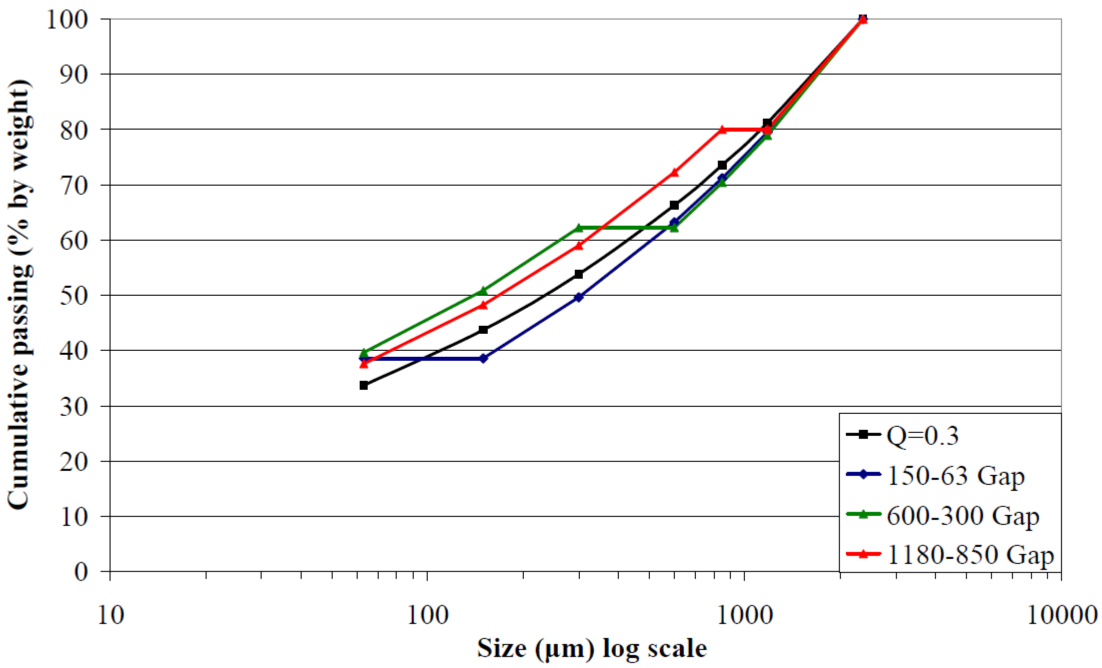


Figure 6.3: Particle size of gap-graded material

6.2.7 Pelletising Techniques

The efficacy of the carbonation reaction may be influenced by the method used for introducing the water and solids. Effective mixing was attempted by spraying water onto the dry powder as it tumbled inside the drum, by adding the premixed material in stages to reduce the growth rate of agglomerates, or reserving the reactive binder for dusting the formed agglomerates.

Low shear-agglomeration imparts minimal force to the powder bed, requiring a high degree of pore saturation to form liquid bridges between particles. Spraying the liquid binder onto the dry powder in the pelletiser allows greater control of agglomerate growth (Albert and Langford, 2007, Gluba, 2003, Kawatra and Ripke, 2002, Wauters *et al.*, 2002a, Wauters *et al.*, 2002b, Amaratunga and Hmidi, 1997). Spraying should also promote carbonation during initial wetting when the degree of pore saturation is low. As wetting progresses the pores begin to saturate and agglomerate growth initiates.

Spray agglomeration is a technique that has been studied extensively in the literature, and is used in many commercial processes including the manufacture of lightweight aggregate. Liquid binder was sprayed onto the tumbling bed of dry powder inside the drum (see figure 6.4). Tilting the drum concentrated the tumbling powder bed, minimising spray wetting the drum wall which led to caking. Water consumption was monitored by placing the water reservoir on a load cell.

The complexity of spray agglomeration can be appreciated by the detailed mathematical modeling devised to optimize numerous variables which include spray angle, spray pattern, droplet size and spray flux (Litster *et al.*, 2001, Gluba, 2003). Optimising these variables is critical to achieve an even liquid distribution, which in turn is essential to maintain control of the process (Gluba, 2003, Litster *et al.*, 2002). Control of many of these variables was beyond the capability of the experimental setup devised. However, the effect of the spray flux was investigated by delivering the full water dose rapidly in 2 minutes, and then more slowly over 8 minutes, leaving 8 and 2 minutes, respectively for the pellets to tumble and compact. Tumbling the dry mix in the drum caused particle segregation and uneven distribution of quarry fines and binder in the formed pellets. This poses an issue for the agglomeration of mixes containing two or more components with different densities. However, this can be overcome by premixing the material together with a small amount of water to prevent segregation. In this instance, the issue was overcome by making pellets entirely from paper ash 3.

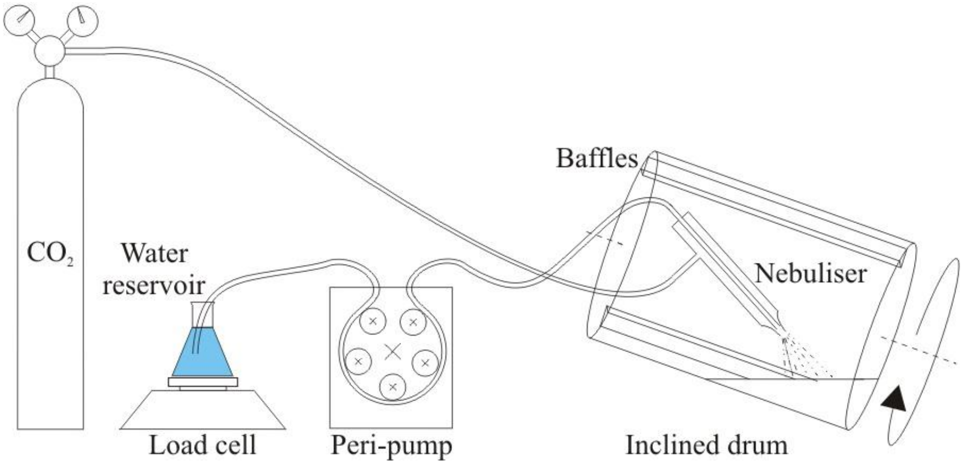


Figure 6.4: Schematic of the apparatus used for spray agglomeration

Seeding was achieved by premixing material and dividing into portions, which were added to the drum in timed increments. This method has previously been used by (Sastry *et al.*, 2003) to control the growth rate of agglomerates.

The efficiency of the carbonation reaction is greatest for materials with high porosity and a large surface area. Size enlargement by wet agglomeration adversely affects all three of these properties. The reaction surface area can be increased by layering the binder onto the outside of the forming pellets rather than by mixing throughout. In diffusion controlled regimes, the carbonation front advances slowly through the material. Therefore, the process may be speeded up by concentrating the reactive material at the pellet surface. Pellets were prepared with 25, 50 and 75% of the binder layered onto the surface of the formed pellets. This was achieved by pelletising mixtures of Hassock sand and silt with 30% paper ash 3, and omitting the appropriate amount of ash from the mixture. Thus, when 50% of the binder content was to be layered onto the pellet surface, only 15% by weight of ash was mixed with the Hassock and water. After ten minutes of pelletising, the remaining ash was added to the revolving drum, and was left to layer onto the pellets for an additional minute. Accordingly, the control mix was left in the drum for eleven minutes.

6.2.8 Partial Drying Carbonation

Consolidation during the pelletising process results in a denser saturated pellet, which can only carbonate via a growing rind mechanism and carbon dioxide slowly penetrates into the structure. Partially drying the material unblocks the saturated pore network, allowing gas to readily penetrate into the structure. This method has been used to enhance carbonation of saturated materials by Soroushian and Hsu (1999) and Liu *et al.* (2003).

Pellets made from Hassock Silt and Sand mixed with CEM1 and paper ash 3 were placed in a drying oven at 40°C for 2, 4, 6 and 8 hours. The remaining moisture content of the pellets was measured according to the British Standard method. These pellets were then cured in the eudiometer for 24 hours. Once oven dried at 40°C, the pellets were also tested for compressive strength. For comparison, pellets were also prepared and immediately oven dried before testing, and another batch was prepared and cured in the eudiometer without oven drying.

6.2.9 Natural Carbonation

Natural carbonation occurs through the reaction of material with carbon dioxide in the atmosphere. The process is considerably slower, given the low concentration of carbon dioxide .

Pellets made from 1:1 Hassock Silt:Sand mixed with CEM1 or paper ash 3 were placed in seed trays with drainage holes raised above the ground on blocks. The trays were placed away from trees and buildings and exposed to natural weathering beginning in June 2008. Samples of pellets were taken after 1, 3, 6 and 12 months, and tested for carbon dioxide uptake and compressive strength.

6.3 Results

6.3.1 Preconditioning

Preconditioning promoted carbonation in both the paper ash 3 and CEM1 bound pellet mixes (see figure 6.5 and 6.6). The CEM1 mixture carbonated rapidly in the first minute, attaining 45% of the maximum uptake of 29%. Exposing the mixture for longer did not increase carbon dioxide uptake. Conversely, the pH of the material continued to drop. The paper ash 3 mixture carbonated steadily until four minutes of preconditioning when a peak of 9% uptake (or 55% of the maximum achievable), when no further increase was measured. Similarly, the pH continued to drop.

However, the final pellet strength was adversely affected. Paper ash 3 bound pellets decreased in strength from 0.03MPa to 0.005MPa after only one minute of preconditioning. After two minutes of preconditioning, the pellets barely registered a compressive strength. The strength of Portland cement mixes decreased from 0.06MPa to 0.04MPa after one minute, and continued to drop to 0.02MPa after three minutes, after which no further decrease was measured.

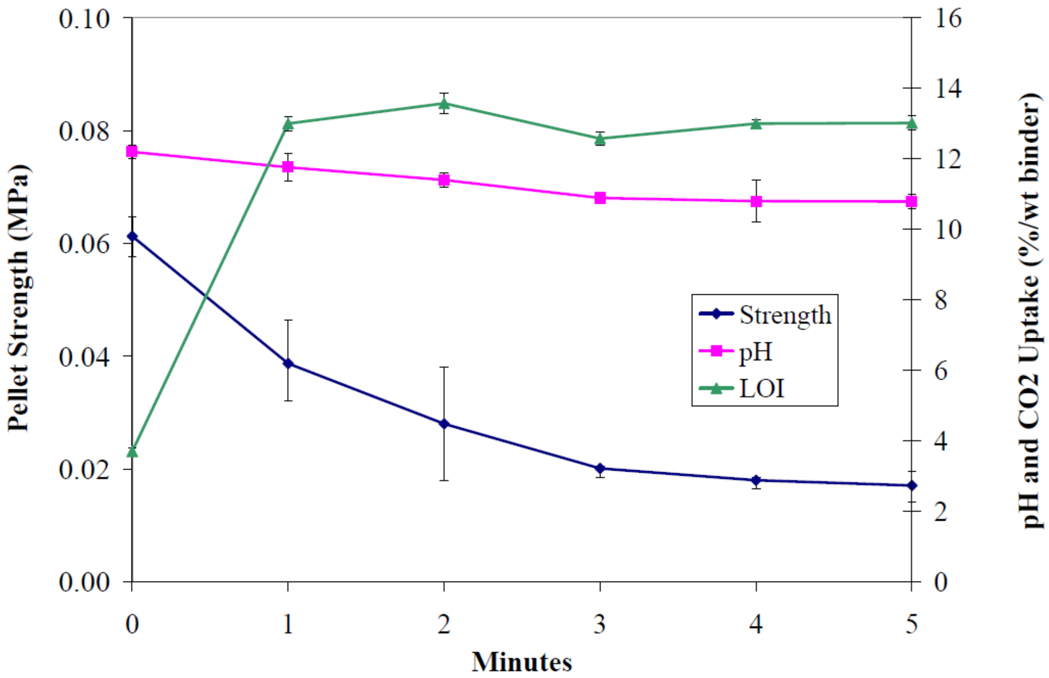


Figure 6.5: Effect of premixing upon carbonation, strength and pH of Hassock and CEM1 pellets (error bars represent the interquartile ranges)

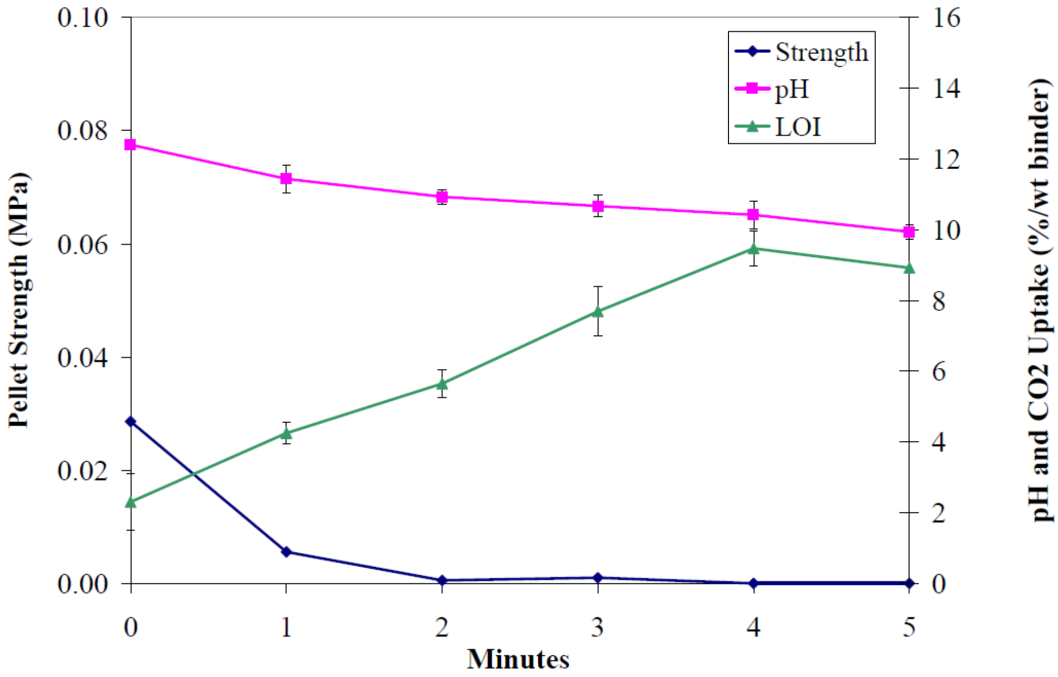


Figure 6.6: Effect of premixing upon carbonation, strength and pH of Hassock and paper ash 3 pellets (error bars represent the interquartile ranges)

Whilst carbonation of the reactive phases had a role in the continued decrease in strength and pH, the rate of carbon dioxide uptake was not directly related.

6.3.2 Cement additives

Cement additives had varying affects upon the water demand for agglomeration (see figure 6.7). Flopam and Conplast reduced the water requirement by 8 and 16% respectively, but only when used in high concentrations. Conversely, Culminal and Floquat dramatically increased water demand due to their thickening effect upon mix water.

The other additives had little or no effect upon the water demand. These included three of the four superplasticisers tested, which are designed to achieve a water reduction of up to 25% in concrete mixes.

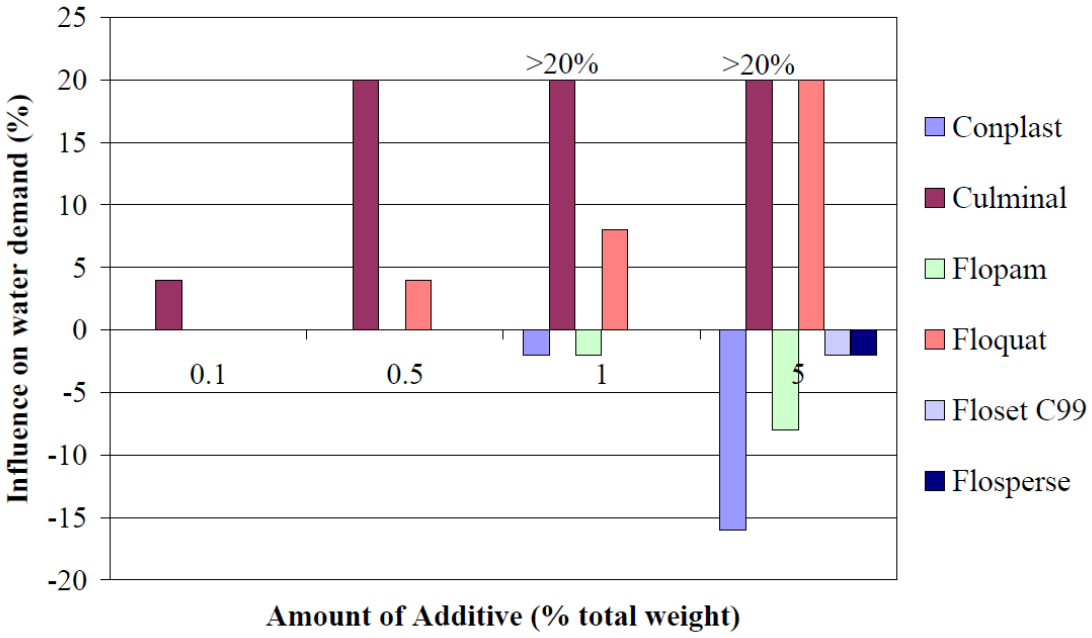


Figure 6.7: Effect of cement additives upon water demand for agglomeration

Pellets prepared with 5% Conplast and 5% Flopam were tested for their carbon dioxide reactivity alongside a control, by measuring the pH and loss of ignition of the green pellets after curing in the eudiometer for 24 hours. The reduction in water content did not promote a higher degree of carbonation (see figure 6.8).

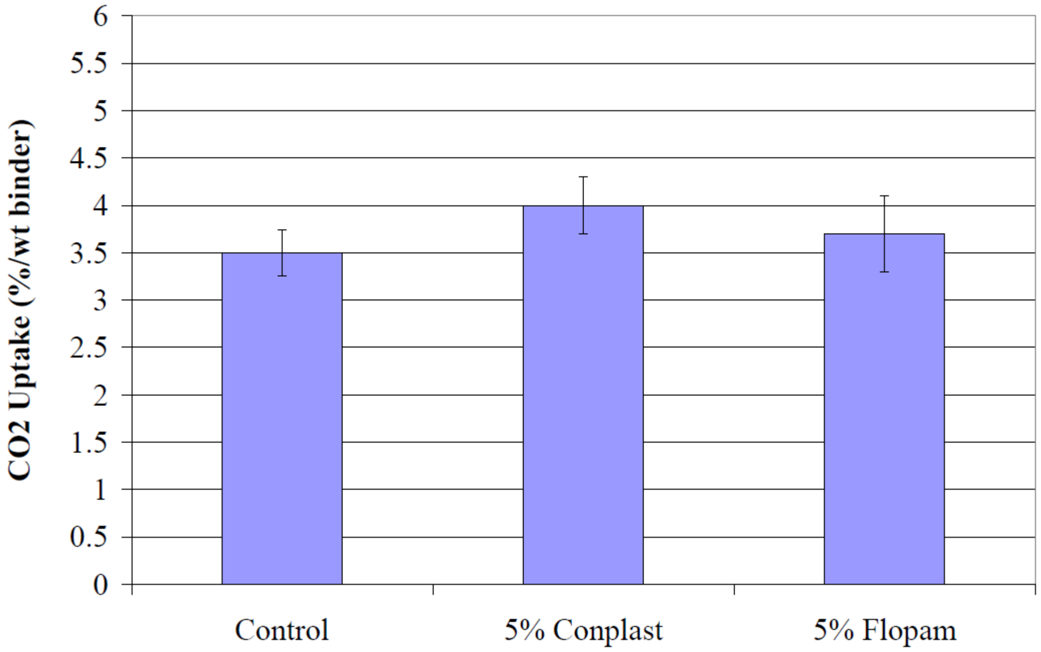


Figure 6.8: Influence of selected cement additives upon the carbonation of pellets

6.3.3 Hydration of carbon dioxide

The carbon dioxide uptake of mortar samples composed of sand and 20% CEM1 doped with three different rate enhancers are shown in figures 6.9-6.11. The maximum CO_2 uptake of the control mortar mix was achieved between 0.1 and 0.15 water/solid ratio. Saturation of the material between w/s 0.2 and 0.3 suppressed the reaction, but an increase in uptake was apparent as the w/s increased further, when the mixture became a suspension.

Sodium hypochlorite did not alter the carbon dioxide uptake when the mortar was in a dry friable state below w/s 0.1. However, when the paste became heavily saturated with water at w/s 0.4, uptake was increased from 4% to 8% in the presence of a 10% hypochlorite solution, and increased to 9% in a 20% solution. A 1% solution had no significant effect upon uptake.

Sodium sulfite was the most significant rate enhancer tested when used in concentrations greater than 1% (see figure 6.10). As with hypochlorite, catalysis was most efficient in a saturated system. At w/s 0.4 uptake was increased from 4% to 10% in a 10% solution and to 19.5% in a 20% solution. During the ten-minute exposure period, approximately 75% of the total uptake for CEM1 was achieved using a 20% sulfite solution.

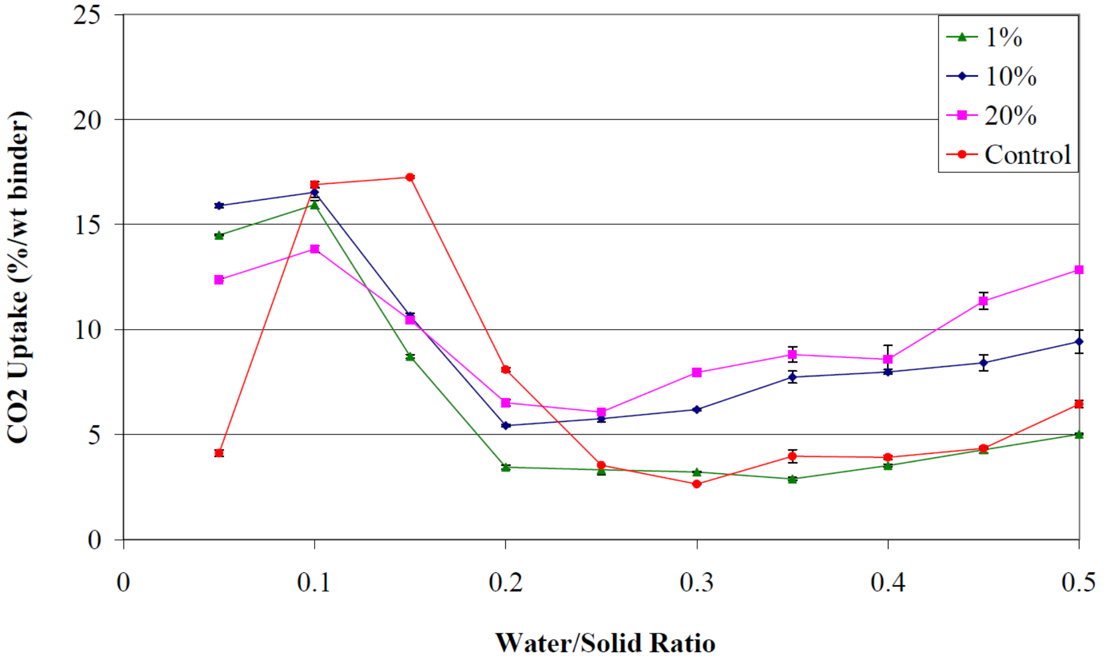


Figure 6.9: Influence of % sodium hypochlorite solution concentration upon the uptake of mortar mixes (error bars represent the interquartile ranges)

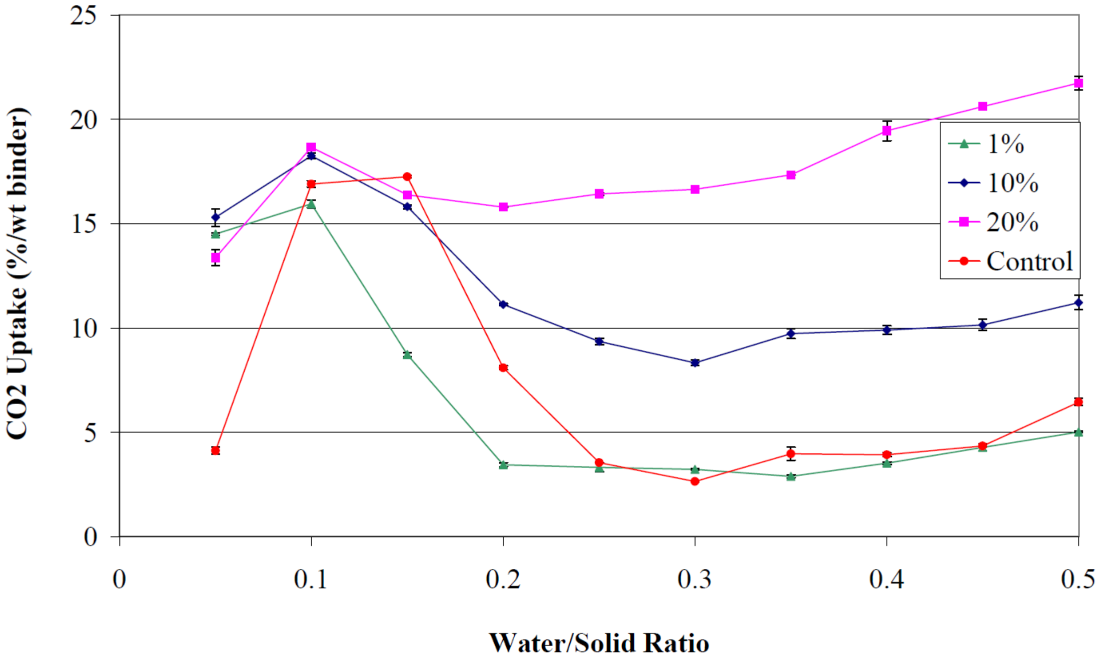


Figure 6.10: Influence of % sodium sulfite concentration upon the uptake of mortar mixes (error bars represent the interquartile ranges)

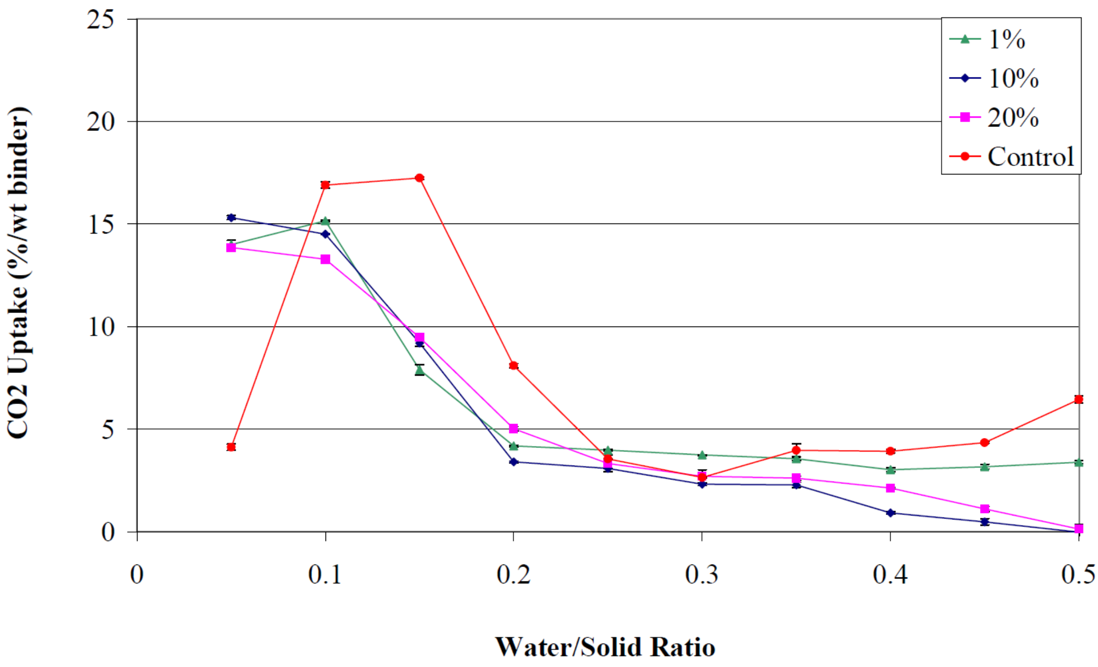


Figure 6.11: Influence of % sucrose concentration upon the uptake of mortar mixes (error bars represent the interquartile ranges)

Sucrose increased carbon dioxide uptake in the dry mortar at w/s 0.05. Uptake was suppressed at higher w/s, which may be due to the increase in viscosity of the solution by the dissolved sucrose.

Mixes of Hassock sand and silt and 10% CEM1 mixed with 10% sodium sulfite and with 10% sodium hypochlorite solutions were pelletised. These were cured in the eudiometer to observe gas uptake. Identical mixes were also prepared, but not pelletised. The pellets prepared with sodium hypochlorite attained a carbon dioxide uptake of 9.6% compared to 4.1% in the control over a 24 hours period (see figure 6.12). Pellets prepared with sodium sulfite achieved 19.1% uptake over the same period. However, the rate of carbonation in pelletised materials was significantly reduced when compared to the unpelletised pastes. Carbon dioxide uptake in the control mortar was 12.3%, but was increased to 17.2% in the sodium hypochlorite mortar, and to 22.8% through the addition of sodium sulfite. The maximum uptake attainable for CEM1 was 29.1%.

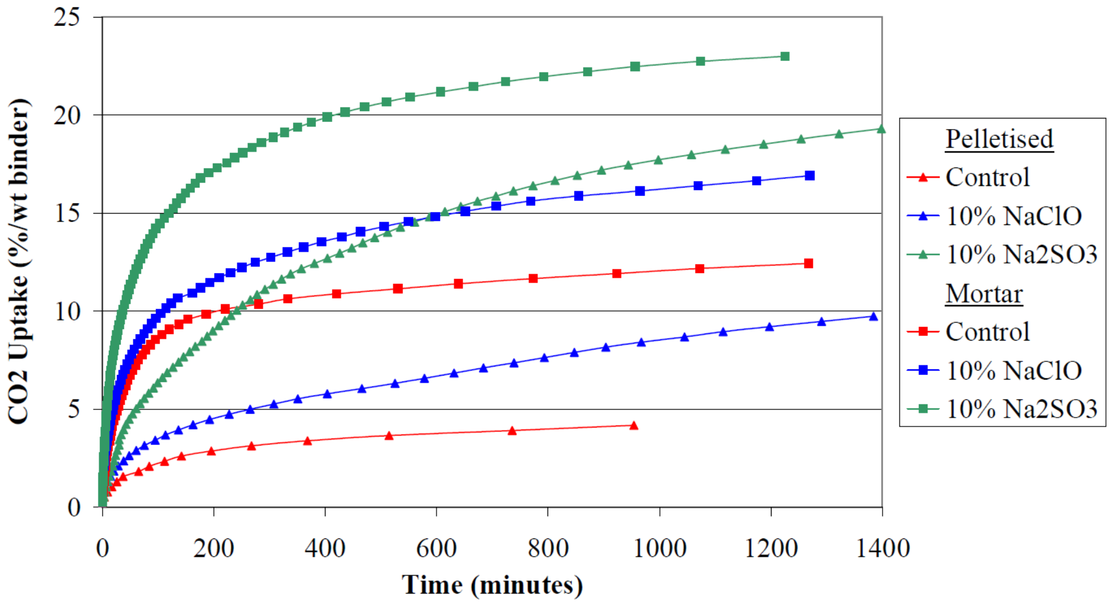


Figure 6.12: Carbon dioxide uptake of mortar and pelletised mixes containing rate enhancers

6.3.4 Alternative Agglomeration Techniques

Spray agglomeration of pellets notably enhanced carbonation (see figure 6.13), although the rate of spray flux had a negligible effect. Where more than one solid component is used in a mix, tumbling of the dry powder can cause segregation due to density differences, with adverse implications for the quality of the pelletised product. Compared to the control, sprayed pellets had substantially lower strength and looser structures, with friable surfaces (see figures 6.13 and figure 6.14a-c). Pellet seeding did not significantly increase carbonation.

Since carbonation of pellets was observed to follow the growing rind model, layering the reactive material as a thin layer upon the surface of the pellet was expected to increase the speed at which carbonation occurred. The results shown are for ash bound pellets, as Portland cement was not suitable for dusting. Cement did not have the same dehydrating effect as the ash, and initiated the rapid growth of the pellets upon dusting. The ash absorbed moisture from the pellet surface, halting growth, and producing a dense, smooth pellet surface. A lime-rich material was deemed the most suitable for dusting the pellets due the dehydrating effect.

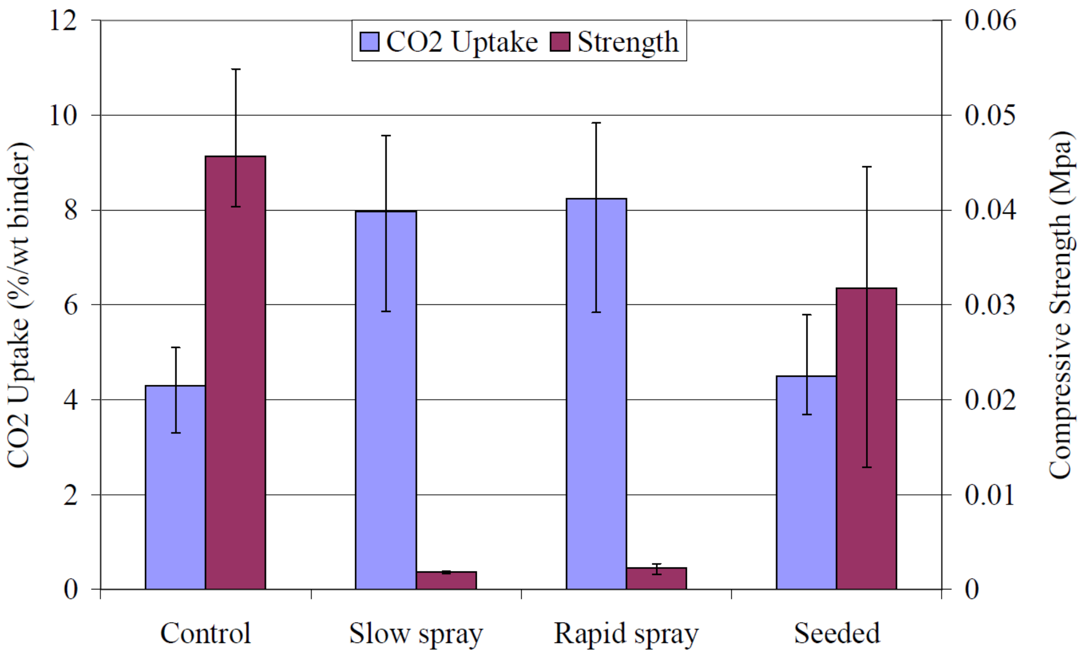


Figure 6.13: Carbon dioxide uptake and compressive strength of pellets manufactured by spray agglomeration and pellet seeding (error bars represent the interquartile ranges)

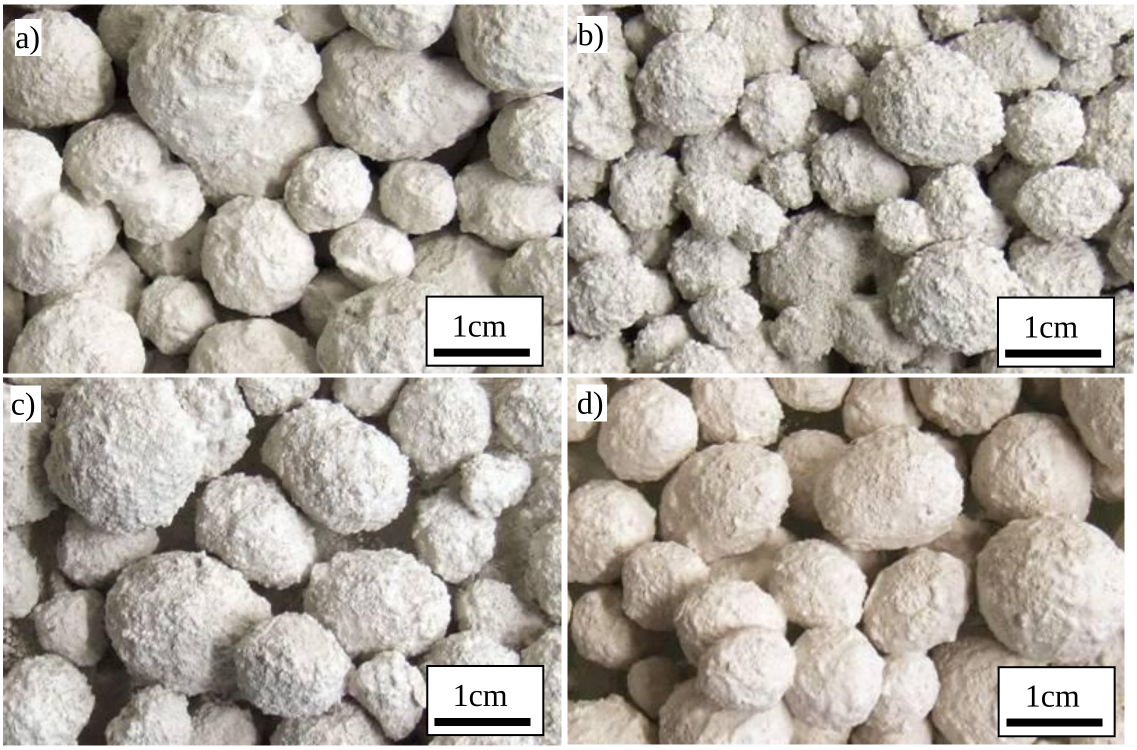


Figure 6.14: Pellets manufactured by; a) preconditioned material, b) slow spray, c) rapid spray, d) seeded

Dusting of the pellet surfaces with the binder increased the strength of the pellets. The greatest increase was observed when 25% was layered onto the surface (see figure 6.15). However, over the 24 hour period of curing, no significant increase in carbon dioxide uptake was observed.

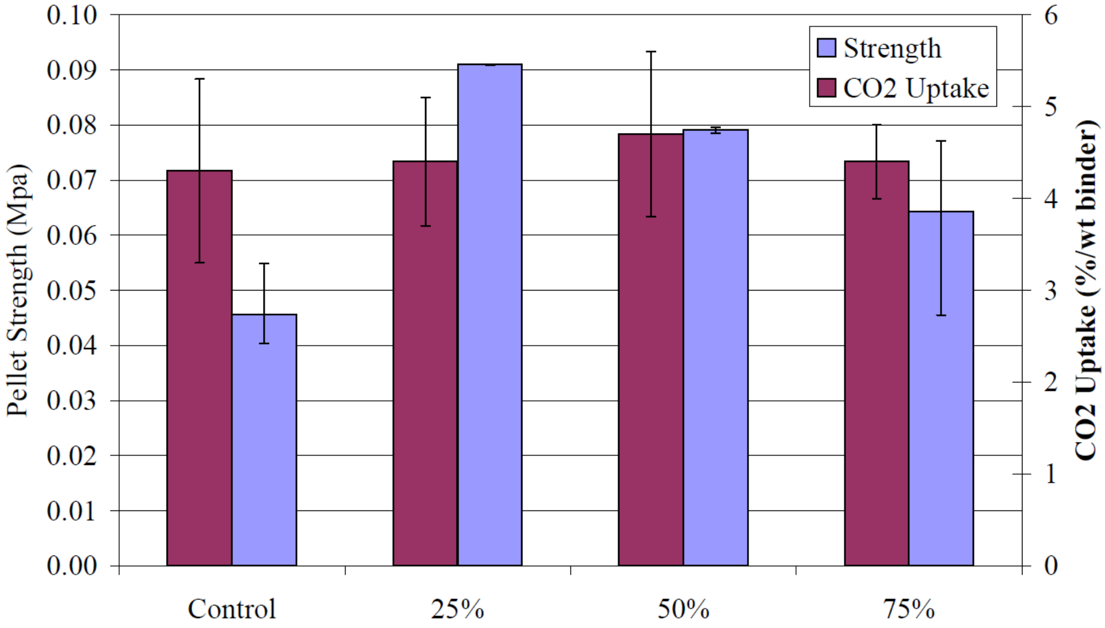


Figure 6.15: Strength and carbon dioxide uptake of pellets dusted with varying amounts of binder (error bars represent the interquartile ranges)

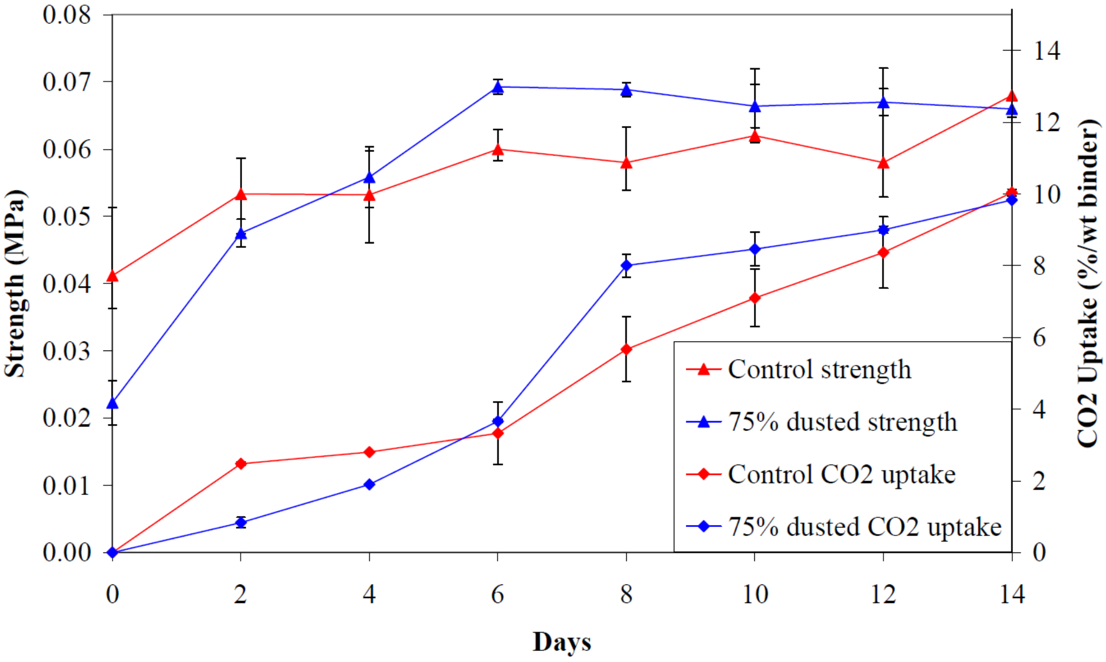


Figure 6.16: Strength, pH and loss on ignition of pellets manufactured by dusting (error bars represent the interquartile ranges)

The carbonation behaviour of the pellets dusted with 75% binder was observed over a period of 14 days of curing in the dynamic flow carbonation chamber (section 5.2.3.3). Samples of pellets were taken every two days and tested for strength and carbon dioxide uptake. The results show that across the period of analysis, the difference between the control and the dusted pellets varied, but was ultimately not significant (see figure 6.16).

6.3.5 Particle Size Distribution

The carbon dioxide uptakes of the Andreasen graded mortars carbonated in the pressurised chamber are shown in figure 6.17. The optimum particle packing for mortars is typically around Q0.3 (Maries, 2008), which is reflected in the significant reduction in carbon dioxide uptake. Gap-grading Q0.3 mortar increased carbon dioxide uptake nearly five-fold.

Carbonation for a longer duration was measured in the eudiometer for each Andreasen mix (see figure 6.18), using the optimum w/s identified from figure 6.17. Carbon dioxide uptake was at its lowest in Q0.3 mortar, achieving less than 6% over a 24 hour period. Uptake in Q0.2 mortar, which contained a greater proportion of silt-sized particles, reached 9.5%. However, a further increase in the silt content in the Q0.1 mortar reduced uptake. Q0.4 and Q0.5 mortars containing more sand-sized particles achieved uptakes greater than Q0.3, but not as high as Q0.2. This suggests that the higher surface area in a fines rich mix may promote carbonation, but that the dominance of fines as in Q0.1 may suppress carbonation due to reduced porosity.

The CO_2 uptake in gap-graded Q0.3 mortar at optimum w/s (derived from figure 6.17) was significantly improved compared to Q0.3 mortar (see figure 6.19). Removing the 150-63μm fraction promoted the greatest increase in carbon dioxide uptake. Opening up the porosity, whilst preserving the silt-sized particle fraction may assist in carbon dioxide permeation into the material, whilst still providing a large reaction surface.

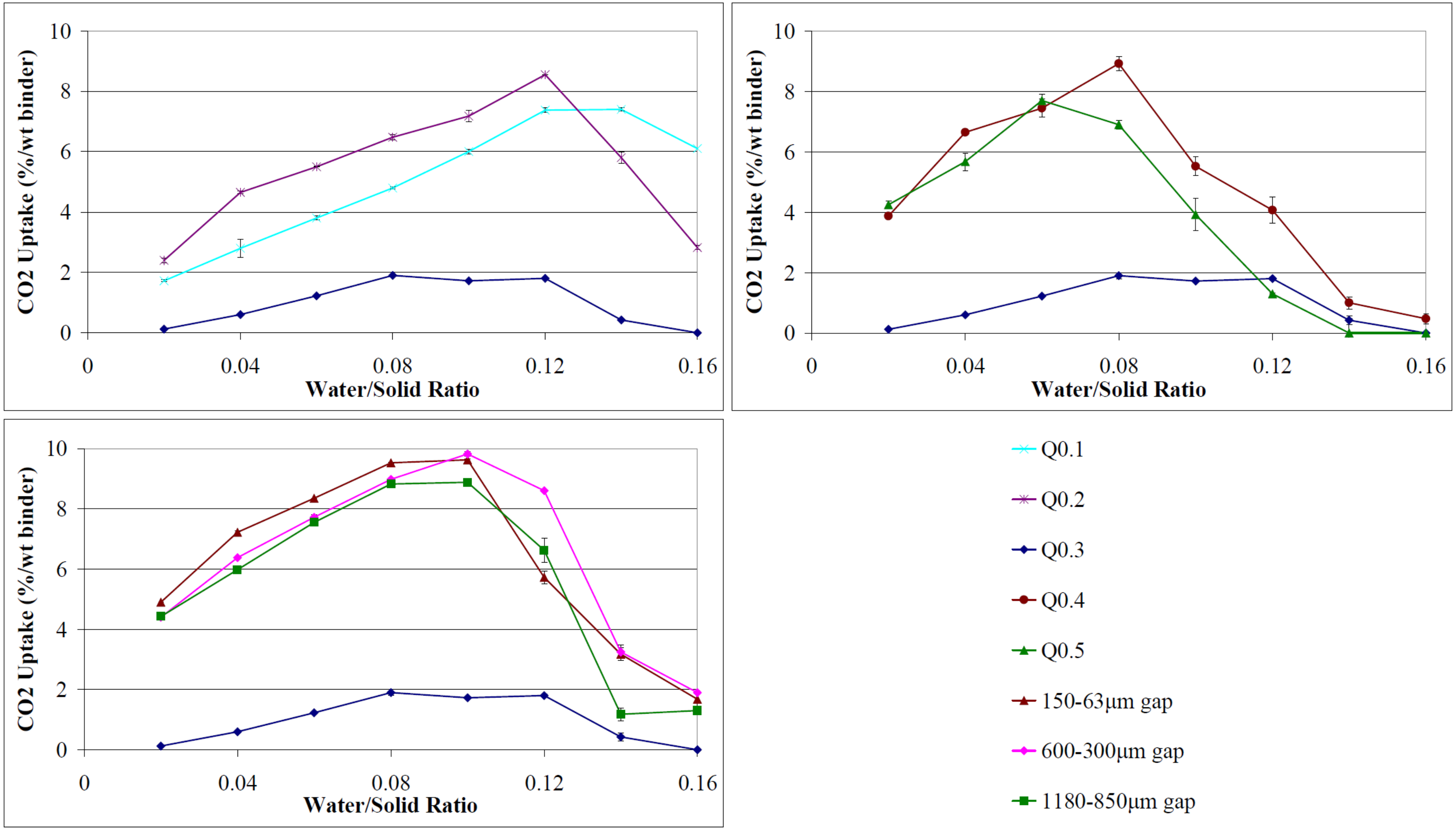


Figure 6.17: Carbon dioxide uptake in Andreasen and gap-graded mortars (error bars represent the interquartile ranges)

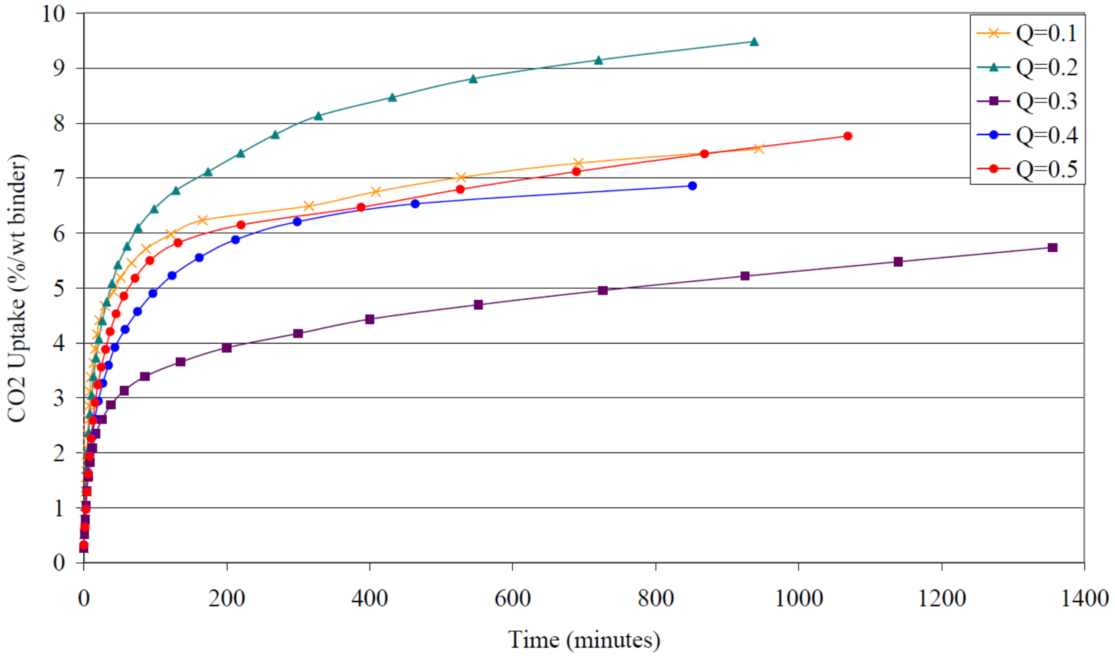


Figure 6.18: Eudiometric measurement of carbon dioxide uptake in Andreasen graded mortars

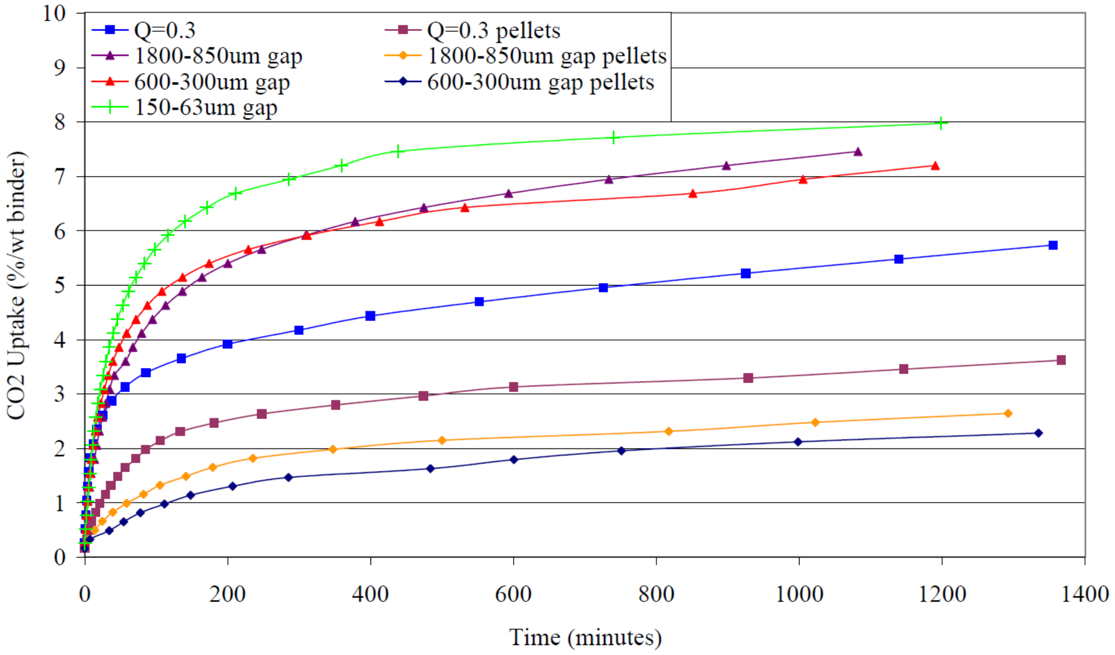


Figure 6.19: Eudiometric measurement of carbon dioxide uptake in Andreasen gap-graded mortars and pellets

Carbonation was substantially reduced in the agglomerated mortar, due to consolidation of the structure and a decrease in reaction surface area as the pellets grew. Furthermore, the gap-graded agglomerates did not exhibit the anticipated increase in carbonation. Removal in the sand sized particles as in Q0.3 minus 1800-850µm and 600-300µm, may result in a reduction in porosity due denser particle packing of the higher proportion of fines grains as the pellets consolidate. Agglomeration of Q0.3 minus the 150-63µm fraction was not possible, again highlighting the importance of the fines for successful agglomeration.

6.3.6 Partial Drying

The speed of carbonation may be enhanced by partially drying the material before exposing to carbon dioxide. Oven drying the pellets resulted in a progressive drop in moisture content with time (see figure 6.20). This drop in moisture content can be related to the increase in carbon dioxide uptake of the pellets shown in figures 6.21 and 6.22.

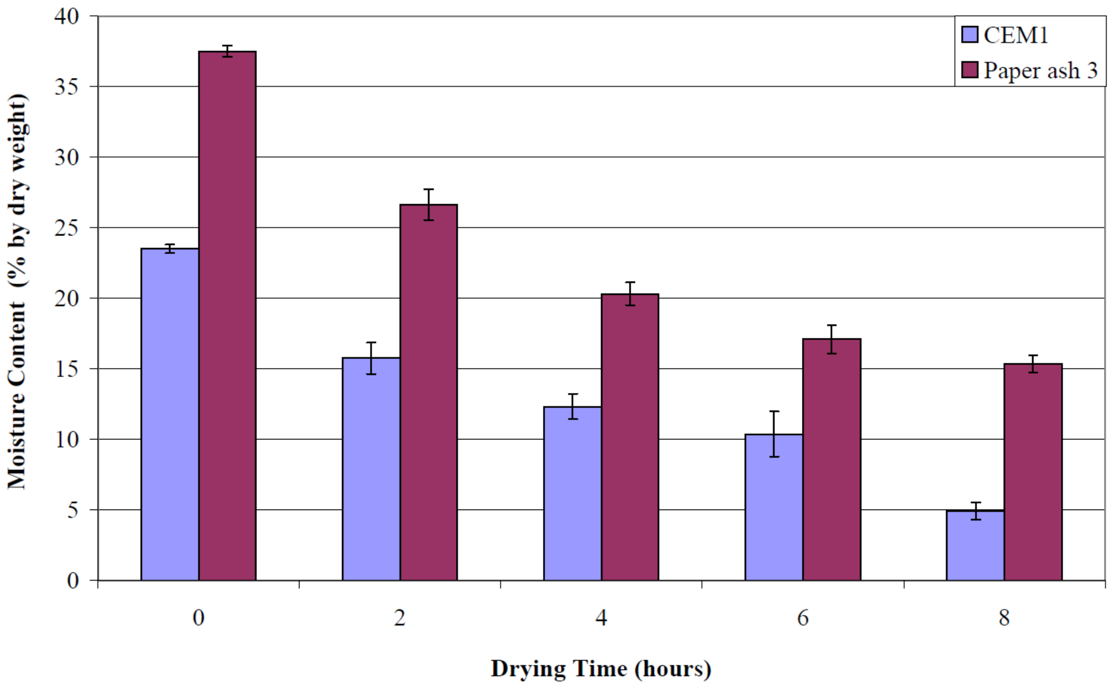


Figure 6.20: Effect of partial drying upon the moisture content of pellets (error bars represent the interquartile ranges)

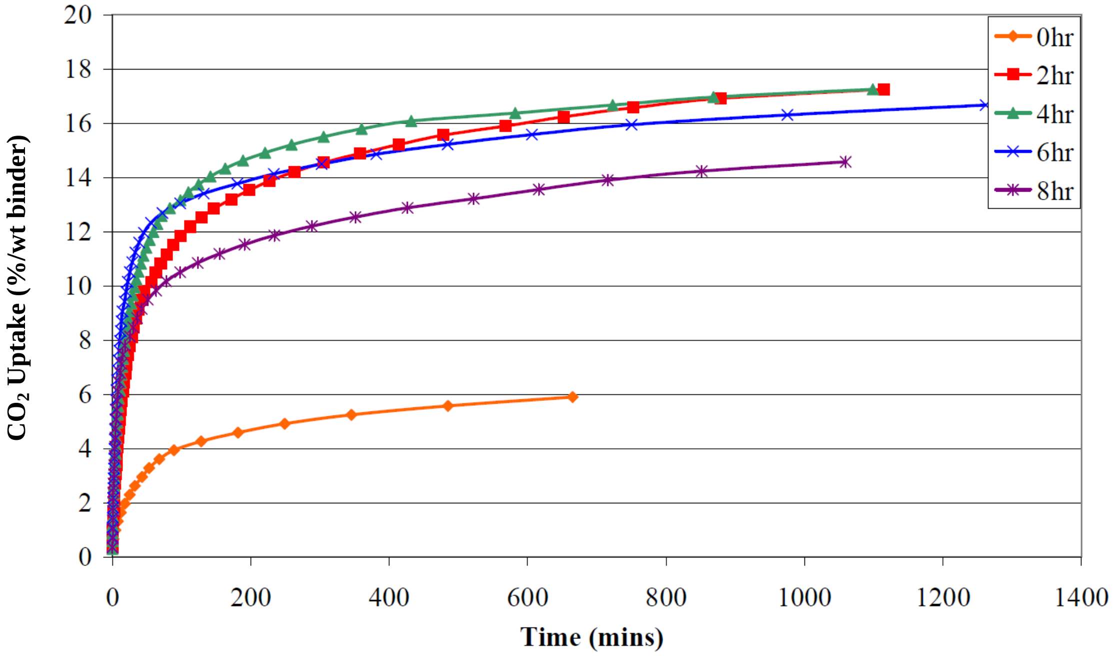


Figure 6.21: Effect of partial drying upon the strength of CEM1 pellets

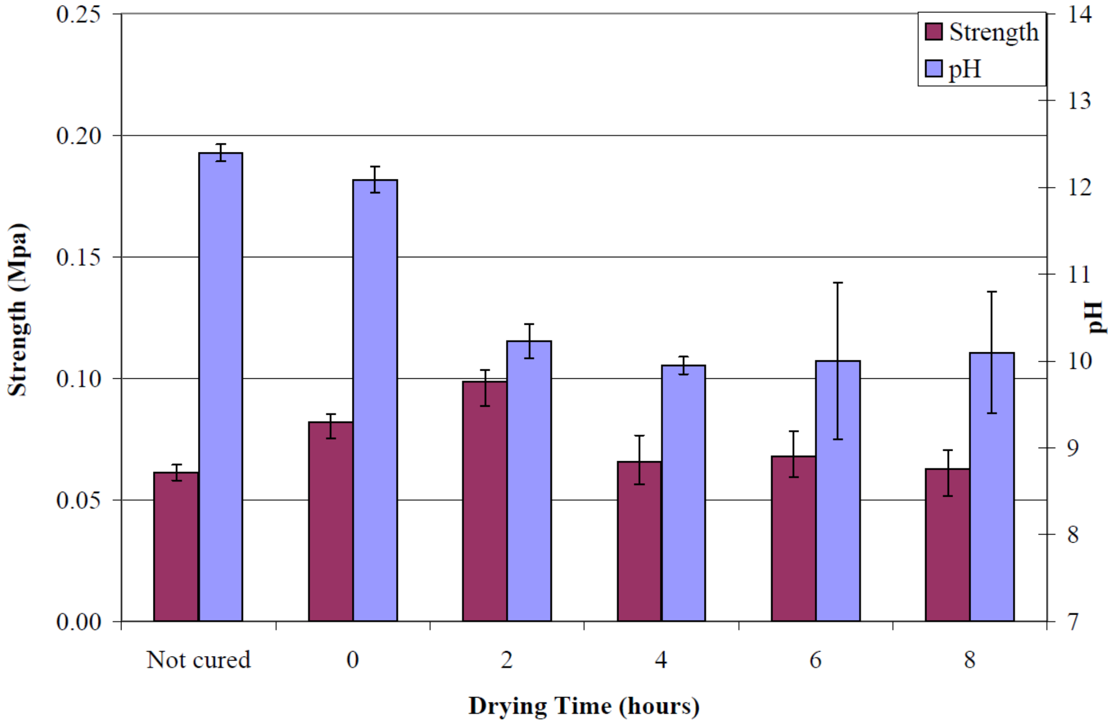


Figure 6.22: Effect of carbonation of partially dried CEM1 pellets upon the upon pH and strength (error bars represent the interquartile ranges)

Maximum carbonation of CEM1 pellets was achieved at 6 hours of drying, when the moisture content had been reduced from 23.5% to 11%. Equally, after 2 hours of drying, at a moisture content of 16%, the carbon dioxide uptake of CEM1 pellets was the same as 4 hours of drying over the 24 hour test period, but the early uptake rate up to 700 minutes was significantly lower. Drying beyond 4 hours resulted in a gradual decrease in maximum carbon dioxide uptake, suggesting that a certain amount of pore water is needed for the reaction to occur efficiently. This trend was matched by the compressive strength of the pellets. Strength development peaked at 2 hours of drying, then decreased and showed no significant improvement over the control.

The paper ash 3 pellets achieved maximum carbonation after 6 hours of drying (see figure 6.23). This may be attributed to the higher moisture content required to pelletise ash-bound pellets (see figure 6.20). At 8 hours, the amount of uptake began to decrease. The strength of pellets are shown in figure 6.24, and indicate that the maximum was reached between 2 and 6 hours of drying, since the results were not significantly different. Again, an optimum moisture content for carbonation, and for strength development, possibly as the result of post-carbonation hydration, is apparent.

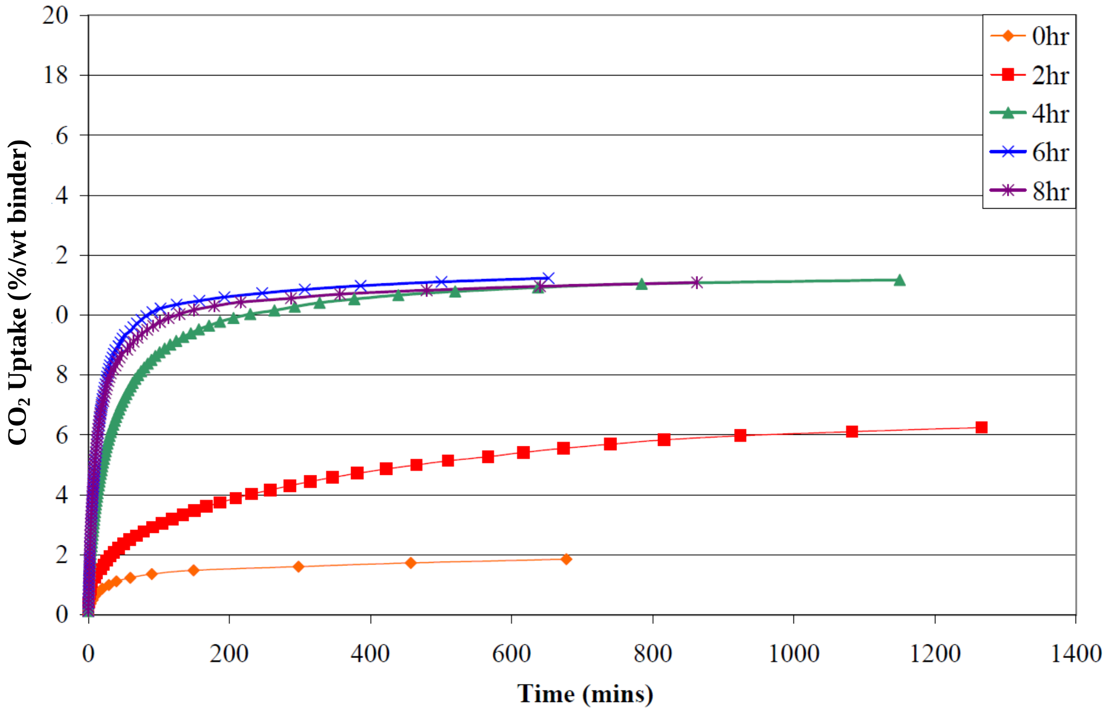


Figure 6.23: Effect of partial drying upon the CO_2 uptake of paper ash 3 pellets

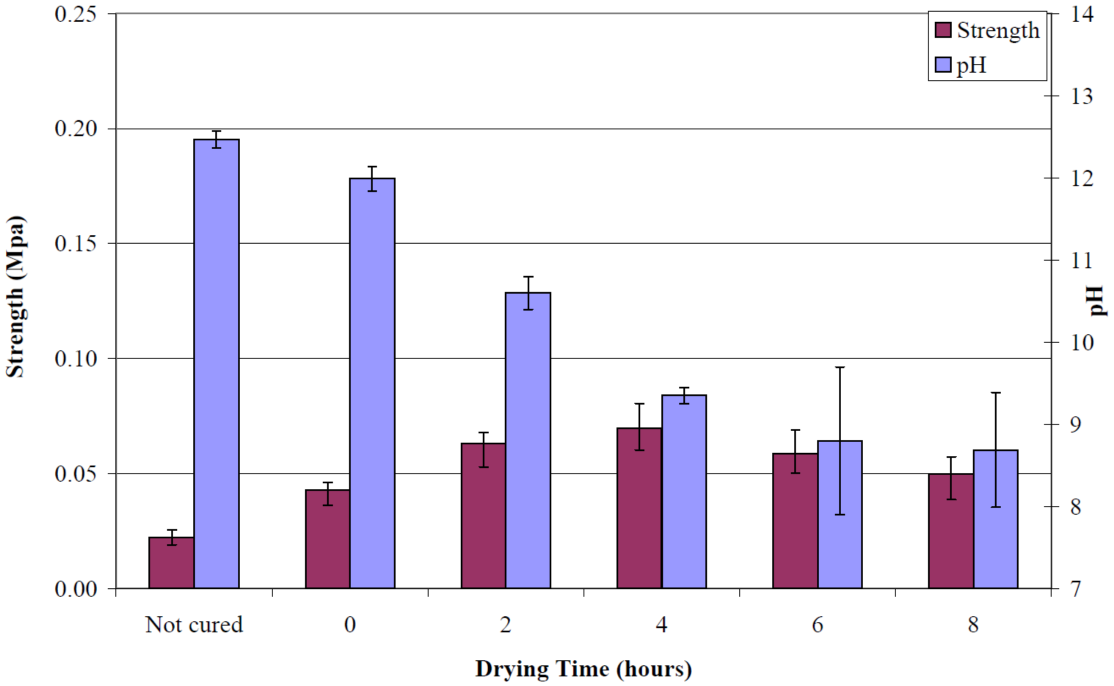


Figure 6.24: Effect of carbonation of partially dried paper ash 3 pellets upon pH and strength (error bars represent the interquartile ranges)

Both the CEM1 and the paper ash 3 bound pellets did not achieve total carbonation. CEM1 has a maximum uptake of 29.1%, whilst paper ash 3 should attain 16.4%. The uptake curves shown in figure 6.21 and 6.23 had levelled off so much that the time elapsed between the last point recorded by the eudiometer and the end of the test was up to 800 minutes. This may be due the formation of reaction surfaces inside the pellets along gas migration pathways, preventing further carbonation. Similarly, the rate of reaction slows as more of the reactive material is converted to carbonate. This suggested that prolonged curing is necessary to achieve total carbonation.

6.3.7 Natural Carbonation

Natural carbonation affects cementitious materials, producing a growing rind of carbonated material around the uncarbonated core.

Samples of pellets bound with CEM1 and paper ash 3 were exposed to natural weathering to promote carbonation. The results are shown in figures 6.25 and 6.26. After 1 month of weathering, the CEM1 pellets achieved 25% uptake, and after 6 months showed no significant increase. The paper ash 3 pellets carbonated more slowly, achieving total carbonation between 6 and 12 months. Maximum strength development for both materials was achieved after one month. This may suggest that hydration accounted for strength development, and subsequent carbonation was inconsequential.

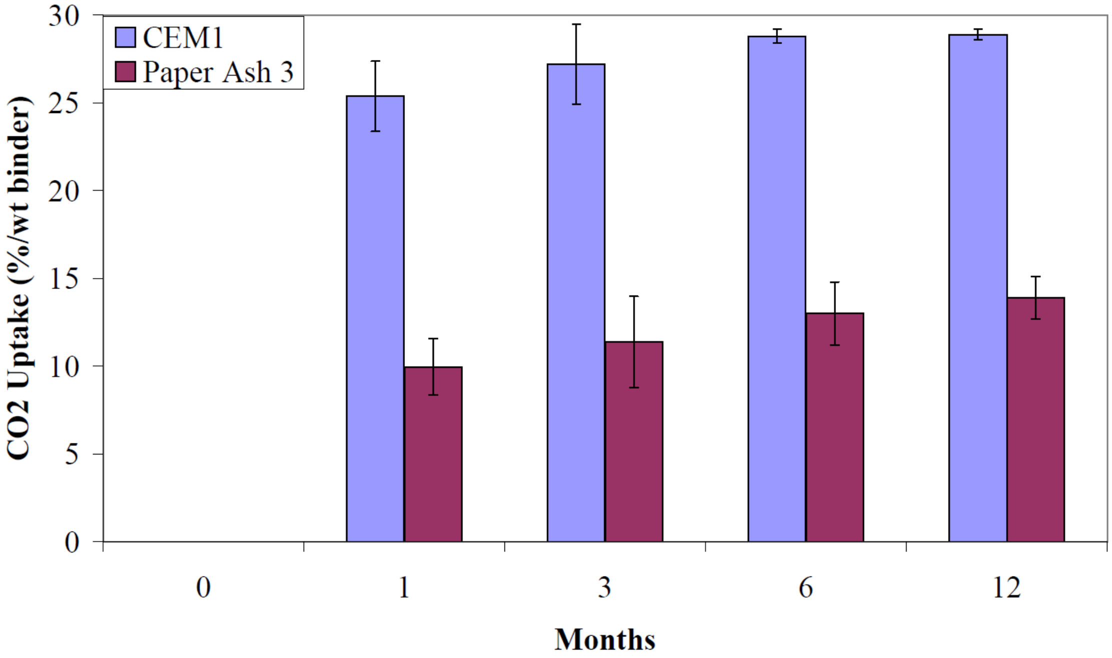


Figure 6.25: Effect of natural carbonation of paper ash 3 and CEM1 pellets upon carbon dioxide uptake (error bars represent the interquartile ranges)

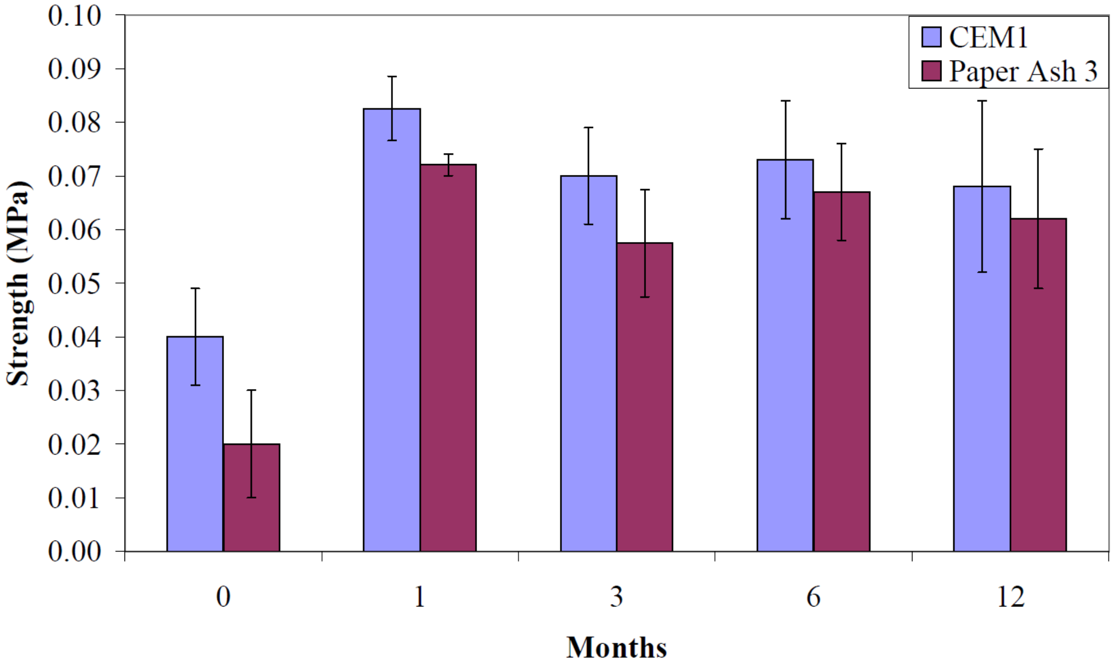


Figure 6.26: Effect of natural carbonation of paper ash 3 and CEM1 pellets upon strength (error bars represent the interquartile ranges)

6.4 Discussion

The importance of moisture content for effective carbonation of materials is well documented in the literature (Cultrone *et al.*, 2005, Russell *et al.*, 2001, Rendek *et al.*, 2006a, Venhuis and Reardon, 2003, Sorochkin, 1975, Berger *et al.*, 1972). Overcoming the detrimental effect of saturated pores upon carbonation is essential for the reaction to work effectively in conjunction with an agglomeration process.

When a reactive material is exposed to CO_2, there follows an induction period during which CO_2 gas dissolves in water, ionizes and starts reacting with species in solution (Maries, 2008). Similarly, as materials compact, carbon dioxide diffusion is reduced. It was considered that by initiating carbonation by preconditioning, the delay caused by the induction period could be shortened or eliminated. However, whilst exposure to CO_2 prior to agglomeration increased CO_2 uptake, strength development of the pelletised product was reduced. This may be explained by consumption of the calcium-bearing cementitious phases, resulting in reduced binding strength in the formed agglomerates. Carbonation during preconditioning can lead to the development of reaction rims in reactive grains, blinding them from further reaction (Jerga, 2004). This was also evident that changes in the grain size and wetting behaviour of the material make the preconditioned material more resistant to agglomeration. Problematic agglomeration of hydrophobic materials may be accentuated by the formation of calcium carbonate which is comparatively less hydrophilic than calcium hydroxide (Beruto *et al.*, 2005, Holuszko and Laskowski, 2004). In order to be effective, crystallisation of a carbonate-cement bridge would have to occur at the precise moment of contact between particles. This is highly unlikely, given the turbulent environment inside the drum and continuous exposure of the grains to carbon dioxide.

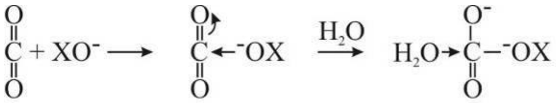
Accelerated carbonation may be promoted by catalysing the hydration of carbon dioxide in water. In a typical system, this follows equation (6.2), where carbon dioxide reacts with water to form carbonic acid.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \qquad (6.2)$$

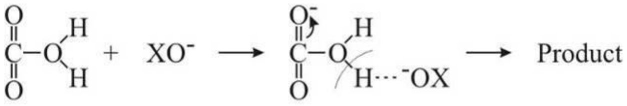
This reaction may be shifted to the left by anionic bases as in equation (6.3) (Roughton and Booth, 1938).

$$CO_2 + OH^- \rightleftharpoons HCO_3^- \qquad (6.3)$$

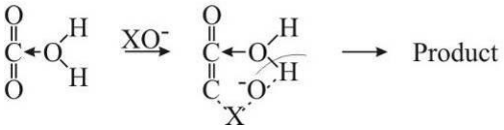
Dennard and Williams (1966) proposed three models for catalysis, shown in equation (4-6); direct interaction between the anionic catalyst and carbon dioxide (equation 6.4), interaction of the anion with water adjacent to the carbon dioxide (equation 6.5), or the anion acting as an electrophilic centre (equation 6.6). No single model explains all catalytic behaviour, and it is likely that different anions act in different ways.



(6.4)



(6.5)



(6.6)

It is generally agreed that the strength of catalysis is related to the charge distribution over the molecule (Sharma and Danckwerts, 1963, Dennard and Williams, 1966). The efficiency of hypochlorite has been previously observed by Maries (1992) and Dennard and Williams (1966), and may be attributed to the strength of a localised charge on the oxygen atom (Sharma and Danckwerts, 1963). Roughton and Booth (1938) and Kiese and Hastings (1939) noted the catalytic power of sulfite, despite it having a delocalised charge. It was postulated by Sharma and Danckwerts (1963), that at high pH, sulfite undergoes a structural metamorphosis which enhances its catalytic strength. Organic molecules exhibit limited catalysis of CO_2 hydration (Sharma and Danckwerts, 1963), as was observed by the negligible effect of sucrose upon carbonation.

Agglomeration behaviour was largely unaffected by the use of chemical wetting agents, superplasticisers and adhesion aids. To have a significant effect upon water demand, additives had to be present in concentrations exceeding normal recommendations for use in concrete. This may have implications for final strength development due to air entrainment and bleeding of the mix water (B.C.A, 1991). Many additives, particularly the adhesive agents, thickened the added water making thorough mixing impossible, and requiring the addition of additional water.

Cement particles flocculate upon mixing with water. Plasticising and dispersant mechanisms prevent flocculation by making the cement grains hydrophilic, allowing more even distribution of the mix water (B.R.E, 2000). Superplasticisers employ similar mechanisms, but are composed of longer chain, high molecular weight surfactants (Mehta and Monteiro, 2006). The weaker water-reducing behaviour of dispersant and plasticisers was apparent from the limited effect of WRDA. Both Ultrazine and Conplast are classified as superplasticers, yet had markedly different effects, and may be due to differences in chemical composition. Ultrazine is a lignosulphonate, whilst Conplast is a sulfonated naphthalene polymer (Borregaard, 2006, Fosroc, 2006). Papayianni *et al.*, (2005) identified significant differences in performance according to the plasticizer type. However, it was clear that the same mechanism that resulted in the effectiveness of anionic superplasticisers was not shared with Floquat, which relies upon cationic coagulation.

The additives only served to increase the hydrophobicity of the highly absorbent fines, producing dough with a ‘greasier’ or ‘oilier’ texture. Yet this was not sufficient to reduce the water demand for agglomeration. This may be due to the need to generate liquid bridges for agglomeration, unlike in concrete. This can only be achieved with sufficient pore saturation, or by putting more energy into the system by aggressive mixing to increase collision energy and reduce the bridging distance between particles. Similarly, the reduced water demand induced by Conplast and Floquat did not promote carbonation in the pellets. This suggests that pellet compaction has a greater influence upon carbon dioxide uptake than moisture content.

The effect of porosity was further highlighted by the decrease in carbon dioxide uptake in mortars with optimum particle packing. Increased surface area has been demonstrated to increase carbon dioxide uptake (Klimesch and Ray, 1997, Arandigoyen *et al.*, 2006). However, decreased uptake suggests that porosity is a stronger control than surface area. Zhang *et al.*, (2004) identified restricted carbon dioxide permeation in materials with tight particle packing. Opening up the tight particle packing by gap-grading increased the rate of carbon dioxide uptake significantly in uncompacted mortar samples. However, in compacted materials, even gap-graded materials exhibited suppressed uptake. The effect of the Fuller constant upon the proportion of coarse and fine particles had implications for agglomeration behaviour. Fines-deficient materials prepared with Q values greater than 0.3 could not be agglomerated. A decrease in the Q value marked a pronounced improvement in the agglomeration behaviour of the material. The importance of a fines-rich, broad particle size distribution for effective agglomeration was noted by Gluba (2003) and Iveson (2002).

Carbonation may be promoted by the progressive wetting of dry powders. Through gradual water addition, the mortar mix at least temporarily reaches the optimum w/s for carbonation. Furthermore, the material does not immediately begin to coalesce and compact, as in mixes where the full charge of water is premixed in prior to agglomeration. However, promoting carbonation of the material in the granular state is detrimental to the final pellet strength and structure. Consumption of the reactive binding minerals was highlighted as the primary drawback resulting from the preconditioning of feed material prior to agglomeration.

Gradual wetting also adversely affected agglomerate nucleation, growth and compaction. The degree of compaction is known to increase with time, densifying the structure and promoting strength development (Oulahna *et al.*, 2003); (Adetayo and Ennis, 2000). Sufficient pore saturation is essential to facilitate compaction by lubricating particle contacts (Iveson and Litster, 1998a, Hjemstad and Schneider, 1996). Whilst the sprayed powder mass exists as a dry crumb, compaction cannot be expected to occur.

Post-agglomeration curing increased the carbon dioxide uptake and strength development of pellets. Natural weathering offers a low-tech and inexpensive curing method, but requires significantly longer to achieve total carbonation. Partial dewatering unblocks the pore network, allowing gas to penetrate further into the sample and promote more complete carbonation, rather than relying upon slow diffusion through the liquid phase (Cultrone *et al.*, 2005, Liu *et al.*, 2003, Russell *et al.*, 2001, Soroushian and Hsu, 1999). The rapid uptake of carbon dioxide in pellets that were force-dried in an oven demonstrated the importance of emptying the saturated pores for carbonation to progress substantially.

6.5 Conclusion

This chapter explored the acceleration of the carbonation reaction in a saturated material. Both agglomeration and carbonation processes are fundamentally controlled by the moisture content of the material. Agglomeration only occurs when there is near total pore saturation to allow liquid bridges to form between grains. Carbonation requires partial saturation for carbon dioxide to hydrate, but equally an open pore network for ingress of gas. To achieve the two simultaneously, several methods were investigated, including preconditioning the material in carbon dioxide, chemical catalysis of the hydration of carbon dioxide, altering the particle size distribution of the material, and post-agglomeration curing.

Carbonating material prior to agglomeration promoted carbon dioxide uptake, but had a deleterious effect upon the strength of the pellets. Conversely, curing of formed pellets promoted improved CO_2 uptake and strength development. However, partial drying of the pellets was necessary to accelerate carbonation.

The catalysis of the hydration of carbon dioxide in water was effective for increasing carbon dioxide uptake in saturated conditions. Of the compounds tested, sodium sulfite, sodium hypochlorite exhibited significant catalytic power. However, in compacted pellets the efficiency of the catalysts was suppressed. Cement additives had a limited effect upon the water demand for agglomeration. Some superplasticisers and coagulants reduced water requirements, but this had no effect upon carbon dioxide uptake.

Spray agglomerating increased the amount of carbonation, but at the expense of final pellet strength. Controlled seeding and layering of the pellets did not increase carbon dioxide uptake and resulted in reduced strength. Dusting agglomerates produced hard outer shells, and whilst this improved pellet strength, there was no increase in CO_2 uptake.

The particle size distribution of powders significantly affected carbonation. Optimum particle packing suppressed CO_2 uptake, indicating that porosity was more significant than surface area. Gap grading increased the CO_2 uptake in uncompacted mortars, but not in compacted pellets.

Post-agglomeration curing was the only effective means of produced carbonated pellets. Therefore, a two-stage manufacturing process is needed. The next chapter will explore scaling up such a process to produce bulk samples for regulatory testing and commercial trials.

Chapter 7 : Scaling-up the Process

7.1 Introduction

Chapter 5 explored a laboratory scale process for producing carbonated aggregate. The moisture content for maximum carbonation was found to be different from that for agglomeration. Therefore, Chapter 6 considered alternative methods for producing carbonated aggregate to improve the efficiency of the process.

The methods examined included altering the rheology using cement additives, changing the grain size of the material to induce agglomeration, and the addition of chemical rate enhancers to promote carbonation. Chemical rate enhancers were found to promote carbonation in saturated materials, but had to be present in high concentrations to maximise carbon dioxide uptake in pellets. The other methods were not found to promote carbonation in an agglomeration process. Partially drying the formed pellets prior to carbonation was found to be the most efficient method.

This chapter examines increasing the scale of the carbonated aggregate process, based upon the optimised laboratory agglomeration process developed in Chapter 5, and the findings of Chapter 6. In this chapter, a pilot scale drum pelletising process is developed. A bespoke pelletising unit is designed and constructed, which is then further engineered operate efficiently. The growth behaviour of pellets in the pilot scale drum is compared to that at laboratory scale.

7.2 Methods

The pelletising process was scaled up through the design of a pilot scale drum pelletiser to produce 200 times the quantity of the laboratory drum.

A laboratory pelletising process is rarely comparable with a full-scale industrial process (Schaafsma *et al.*, 1998). To effectively set up a full scale process, comparative experimentation of one scale with another is needed (Iveson *et al.*, 2001a). Larger drums are noted for showing slower growth rates, high breakage and attrition and segregation of materials due to differences in density (Venkataramanaa *et al.*, 2002, Litster and Sarwono, 1996, Faure *et al.*, 2001).

A flowchart showing the initial process adopted to produce pellets on a larger scale is shown in figure 7.1. First, the raw materials were measured for moisture content, and batched according to their dry weight. The materials were premixed, and water added before pelletising. Carbon dioxide was added at ambient pressure to initiate the carbonation process. At the end of pelletising, dry ash was added to coat the pellets, and improve handling. The pelletised product was cured in a dynamic carbon dioxide environment. Each of these stages is examined in more detail.

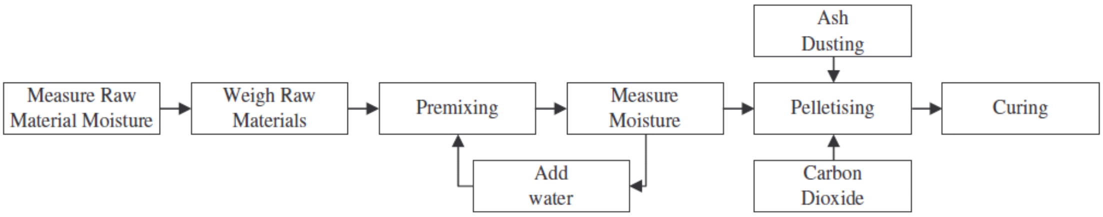


Figure 7.1: Pilot scale pelletising process flowchart

7.2.1 Raw Materials

Hassock sand and silt were used as examples of non-reactive wastes, and paper ash 3 was used as a reactive waste binder. The mix contained 35% Hassock sand, 35% Hassock silt, and 30% paper ash 3. The typical moisture content to agglomerate the material was 41%.

7.2.2 Moisture content measurement

A fast and accurate method for measuring moisture content on site was needed. The British Standard, method for oven drying requires at least sixteen hours, which is not appropriate where time and available facilities are limited.

A method using a microwave drying oven was trialled. A 500g sample of material was weighed on a top-pan balance, microwaved at medium power for ten minutes, and reweighed. The process was repeated until a constant weight was achieved. This method produced results within 1% of the conventional oven drying method specified in BS1377-2.

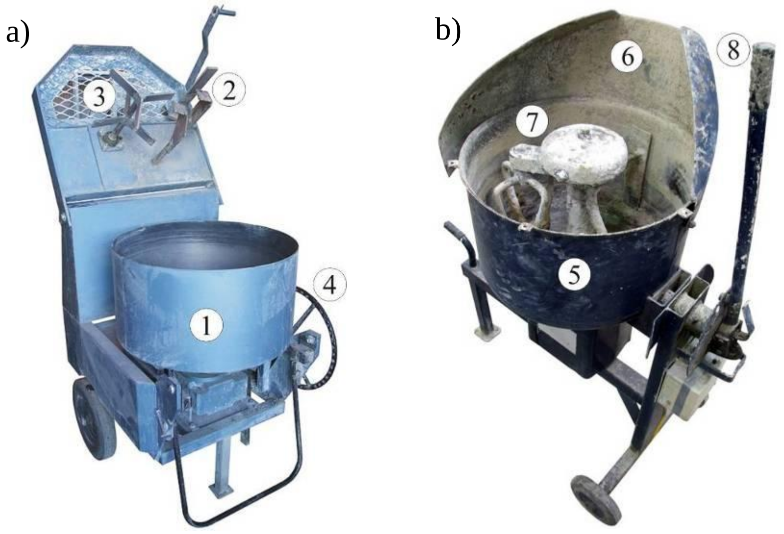
7.2.3 Premixing

Stockpiled raw materials naturally dry in the air and drain of water under gravity, resulting in variations in moisture content. Stockpiles of material must be thoroughly mixed to homogenise the material, before testing the moisture content. The mix ingredients had to be combined according to their dry weights. A top-pan balance was used to weigh the mix components.

During the first trials, the mixes were premixed by hand with a spot and shovel. The results were pellets that did not have a homogeneous mix of binder (see figure 7.2). These pellets had a dry strength of 0.02MPa, and disintegrated when placed in water. A premixer capable of achieving thorough mixing of the wet fines and the dry binder was necessary. Subsequently, motorised mixers were used.

Figure 7.2: Pellets made using manually premixed feedstock

Pan mixers produced by Creteangle Ltd (see figure 7.3a) have a motorised pan, with static blades and freely rotating mixer paddles to induce mixing. The stirring action of the blades induced agglomeration of the wet material in the pan, producing a poorly mixed paste.



(1) – Rotating pan
(2) – Static blades
(3) – Mixing paddle
(4) – Pan tipping wheel
(5) – Fixed pan
(6) – Tipping chute
(7) – Mixing head
(8) – Tipping handle

Figure 7.3: Premixers used; a: Creteangle mixer, b: Utranazz mixer

Utranazz Ltd manufacture a pan mixer with a static pan and a rotating mixing head (see figure 7.3b). The head is fitted with horizontal and vertical scraping blades, and a freely rotating mixing ‘claw’. The increased shear of the process encouraged more aggressive mixing, producing a more uniform paste with no undesirable agglomeration. The Utranazz was adopted as the premixer, and mixes were prepared at the maximum working capacity of 40 litres. These pellets were stable in water, and had a dry strength of 0.1MPa.

7.2.4 Pelletising

Pelletising trials were conducted in a bespoke pilot drum pelletiser. The basic specifications of the machine compared to the laboratory drum pelletiser are shown in table 7.1.

To compare the pilot scale drum with the laboratory process, a series of comparative experiments were performed. These included altering mix and machinery variables, comprising drum linear velocity, mixing time, and moisture content.

In accordance with the experiments conducted in chapter 5, linear velocity increments of 0.11, 0.21, 0.31, 0.42, and 0.52m/s, and mixing times of 2, 5, 10, 20 and 30 minutes were used. The moisture content of the material was varied from 38% to

43%. The control mix was made with 41% moisture at 0.31m/s for 10 minutes. Materials sampled from the same stockpiles were used for both the pilot scale and laboratory scale experiments, eliminating any influence of material variability. All mixes were prepared in triplicate.

Table 7.1: Comparison of pelletiser specifications at different scales

	Drum Pelletiser	**Pilot Plant**
Length (cm)	20	220
Diameter (cm)	20	92
Working Capacity (dm^3)	0.5	200
Effective Speed (rpm)	30	9
Linear Velocity (m/s)	0.29	0.23
Residence Time (mins)	20	20
Process	Batch	Continuous

The formed pellets were tested for particle size distribution according to British Standard BS 812-103.1 (1985).

7.3 Pilot Scale Plant Development

A bespoke drum pelletiser was designed and constructed specifically for simultaneous carbonation and pelletising in a continuous process (see figure 7.4). The original design was produced by David Chapman (Aircrete Engineering Ltd, Essex) and built by Alchrist Engineering Ltd, Grays, Essex.

(1) - Trailer
(2) - Control cabinet
(3) - Safety cage
(4) - Pelletising drum
(5) - Feed system
(6) - Discharge system

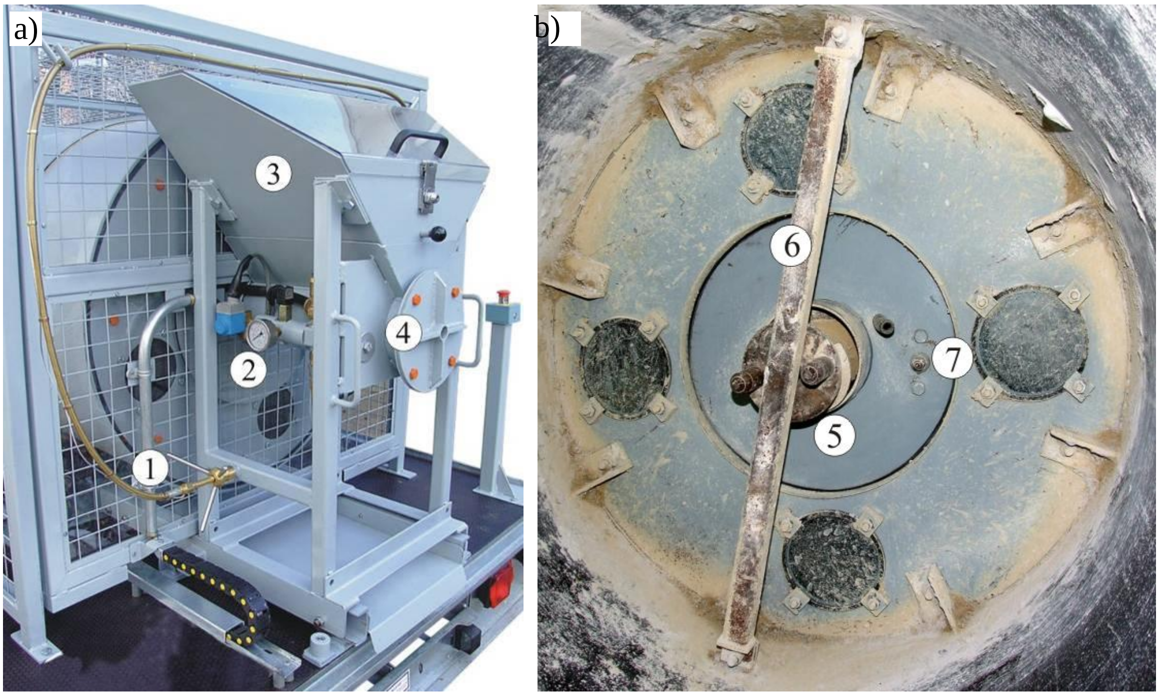
Figure 7.4: General view of prototype carbonation processor 'pilot plant'

The plant was pelletising drum mounted upon a trailer for mobility, equipped with feed and discharge mechanisms and a carbon dioxide gas delivery system. The completed plant was tested, and modifications were made to the design of the drum, feed system and discharge system to improve the operation of the plant.

7.3.1 Feed System

Premixed material was loaded into the feed hopper on the plant (see figure 7.5a). A screw conveyor at the base of the hopper drew material into the pelletising drum (see figure 7.5b).

Carbon dioxide was supplied from cylinder banks via a reinforced hose to the delivery manifold on the pilot plant. The manifold was fitted with a pressure gauge, low pressure sensor, high pressure burst valve and a solenoid valve to turn the flow on and off. Gas was injected into the drum through a nozzle mounted alongside the screw conveyer.



(1) – CO_2 delivery hose, (2) – Gas delivery manifold, (3) – Feed hopper, (4) – Screw conveyer tube, (5) - Screw conveyer, (6) – Drive beam, (7) – CO_2 delivery nozzle

Figure 7.5: Pilot plant feed system, a: external view, b: internal view

Screw conveyers were employed as they provided a ‘seal’ to retain the carbon dioxide gas inside the pelletising drum, compared to an open chute. However, as both the raw feed and the pelletised product were wet and cohesive, the conveyers struggled to effectively transport the material. Adhesion of the feed to the screw flights was a problem. The material would also form a thin veneer in the gap between screw flight and the conveyor tube. Regular cleaning was necessary to remove this material as this resulted in reduced efficiency, or caused the screw to seize.

The efficiency of the feed system was hampered by the movement of the raw feed in the hopper (see figure 7.6). Cohesion of the feed resulted in bridging across the shallow sloping walls of the hopper (figure 7.6a). Furthermore, the screw itself was not sufficiently exposed to ‘bite’ into the material in the hopper.

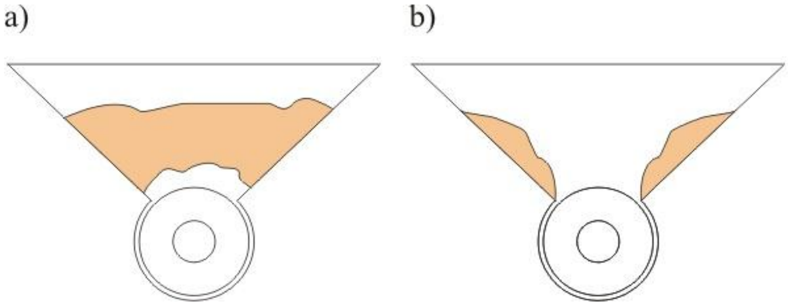


Figure 7.6: Issues with the pilot plant feed system, a: bridging of wet material, b: adhesion to hopper sides

7.3.2 Drum

The pelletising drum measured 2.2m in length and 0.9m in diameter, and was supported on four wheels. A three-phase electric motor was connected to one wheel through a reduction gearbox. A inverter located in the control cabinet allowed variation of the drum speed between 2 and 11rpm (0.1 and 0.5m/s linear velocity).

Drum residence time was controlled by the inclination angle of the plant, which was adjusted using the jockey wheel at the front and the two jacks at the rear of the trailer, and measured using a digital inclinometer located in the control cabinet. Material delivered by the feed screw conveyer tumbled under gravity over the smooth inner drum surface towards the discharge end.

The influence of the angle of the drum on the residence time was negligible. On a level gradient, material began discharging within 2 minutes of loading. This was due to the influence of the feed rate of material upon residence time. Material conveyed into the drum initially accumulated as a heap at the feed end. The rotation of the drum caused the material to naturally find its own level. Continued feeding pushed the material already inside the drum towards the discharge scoops before it had sufficient time to agglomerate. When loading ceased, the excess material in the drum discharged, leaving a residue which could only be removed by tilting the drum steeply towards the discharge end.

Experiments with the laboratory scale drum revealed that for optimum pellet strength to be achieved, mixing for twenty minutes was required (see Chapter 5). In order to increase the retention time in a fully loaded drum, several potential solutions were designed and tested (see figure 7.7).

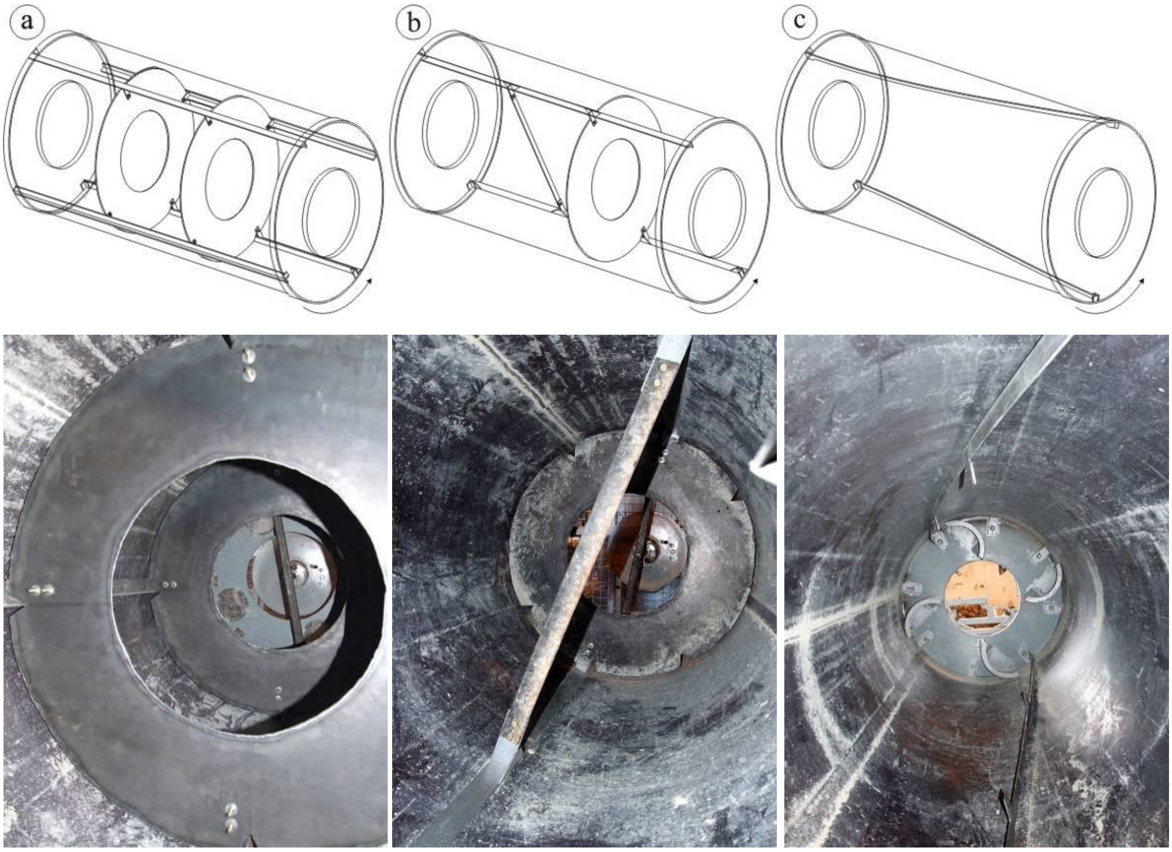


Figure 7.7: Experimental drum retention methods trialled, a: dual retention rings and lifter bars, b: single retention ring, c: helical lifter bars

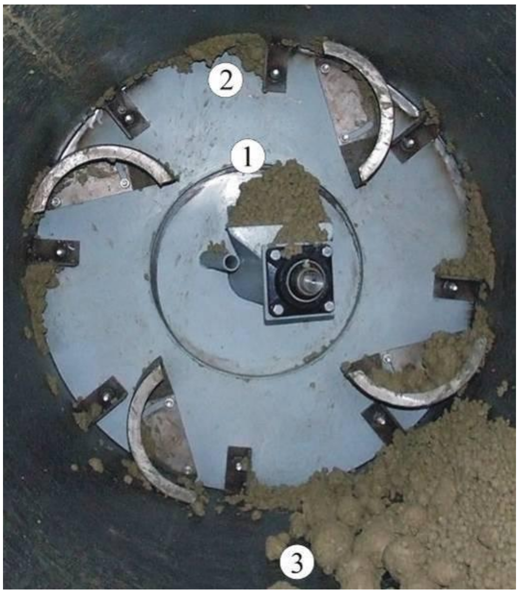
Blocking the passage of material by installing weirs was initially examined. Four lifter bars fashioned from 40mm angle iron were bolted longitudinally inside the drum, to serve as support for the weirs and promote bed tumbling. By inducing mixing in this way, the drum speed could be slowed without compromising effective tumbling. Reducing the speed would slow material transit. Two metal rings cut from 4mm steel sheet were bolted to the lifter bars, effectively dividing the drum into three equal compartments (see figure 7.7a). The rings had a radial gap with the drum surface of 25mm (being the maximum pellet diameter permitted by the discharge conveyer). These allowed the pellets to pass underneath, reducing the passage of material to a steady trickle.

The accumulation of wet material on the lifters was excessive. Furthermore, the second ring nearer the discharge end served no purpose as the throughput was already limited by the first. The second ring and the lifter bars were removed and discarded. Two flat bars were bolted in place of the lifters to act as supports for the remaining ring (see figure 7.7b). Accumulation of the wet material was dramatically reduced, but the remaining retention ring failed as agglomerates in the feed rapidly grew larger than 25mm. Many of these agglomerates arose from compaction of the material in the feed screw. In the confined space of the drum compartment, the oversized pellets, unable to pass through the annular gap, accelerated the rate of growth and resulted in accumulation of a large volume of material.

The retention rings were removed and replaced with curved lifter bars cut from 4mm steel. The bars formed a shallow flight helical screw, curving through 45° along their length to induce the material to tumble back towards the feed end as the drum rotated (see figure 7.7c). Although effective in this respect, accumulation upon the bars was a problem once again.

The accumulation of material inside the drum was a continuing problem, particularly around the support brackets for the end covers (see figure 7.8). This became more problematic as the fixings and bucket lifters became roughened with corrosion. Regular cleaning of the drum and conveyers was essential to maintain performance.

In conclusion, a smooth internal drum surface with as few accumulation points as possible would be most effective.



(1) Blocked discharge hopper
(2) Accumulation around fixing points
(3) Oversized (>25mm) pellets

Figure 7.8: Issues with the internal drum

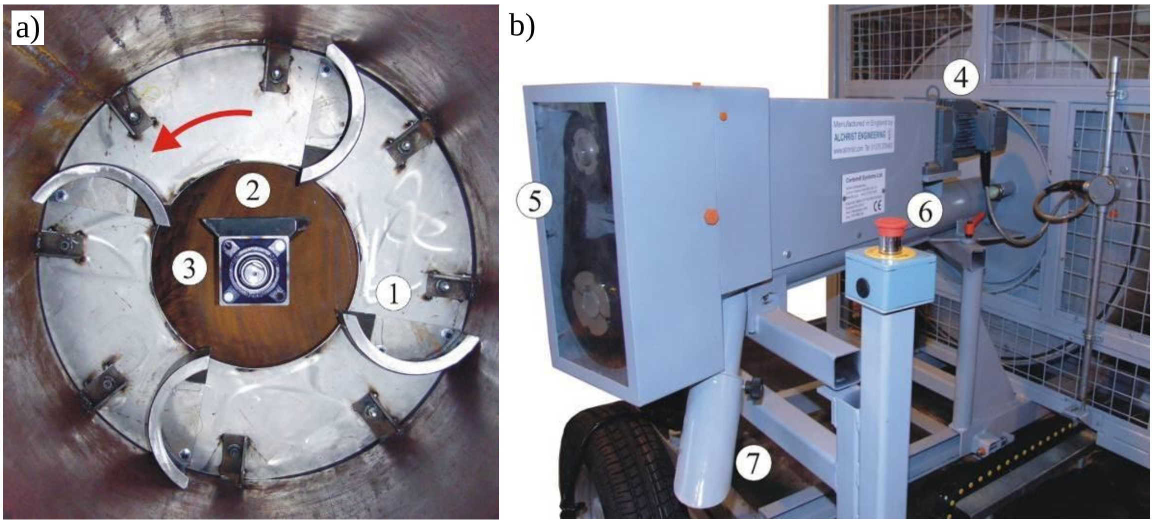
7.3.3 Discharge System

Pellets were discharged via bucket lifters, which scooped pellets from the base of the drum and deposited them into a hopper mounted at the end of a second screw conveyor (see figure 7.9a). The screw conveyer was driven by a second three phase motor and separate inverter. Pellets falling into the receiving hopper were drawn along the conveyer and exited through the offset discharge tube (see figure 7.9b).

The radial gap between the screw shaft and the housing tube permitted a maximum pellet diameter of 25mm. As the plant design had been based upon experiments in the laboratory, the formation of pellets of this size was rare. However, at a larger scale the reduced efficiency of the premixing and compaction in the feed screw resulted in the growth of a greater proportion of larger pellets (see figure 7.8).

The discharge conveyer was unable to cope with the throughput of material and frequently became blocked (see figure 7.8). Furthermore, the screw crushed and abraded larger pellets, depositing wet cementitious material inside the discharge tube.

Periods of plant inactivity allowed this to harden and the screw to cease and prevent its removal for cleaning.



(1) – Bucket lifter, (2) – Receiving hopper, (3) Screw conveyer tube, (4) – Drive motor, (5) – Drive pulleys, (6) – Screw conveyer tube, (7) – Discharge nozzle

Figure 7.9: Pilot plant discharge system (a) – internal view, (b) – external view

A gravity chute was constructed from 100mm diameter plastic pipe to replace the screw conveyer (see figure 7.10a). The pipe was slung on articulating brackets mounted on the front support frame and the drum cage. A new discharge end cover was cut from sheet steel, and the chute aperture sealed with a flexible rubber socket. Despite increasing the maximum pellet size tolerance and the use corrosion free materials, blocking was a regular occurrence, due to pellets sticking as they impacted the hopper after tipping from the bucket lifters. Increasing the fall angle of the chute failed to rectify the problem, and a vibrating motor was added to assist in conveying the wet pellets.

Vibration conveying was effective at transporting pellets that were surface dry. However, the four bucket lifters deposited pellets in sudden bursts into the hopper each quarter turn of the drum, rather than as a constant trickle. This sudden periodic influx of material formed plugs in the chute, which consolidated into a solid mass due to the vibration. A discharge system feed by bucket lifters was deemed unsuitable for dealing with wet pellets.

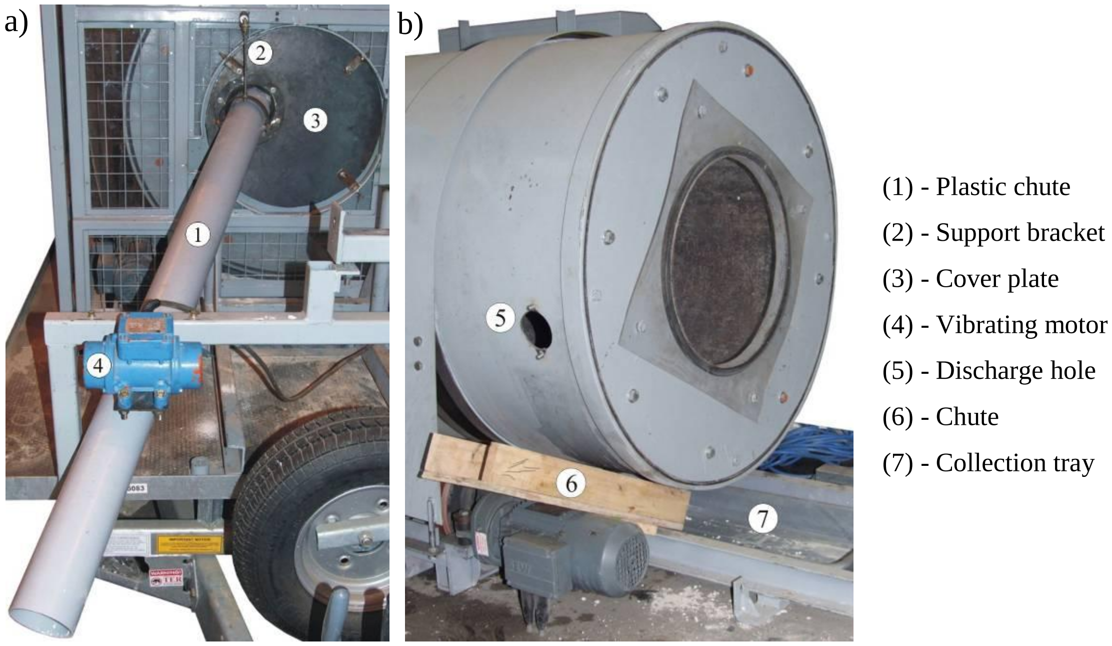


Figure 7.10: Discharge systems trialed; (a) – vibrating chute, (b) – gravity system

The discharge of wet pellets was facilitated using a simple gravity system. A discharge hole cut into the side of the drum (see figure 7.10b), allowed pellets to fall onto a chute and into a collection tray. This minimised the forces on the pellets and allowed them to discharge effectively. A blanking plate bolted over the hole allowed the pellets to tumble inside the drum for the required duration, after which the plate was removed, and the pellets allowed to discharge. However, this only allowed for batch processing, rather than continuous operation.

7.3.4 Dusting

The green pellets were very deformable and had a tendency to stick together during storage. This became a major issue during the curing stage when large quantities of pellets were stacked in heaps. Dusting the pellets with paper ash improved green strength and eliminate adhesion. The latter was particularly important as it reduced the friability of the pellet surface, and improved the appearance of the pellets.

Using the pilot plant as a batch mixer, the wet feed was loaded and pelletised. When the pellets had grown to the required size, ash was sprinkled onto the tumbling bed until an even coating was achieved. Further tumbling allowed this outer layer to consolidate and form a dense outer skin on the pellets.

7.3.5 Curing

Chapters 5 and 6 identified that carbonation was not occurring within the timescale of agglomerate formation, and that a separate curing step was deemed necessary. Partial drying of pellets was also found to accelerate the carbonation of pellets. A curing chamber was constructed from a 1100 litre waste bin (see figure 7.11).

The bin was converted by replacing the roll-top lid with a sheet steel cover, which bolted down onto the bin rim, compressing a foam gasket. A hinged hatch allowed loading and inspection without removal of the entire cover. Inside the bin, a false bottom fashioned from steel sheet perforated with 5mm holes provided a cavity underneath for carbon dioxide gas injection. The humidity of the atmosphere inside the chamber was desaturated to promote efficient carbonation using an domestic dehumidifier unit. The unit gently warmed the chamber, and removed excess moisture, which was discharged through a drain pipe in the side of the bin. Pellets were carbonated inside the chamber until they were strong enough to shovel into bags. This was typically 2-3 days.

(1) – CO_2 cylinder
(2) – Steel lid
(3) – Loading hatch
(4) - CO_2 flow regulator
(5) – Internal false bottom,
(6) – Dehumidifier drain pipe

Figure 7.11: Pilot scale carbonation chamber

7.3.6 Influence of scale on the agglomerate growth

Chapter 5 established the importance of the mix and machinery variables upon the pelletised product. The difficulties of scaling up have been previously noted, and experimentation is often needed to create a reliable model (Arslan and Baykal, 2006a, Iveson *et al.*, 2001a, Schaafsma *et al.*, 1998).

Using materials sampled from the same stockpiles, the effects of rotation speed (linear velocity), moisture content of the mix and mixing time upon particle size of the product were compared in the laboratory pelletising drum and the pilot scale pelletising drum.

Table 7.2 shows the variables investigated, and the common link between each. Thus when rotation speed was considered, mixing time was maintained at 10 minutes, moisture content at 40%.

Table 7.2: Pelletising variables investigated

Variable	**Increments**					
Rotation Speed (rpm) [linear velocity m/s]	0.1	0.21	**0.31**	0.42	0.52	
Mixing Time (mins)	2	5	**10**	20	30	
Moisture Content (%)	38	39	**40**	41	42	43

Increments in ***bold type*** *indicates the common factor*

The moisture content of the mix, the linear velocity of the drum and mixing time had a significant influence upon the particle size distribution and shape of the pellets (see figures 7.12 to 7.15). At pilot scale, increasing the moisture content from 38% to 41% resulted in a steady increase in pellet growth from 8 to 23mm. Increasing the moisture beyond 41% caused growth to accelerate rapidly, and the variation between batches to increase. This suggests decreasing mixing efficiency and liquid distribution as the moisture content increased. Pilot scale batches generally had more variability than at laboratory scale suggesting an overall decrease in mixing efficiency as the process was scaled-up. At laboratory scale, pellet size steadily increased between 38% and

42%. Increasing to 43% moisture caused the growth rate to increase. Variability at laboratory scale was considerably smaller, due to the greater accuracy of weighing and mixing materials.

Pellet size increased steadily with linear velocity. The steeper incline of the pilot scale graph suggests that at the same linear velocity, the larger drum imparts more force into the pellets. Similarly, greater variation between pellet batches was observed at pilot scale.

Although the size of pellets was larger at pilot scale, the same growth pattern at both scales was apparent over time. During the first five minutes, growth was slower, followed by a period of more rapid growth until ten minutes. From ten to thirty minutes, the rate of growth gradually decreased. This suggests an initial induction and consolidation phase, followed by a phase of steady growth, and slowing of the pellet growth as maximum consolidation is reached.

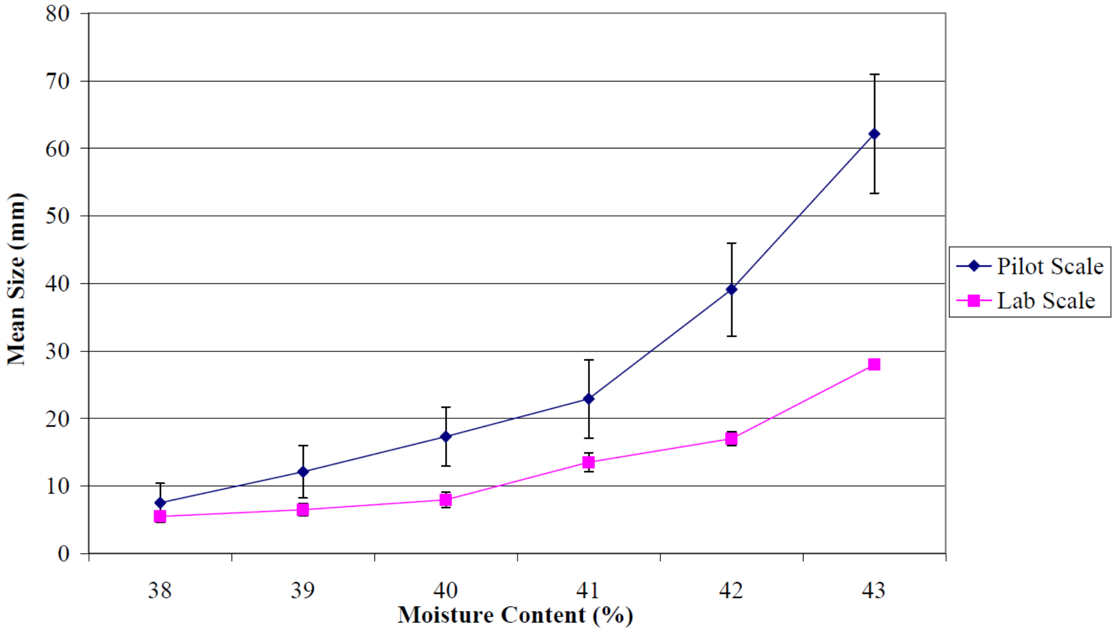


Figure 7.12: Influence of moisture content upon the particle size distribution of pellets manufactured at different scales (error bars represent the interquartile ranges)

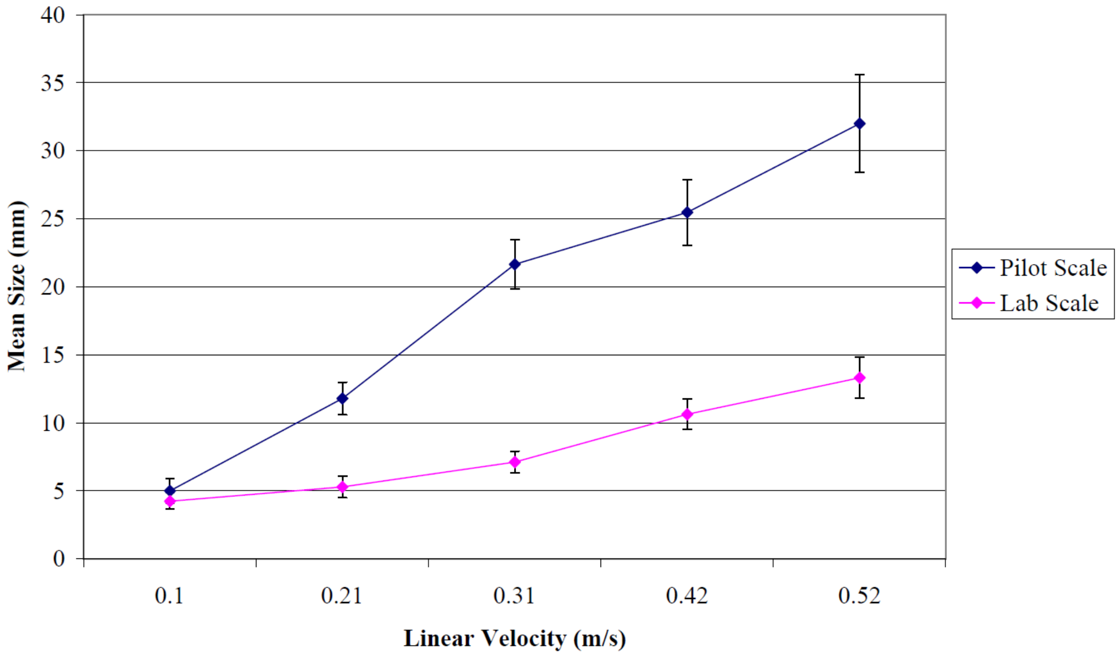


Figure 7.13: Influence of linear velocity upon the particle size distribution of pellets manufactured at different scales (error bars represent the interquartile ranges)

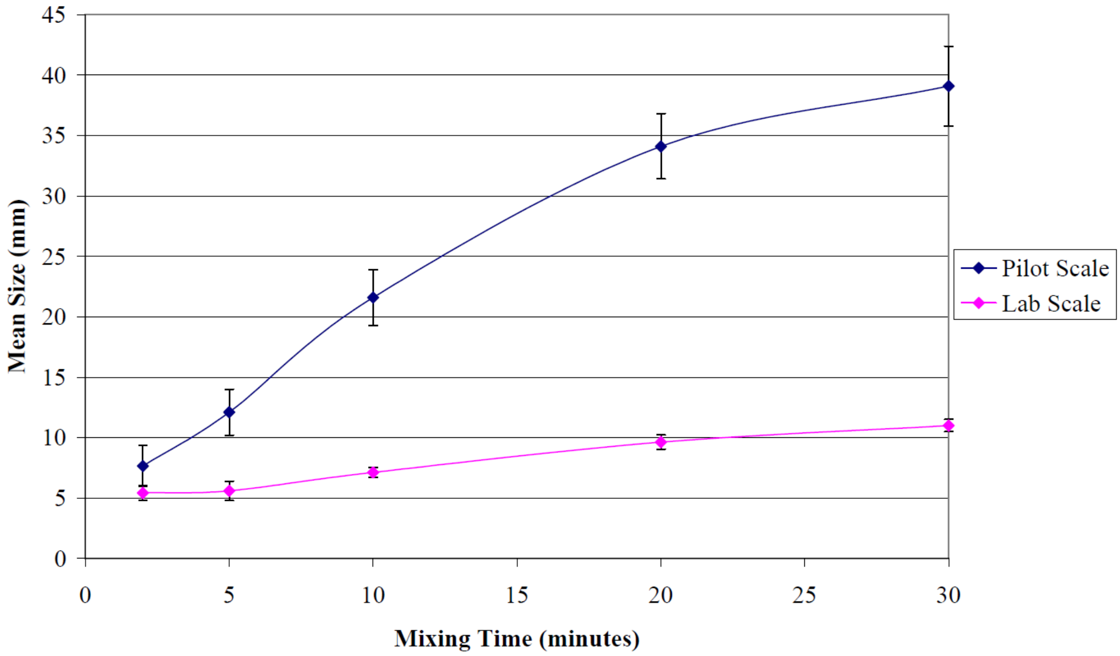


Figure 7.14: Influence of mixing time upon the particle size distribution of pellets manufactured at different scales (error bars represent the interquartile ranges)

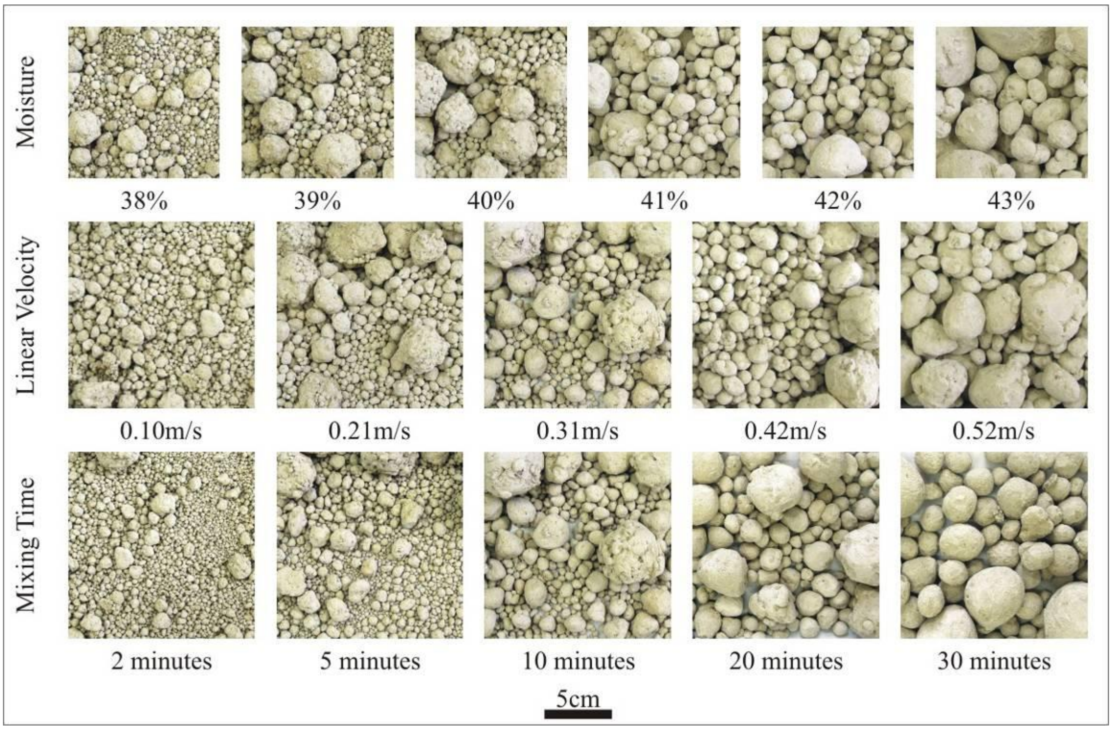


Figure 7.15: Pellets made in the pilot scale pelletiser

Pellets produced at pilot scale tended to grow larger, due to the larger volume of raw material available to agglomerate. Any differences in scaling up were largely due to the effect of having a larger batch size in the pilot scale drum compared to the laboratory. Increasing the batch size from 25kg to 50kg reduced the moisture requirement to form pellets of a given size by 2%. This was due to increased forces inside the drum brought about by a larger mass of material, which promoted consolidation, and reduced the amount of moisture required to form liquid bridges between particles.

7.4 Discussion

A pelletising drum with a working capacity of 200 kilograms per hour was designed and built with the intention of producing carbonated pellets. The results of chapters 5 and 6 found that it was not possible to simultaneously carbonate and pelletise materials as the two processes required different moisture contents.

Much of the design of a pilot scale pelletising drum was motivated by the intention to integrate both the carbonation and agglomeration processes. In particular, screw conveyors were chosen as they would help to retain gas inside the drum, despite the fact that they are best suited to conveying dry materials. Ultimately, the two processes were deemed incompatible, rendering many of the pilot plant's features inefficient for pelletising alone.

Premixing was found to be a key step in the production of pellets with the required particle size distribution and strength properties. Manual mixing of the raw material did not achieve even distribution of binder throughout. Mechanical mixers had varied performance. A forced action pan mixer was the most efficient trialled. A mixer imparting a large amount of shear to the mix appeared to be the most appropriate.

The properties of the raw material presented the greatest challenge for the design of the plant. Premixed quarry fines and paper ash had the consistency and adhesive properties of soft clay. Adhesion of this material to the screw conveyors and to the fixing points inside the drum, suggested the need for a scraping arm and a plain internal drum surface. As the pellets were soft after pelletising, conveying them out of the drum was equally problematic. Screw conveying caused the pellets to break up. However, the pellets were too adhesive for use with a gravity chute. Vibration conveying caused the pellets to consolidate into a solid mass. Belt conveying is probably the only practical solution.

Operating the plant as a continuous process was hampered by the lack of control on the retention time of the material in the drum. Residence time was controlled by the feed rate, rather than as intended by the inclination of the drum. Similarly, the drum was apparently too short in length. Typically, the size of a drum is calculated based upon the required residence time (Miller, 2005). Consequently, batch processing was the only method of retaining the pellets for sufficient time to grow and compact. Operating as a continuous process had the additional problem of maintaining a constant feed of material into the mixer from a batch premixer. A fully-fledged continuous process would require silos for as-received material storage, and automated batching, premixing, and feed systems. Most agglomeration plants operate continuously as it allows high production rates, minimal user input, and consistent product properties. Batch processing is suited to producing small quantities of a wide range of products, although requiring increased maintenance and cleaning (Gantner, 2003).

Transferring a laboratory pelletising process to full-scale is rarely a direct move. Comparative experimentation is often necessary to understand the relationship (Iveson *et al.*, 2001; Schaafsma *et al.*, 1998). In this case, experiments were conducted on the two machines to observe the effects of comparative linear velocity, moisture content of the feed, and mixing time. Scaling up the pelletising process from the laboratory was readily achieved using the same variables, e.g. linear velocity of the drum, moisture content and mixing time. However, this could only be achieved when the pilot scale machine was modified to closely match the design of its laboratory-based counterpart. However, a faster pellet growth rate was observed in the larger drum, and greater variability between batches was observed.

As was highlighted in chapters 4 and 5, wastes often vary physically, mechanically, and chemically. Rarely were two batches of material alike. Primarily, the moisture content was the biggest issue, which would often vary in a single stockpile. However, previous observations have shown that the particle size distribution of the materials can also vary. On site, constant monitoring of the moisture content of the raw materials was necessary to achieve a product with the same particle size distribution. A full scale plant would require the product to be screened after pelletising, and the oversize and undersize returned to the premixing stage.

7.5 Conclusion

The scaling-up of laboratory carbonation-agglomeration process to pilot scale was examined in this chapter.

Premixing was found to be a key step in producing the required product. Working at pilot scale was complicated by the need to deal with larger quantities of materials in their as-received state, with little or no preparation.

Scaling the pelletising process from laboratory to pilot scale was achieved using the same operating and mix variables. This required the machinery to be closely matched, and the same batches of raw materials to be used. However, the rate of pellet growth was higher in the larger drum, and greater variability was observed.

In the previous chapter, it was identified that carbonation and agglomeration are more effective as separate processes. Pellets are initially formed and then carbonated in a two-stage process. This rendered many of the design features of the specialized pilot plant defunct. A simple drum or disc pelletiser is best suited for use in a pilot scale process to manufacture carbonated aggregate.

The next chapter will examine the mechanical and chemical properties of pellets produced using this pilot scale process. Potential market end-uses for these pellets are also explored.

Chapter 8 : Aggregate Testing

8.1 Introduction

Scaling up the process for manufacturing pellets using accelerated carbonation was explored in the previous chapter. At a larger scale, the conveying of the material before and after pelletising was troublesome. The equipment used to pelletise the material should closely match that used in the laboratory development stage. In Chapter 6, it was found that the carbonation reaction could not be accelerated sufficiently to combine the pelletising and carbonation processes. The optimised pilot scale process employed three stages, comprising premixing the waste and binder together, pelletising the premixed material, and finally curing the pellets in carbon dioxide.

This chapter examines the mechanical and chemical properties of aggregate produced in the pilot scale process. Testing is performed according to British Standards alongside commercial lightweight aggregates. The potential use of the aggregate in concrete is explored.

8.2 Materials and Methods

8.2.1 Materials

Quarry fines known as Hassock silt and Hassock sand were used as examples of waste which were not reactive with carbon dioxide. These were mixed with incineration ash from a paper recycling facility, previously referred to as paper ash 3.

8.2.2 Pellet Manufacture

Two mixes were manufactured; 35% Hassock sand and 35% Hassock silt with 30% paper ash 3, and 25% Hassock sand and 25% Hassock silt with 50% paper ash 3. The moisture contents required for the mixes were 40% and 51% respectively. Chapter 6 identified that reserving 25% of the binder, and using it to dust the surface of the formed pellet enhanced both the initial and the final strength of the pellets.

The moisture contents of the materials were measured according to the modified British Standard method described in chapter 7. Using these values, the materials were weighed out according to their dry weights. A Utranazz pan mixer was used to blend the materials together, before adding required amount of additional water.

A 3.2 cubic metre drum pelletiser, capable of producing 200 kilograms per hour was used to manufacture the pellets for testing. Development of this pelletiser was described in chapter 7. In accordance with the findings of chapter 5 and chapter 7, the pelletiser was operated at a linear velocity of 0.32m/s, with a residence time of 10 minutes. .

After pelletising, the 25% of binder reserved, was thrown into the drum to coat the tumbling pellets. A further five minutes of mixing was needed to layer the material onto the pellet surfaces. The pellets were divided into two separate portions, which were cured in the pilot scale carbonation chamber or allowed to naturally carbonate in the open air for 7 days.

8.2.3 Pellet Testing

British Standard BS EN 13055 outlines the requirements for lightweight aggregate (LWA). Accordingly, the required British Standards methods were used to test the pellets, which are summarised in table 8.1. Each test was performed in triplicate. Chemical tests were performed in duplicate by Bureau Veritas Ltd as indicated in table 8.1. Individual pellet crushing strength was measured according to the method described in Chapter 5, based upon a sample size of twenty pellets. CO_2 uptake and pH were measured in triplicate according to the methods described in Chapter 3 .

Table 8.1: Physical and mechanical tests applied to pellets

Test	British Standard	Method Summary
Acid soluble sulfate*	BS EN 1744	Acid digestion in dilute acid and precipitation of sulfur using barium chloride. Precipitate heated to 925°C and weighed.
Bulk density	BS EN 1097-3	Uncompacted weight of oven dried aggregate is measured as a unit volume and expressed in kg/m^3.
Freeze-thaw	BS EN 13055	Measure disintegration of aggregate subjected to 20 consecutive cycles of freezing at -18°C and thawing at 20°C.
Particle density & water absorption	BS EN 1097-6	Density is measured by weighing the aggregate in an oven dried, saturated and water immersed state. Particle density is defined as the ratio of the oven dried mass to the volume it occupies in water including sealed and water accessible voids
Total sulfur*	BS EN 1744	Acid digestion of the aggregate with bromine and precipitation of sulfur using barium chloride. Precipitate heated to 925°C and weighed.
Water soluble chloride*	BS EN 1744	Aggregates are leached in water in a 1:1 ratio, the chloride precipitated using excess silver nitrate, and back-titrated with thiocyanate solution.

*Tests performed by Bureau Veritas Ltd

8.3 Results

8.3.1 Pellet Testing

The pellets manufactured were rounded to sub-rounded in shape, with rough surfaces (see figure 8.1). The properties of the pellets are compared with commercial lightweight aggregates; sintered PFA (Lytag), autoclaved PFA (Aardelite), and expanded clay (LECA), in table 8.2. The modes of production of these aggregates are described in table 2.4.

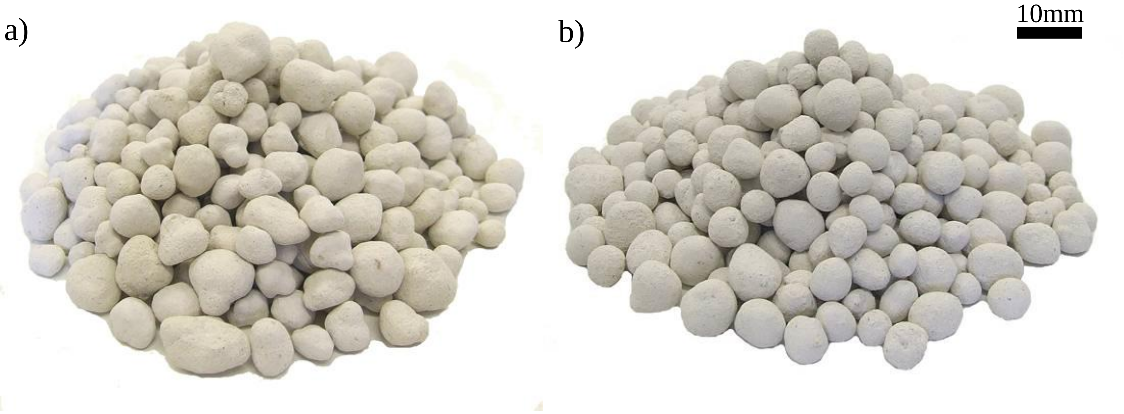


Figure 8.1: Final pelletised product; a: 30% ash pellets, b: 50% ash pellets

Table 8.2: Pellet testing results

	30% Ash Weathered	**30% Ash Carbonated**	**50% Ash Weathered**	**50% Ash Carbonated**	**Lytag**	**LECA**	**Aardelite**
Acid Soluble Sulfate (%)*	0.23	0.23	0.28	0.28	ND	≤0.5[†]	ND
Particle density	2.5	2.5	2.4	2.4	1.7	1.0	2.1
Bulk density (kg/m^3)	890	918	824	854	734	350	720
CO_2 Uptake (% by weight of binder)	13.0	15.3	14.6	16.6	-	-	-
Freeze-thaw (% disintegration)	12.3	10.4	8.9	3.2	3.8	4.3	10.5
pH	11.6	11.6	11.9	11.7	8.8	7.2	8.9
Individual Pellet Strength (MPa)	0.12	0.13	0.13	0.17	0.43	0.09	0.09
Total Sulfur (%)*	0.08	0.07	0.1	0.1	ND	≤0.32[†]	ND
Water Absorption (%)	25.0	27.0	28.6	27.8	18.0	30.3	21.2
Water Soluble Chloride (%)*	0.01	<0.01	<0.01	<0.01	ND	≤0.04[†]	ND

** = tests performed by Bureau Veritas Ltd, [†] = values quoted by Maxit Group (2008), ND = not determined*

The compressive strength of the carbonated pellets increased with the reactive binder content, and as a result of exposing the pellets to accelerated carbonation opposed to natural weathering. Strength increased in the order: 30% paper ash naturally weathered < 30% paper ash accelerated carbonated < 50% paper ash naturally weathered < 50% paper ash accelerated carbonated. The weakest pellets had a compressive strength of 0.12 megapascals, which was 33% stronger than LECA and Aardelite, but weaker than Lytag.

Increasing the reactive ash content reduced the bulk densities of the pellets. However, accelerated carbonation increased bulk density compared to the naturally weathered pellets. However, all the pellet batches were well below the 1200kg/m^3 bulk density limit for LWA (BS EN 13055-1:2002). Particle density was also reduced by increasing the paper ash content.

Freeze-thaw disintegration was also affected by the binder content and method of curing. Pellets with a higher compressive strength were found to exhibit less disintegration. Naturally carbonated pellets made with 30% paper ash disintegrated by 12.3%, whilst accelerated carbonation pellets made with 50% paper ash disintegrated by 3.8%. The extent of disintegration is clearly evident in figure 8.2. Disintegration of the commercial aggregates was limited to surface fragmentation, rather than complete splitting of the pellets. Aardelite was 10% fragmented after testing, whilst Lytag and LECA disintegrated by around 4%.

30% Weathered 30% ACT 50% Weathered 50% ACT

Figure 8.2: Pellets subjected to freeze-thaw testing

Accelerated carbonation curing of the pellets increased carbon dioxide uptake compared to natural weathering. Paper ash 3 attained a maximum carbon dioxide uptake of 22.7% when repeatedly carbonated in a pressurised vessel (according to the method described in 4.2.2.2). Natural weathering resulted in 13% and 14.6% carbon dioxide uptakes for 30% and 50% paper ash pellets respectively. Pellets subjected to accelerated carbonation achieved around a 2% greater increase in weight. The pH was higher for pellets containing more reactive binder.

Water absorption of the pellets varied between 25 and 28.6%. These fell within the range of the commercial aggregates between 18 and 30.3%.

The chloride and sulfate content of the pellets were compared to the published specifications for LECA aggregate. The sulfur content of the pellets was increased as the paper ash content increased. Total sulfur values for the pellets did not exceed 0.1% by weight, which was three times less than the specified limit for LECA. Acid soluble sulfate levels were approximately half that of LECA. Water soluble chloride levels were no greater than 0.01% and in many cases below the limit of detection. LECA exhibited water soluble chloride levels of 0.04%.

8.3.2 End Uses

LWA is a premium product used in specialist applications including lightweight structural concrete in bridges and in horticulture as plant substrates (Chandra and Berntsson, 2003). Carbonated aggregate was trialled in lightweight structural concrete, and through collaborative research projects in a horticultural application (Molineux *et al.*, 2009). Typical uses of LWAs are summarised in table 8.3.

Table 8.3: Typical uses for lightweight aggregate (source: Chandra and Berntsson, 2003)

End Use	Description
Lightweight structural concrete	Lightweight aggregate concrete (LWAC) is about 28% lighter than normal weight concrete. Therefore, less reinforcing and reduced cast section thickness can be achieved.
Floor and roof screed	Screeds benefit from reduced weight and enhanced thermal and sound insulation.
Geo-fill	Using LWA for geotechnical fill reduces weight and pressure, from back-fill, to structures.
Filter medium	LWAs are suited to filtration systems, particularly those incorporating a biological element due to the high surface area of the vesicular structure.
Pipe bedding	Low bulk density and good frost resistance protect underground pipes, and allow easy removal for future inspection.
Lightweight Blocks	Good thermal insulation and low bulk density produce blocks which are safer to handle and reduce heating costs. Block products on the market include Hemelite.
Insulation	The vesicular structure of LWAs give them excellent thermal insulation properties, which are imparted to the concrete, or used to fill cavities in masonry.
Horticulture	The high water absorption of lightweight aggregate allows them to act as a water storage medium to support plant growth. Lower bulk density makes them more stable in sloping applications such as vegetated (green) roofs.

8.3.2.1 Lightweight aggregate for concrete

Concrete cubes were made from the four pellet batches, and from Lytag and LECA aggregate for comparison. Mixes were prepared according to a recommended mix for lightweight concrete using Lytag aggregate (Lytag, 2004), using quartz sharp sand conforming to BS EN 12620, and Blue Circle 52.5 Portland Cement. This mix formulation is presented in table 8.4. Aggregate and water doses were altered to account for variations in the bulk density and water absorption of the different aggregates. The water addition was based upon the requirement to achieve a concrete slump of 70mm. The aggregate was soaked in the mix water for thirty minutes, before adding and mixing the sand, and finally the cement. Mixes were prepared in a plastic bucket, and blended by hand with a trowel.

Concrete cubes were prepared according to BS EN 12390-1 (2000) and BS EN 12390-2 (2000), using 100mm moulds. The cubes were demoulded after 24 hours and immersed in water for the remainder of the curing period.

Table 8.4: Mix design for 10cm concrete cubes*

	30% Ash Hydrated	**30% Ash Carbonated**	**50% Ash Hydrated**	**50% Ash Carbonated**	**Lytag**	**LECA**
Volume of mix	$3dm^3$ + 25% overfill					
Cement (kg)	1.35	1.35	1.35	1.35	1.35	1.35
Dried Sand (kg)	2.25	2.25	2.25	2.25	2.25	2.25
Dried aggregate [0.88 x bulk density] (kg)	2.44	3.03	2.94	2.82	2.72	1.06
Water [70mm slump + absorption of aggregate] (kg)	1.11	1.46	1.41	1.48	1.43	0.90

** according to the recommended mix design for lightweight concrete specified by Lytag (2004)*

After 28 days, cubes were tested for compressive strength immediately after removal from the water bath according to BS EN 12390-3 (2002). An Avery-Denison 7226CB compression testing machine was used, operating at a loading rate of 2.5kN/s. Strength and wet density values for the cubes are shown in table 8.5.

The cubes exhibited a satisfactory mode of fracture, as specified in BS EN 12390 (see figure 8.3a). All four exposed faces were cracked approximately equally, with minimal damage to the faces in contact with the compression machine platens. Fractures were propagated through the aggregate particles, rather than around the pellets, indicating good bonding with the cement paste. Cube fracture revealed that, despite the high compressive strength of the aggregate, the feed was not uniformly premixed. As figure 8.3b shows, inclusions of uncombined Hassock silt occasionally occurred in the pellet cores.

Table 8.5: Density and compressive strength of concrete cubes

	30% Ash Hydrated	**30% Ash Carbonated**	**50% Ash Hydrated**	**50% Ash Carbonated**	**Lytag**	**LECA**
Compressive Strength (Mpa)	20.5	19.0	24.0	23.0	29.0	22.5
	21.0	19.0	24.0	22.0	28.0	22.0
	21.5	17.0	23.0	24.5	28.0	22.0
Density (kg/m^3)	2020	2020	1970	1995	1840	1570

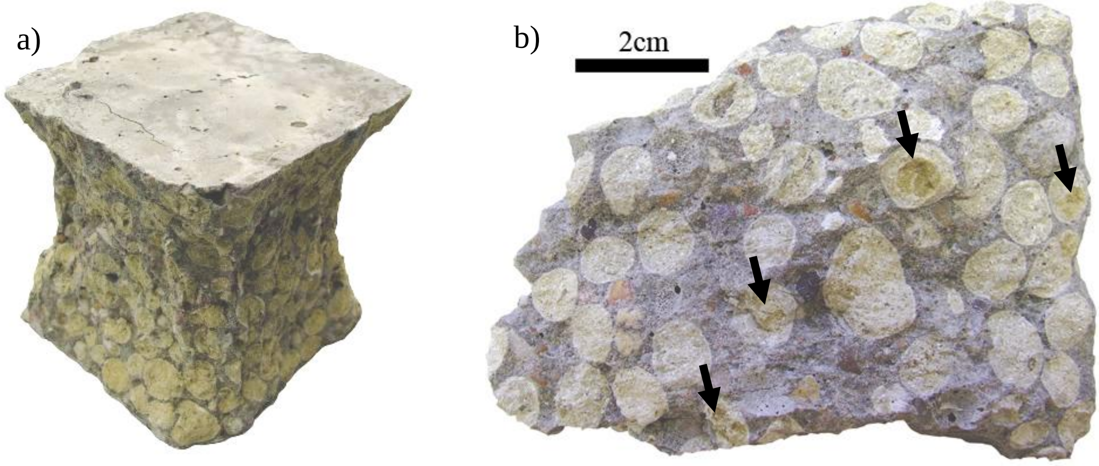


Figure 8.3: Concrete test cubes, a) satisfactory failure of a concrete cube, b) cube fragment

8.3.2.2 Green roof application

Green roofing involves installing drainage and growing layers to allow planting, resulting in improved aesthetic and building insulation properties, and environmental benefits (Johnston and Newton, 1997). A lightweight, absorbent medium is required to support plant growth without placing excessive load on the roof structure.

Green roofs are classified as either intensive or extensive. The former have deep growing medium which are planted with trees and landscaped with ponds, paved areas and seating. The latter have a shallow growing medium, and are generally left to nature with minimal maintenance. Extensive roofs can be carpeted with thin Sedum (hardy alpine) mats, or covered with a thicker substrate which is plug planted or left to naturally colonise (Livingroofs.org, 2004). Substrate-based roofs comprise several layers for ventilation, insulation and growing (see figure 8.4a).

Royal Holloway College at the University of London undertook a study of recycled materials for use in green roofs. Carbonated aggregate was compared along with other experimental substrates to crushed brick which is traditionally used. The experimental substrates were comparable or out-performed the crushed brick in terms of bulk density, contaminant release and water holding capacity (Molineux *et al.,* 2009). Accelerated carbonated aggregates were supplied for a pilot-scale green roof trial in the south-east of England. Carbonated aggregates are being trialled for their ability to sustain plant growth over extended timescales. A pilot scale trial was set up on a roof in London during spring 2008, for monitoring over a period of 15 months (see figure 8.4b). As of autumn 2009, the performance of carbonated pellets was comparable to the control and the other substrates (Molineux, 2009).

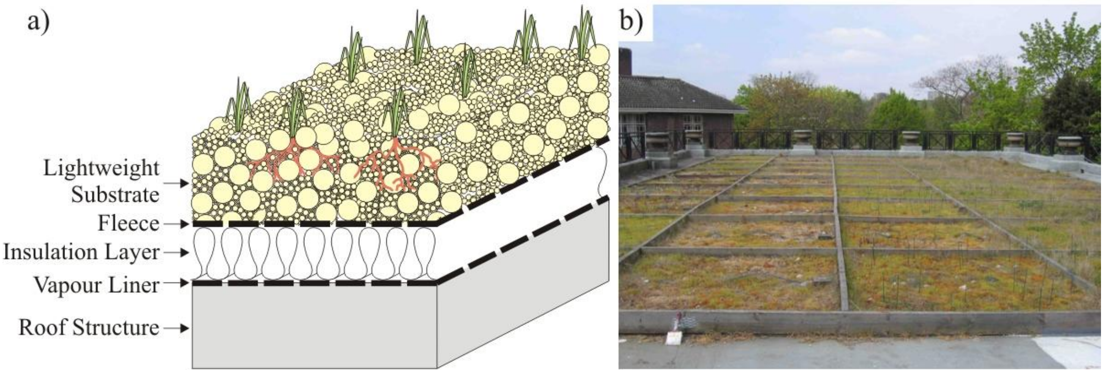


Figure 8.4: Green roofs, a: Anatomy of a green roof (modified from Livingroofs, 2004), b: green roof test plots incorporating carbonated aggregate (courtesy of Chloe Molineux, University of London).

8.4 Discussion

8.4.1 Aggregate properties

Commercial lightweight aggregates have highly varied bulk density and strength properties, which are generally end-use specific. LWA's are typically classified by low bulk density and low strength for 'insulation' applications, medium density and strength for 'blockwork' production, and high density and strength for 'structural' use (IStructE, 1987). Typical weights for LWA vary between 80 and 900kg/m^3 (Mehta and Monteiro, 2006). The carbonated aggregates fell near the upper threshold of this range, suggesting their use may be limited to structural applications. Bulk density may be reduced by increasing the binder content in this instance, although this may not apply if other binders such as cement are used. Equally, accelerated carbonation increased the bulk density compared to pellets which were allowed to naturally weather. Growth of calcium carbonate in the pore space would account for an increase in bulk density.

Freeze-thaw disintegration of the carbonated aggregate was found to be generally higher than the commercial aggregate tested. However, disintegration was reduced to a comparable level by increasing the binder content, and subjecting the pellets to accelerated carbonation. Assuming the pellets to be analogous to normal concrete, susceptibility is affected by the water/cement ratio, cement content, porosity, moisture content, and the environment of exposure (including temperature cycles, wet/dry cycles and the presence and type of salt) (Concrete Society, 2005, Chandra and Berntsson, 2003, B.R.E, 2001, Concrete Society, 1999).

Porosity is generally regarded as being a key controlling factor upon freeze-thaw durability. However, this is dependent upon the size distribution of the pores. The finer capillary pores between 1 mm to 30 nm are responsibility for much of the damage when they become saturated (C.I.R.I.A, 2001). The increased amount of calcium carbonate caused by accelerated carbonation may contribute to filling these pores. Conversely, freeze-thaw behaviour improves in concretes with a lower water/cement ratio (w/c) and cement content, due to a decrease in the quantity of cement paste and reduced porosity from excess water (Concrete Society, 2005, C.I.R.I.A, 2001). At a paper ash binder content of 30%, a mix water content of 40% was required, representing a w/c of 1.3. When the paper ash content was raised to 50%, mix water only increased to 51%, being a w/c of approximately 1. The combined effect of reduced w/c and therefore excess void space, and further closure of these voids due to carbonation, is likely to account for enhanced freeze-thaw resistance in the higher binder content mixes exposed to accelerated carbonation curing.

Carbon dioxide uptake of the pellets was promoted by accelerated carbonation curing. However, this had more important implications for the strength and freeze-thaw durability of the pellets, rather than carbon dioxide uptake, which was only increased by around 2%. Over a period of seven days, the amount of carbonation occurring was around 70% of the maximum achievable. Carbonation was promoted by partial drying in the laboratory to a similar extent within a 24 hour period. This suggests that the pilot scale curing method was not as efficient, or that the reaction slows down substantially after the first 24 hours, and further curing is unnecessary.

Water absorption of the pellets was high compared to the commercial aggregates, and significantly greater than the range for normal weight aggregate of 1-5% (Smith and Collis, 2001). High water absorption may result in increased susceptibility to freeze-thaw, but this also affected by the size range of the pores (C.I.R.I.A, 2001). Equally, drying shrinkage of concrete is also known to increase with aggregate absorption (Smith and Collis, 2001). Conversely, absorbance of water from the concrete during the curing phase, may help to reduce the w/c in the cement paste (Chandra and Berntsson, 2004).

Aggregates with a rounded shape impart improved workability and aid of the compaction of concrete (Smith and Collis, 2001). Conversely, the contact between the cement paste and an angular aggregate may be greater, yet a higher w/c is required to achieve the same workability, reducing strength (Mehta and Monteiro, 2006). The contact between aggregate and cement paste is improved by a rough surface texture. This has a significant effect upon flexural strength which can have implications for the use of lightweight concrete in structural applications. Compressive strength can also be affected, as the bond with the cement paste may not be strong enough to realise the maximum strength of the concrete (Mehta and Monteiro, 2006)

British Standard guidance on total sulfur imposes a limit of 1% by weight of the mortar product (BS EN 13139). The acid soluble sulfate content of lightweight aggregates should not exceed 1% according to BS 8500. The interaction between sulfate ions and concrete can result in sulfate attack. This is normally associated with the formation of ettringite and gypsum through a reaction of sulfate ions with the cement hydration products. Formation of both ettringite and gypsum can be destructively expansive, as they occupy a greater space than the original constituent Sulfate attack can also result in the formation of a calcium silicate carbonate sulfate hydrate known as thaumasite. Formation of thaumasite occurs as the calcium silicate hydrate gel in the hydrated cement is consumed, resulting in the formation a soft pulpy mass and a significant loss in strength (B.R.E, 2005).

In a study upon the effects of contaminated soil upon concretes, concentrations of sulfate in the soil above 12,000mg/kg were considered to be a high risk of causing sulfate attack in concrete (B.R.E, 1994). The carbonated aggregates did not exceed 1000mg/kg, suggesting that sulfate attack was unlikely. However, paper ash 3 was found to leach low levels of sulfate in chapter 4. Equally, in other wastes including other paper ashes, the levels of sulfate were over an order of magnitude higher. The use of these wastes to make carbonated aggregate may pose a significantly greater risk.

Penetration of chloride ions results in the initiation of corrosion of steel reinforcing bars (Mehta and Monteiro, 2006). Cement paste degradation also occurs through the reaction of the calcium hydroxide in hydrated cement with chlorides to form soluble calcium chloride, which then leaches out, increasing permeability and susceptibility to further chemical attack. Crystallisation of potentially damaging chloride crystals within the concrete can also occur as a result of repeated wetting and drying (Chandra and Berntsson, 2003).

The low chloride leaching of the paper ash binder (see chapter 4), resulted in leachate concentrations lower than that of LECA. Chloride content should not exceed 0.1% of dry mass of mortar according to BS EN 998-2, or 0.2% of the mass of cement in concrete containing pre-stressed steel reinforcement (BS EN 206). Concrete exposed to contaminated soil was found to be at high risk, when chlorides were present in concentrations exceeding 1% (B.R.E, 1994). The other wastes studied leached chlorides in concentrations up to two orders of magnitude higher than paper ash 3, which may pose a more serious issue.

8.4.2 Pellet strength

Pellet strength was proportional to the binder content, and the degree of cementation promoted by accelerated carbonation curing. The strength of spherical particles can be attributed to a combination of surface friction of interlocking particles, electrostatic forces, and chemical bonding (Kapur and Fuerstenau, 1967).

Tensile failure is considered to be a key mechanism of particle breaking upon crushing (McDowell and Humphreys, 2002, Tang *et al.*, 2001). The mode of failure observed was of sudden fracture of pellets into typically two hemispherical fragments, or into a number of segments or quandrants, together with some fines. Fracture lines developed longitudinally in the sphere, in the direction of applied force (see figure 8.5). These fracture lines coincide with the maximum tensile stress induced within a sphere occurring at some point along the axis passing through the two loading points (Li *et al.*, 2000).

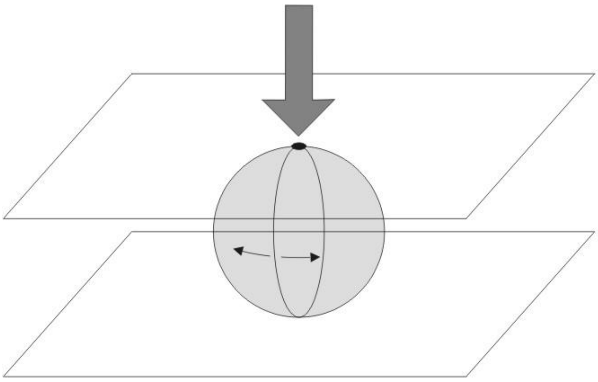


Figure 8.5: Schematic of single pellet strength test

Failure may not occur only by tensile cracking at the centre but by the development of localised crushing zones at the points of contact (Tang *et al.*, 2001), which would explain the generation of fines. It has been suggested that the development of so called crushing cones, converging to a point towards the centre of the sphere away from the loading point, may act like a wedge and be responsible for the eventually splitting of the pellet (Kapur and Fuerstenau, 1967). Conversely, simulations of the failure of spherical particles, suggest that cracks propagate towards the centre of the particle, and radiate outwards as more force is applied, leading to the development of a fracture line connecting the two loading points (Tang *et al.*, 2001).

These modes of failure apply to homogeneous materials. As has been demonstrated in previous chapters, the heterogeneity of the pellets is dependent upon a number of factors, including that of the raw materials and the degree of mixing of the different components. The range of failure modes, such as splitting into halves, wedges or quadrants, indicated the variability between particles. Figure 8.3 clearly demonstrates the variability as a result of inadequate mixing. A heterogeneous structure results in indirect transmission of stresses through the body of the pellet (Tang *et al.*, 2001, Kapur and Fuerstenau, 1967).

Rarely are pellets true spheres, and variations in size and shape influence strength. It has been observed that smaller particles exhibit proportionally greater strength, due to reduced number of flaws and irregularities (Nakata *et al.*, 2001). The variation in fracture load with pellet size is shown in figure 8.6. The lack of correlation between size and failure load suggests heterogeneity, which may be attributed to uneven binder and water distribution, and to inefficient mixing. Variations in the size, shape and the orientation of flaws lead to unrepeatable stress distributions, and scattering of the strength data (Li et al, 2000).

The pellet surface is likely to play a key role in stress distribution. Kapur and Fuerstenau (1967) highlighted that the highly compacted outer region of the pellets has a disproportionate effect on strength. Similarly, in chapter 6 the results of layering the reactive binder onto the surface of the pellet after forming rather than mixing it evenly throughout the material before pelletising, found that strength was increased. This would suggest that a crust forms on the pellet, which may be attributed to the formation of a carbonated rim in the initial stages of carbon dioxide exposure. During loading, stress may be conducted through the hardened crust, rather than through the pellet core. However, once the crust fractures, the comparatively weaker pellet core undergoes sudden failure.

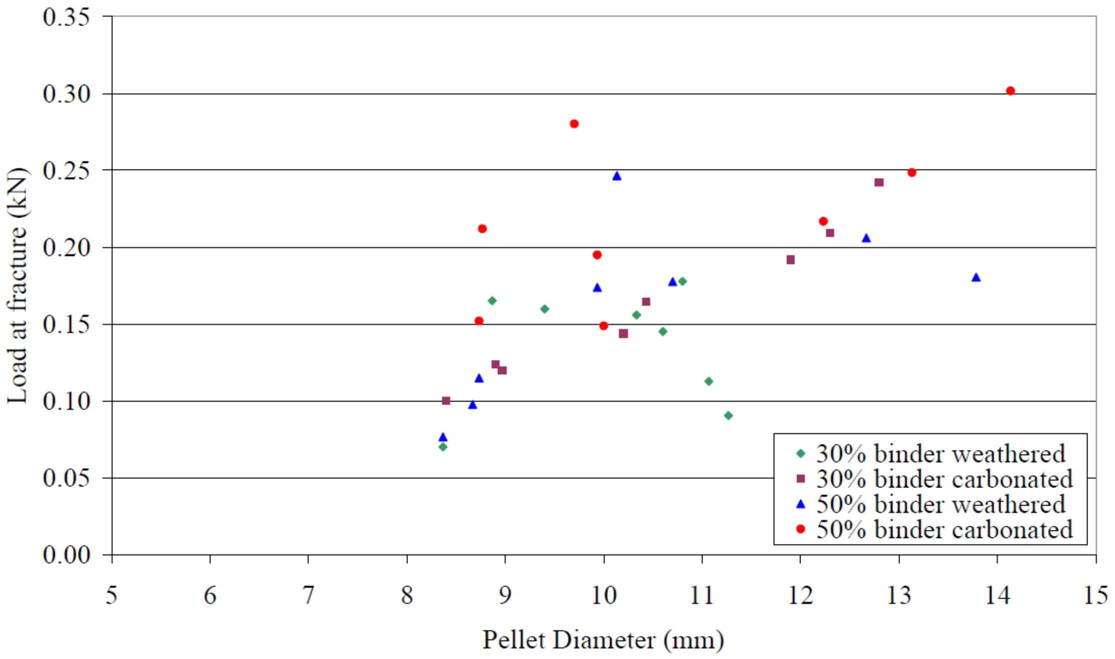


Figure 8.6: Variation in pellet fractures loads with pellet diameter

8.4.3 Use of aggregate in concrete

British Standard (BS 8500-1:2006) allocates concrete to specific applications based upon compressive strength (see table 8.6). Exposure classes recommended the severity of the service environment to which the concrete is subjected. Thus, low strength concrete is only deemed fit for X0 applications, where concrete is used in non-aggressive environments. Progressively higher strength concrete may be exposed to increased risk of wetting and drying, freeze-thaw or aggressive chemicals.

The exposure classes of the manufactured concretes are shown in table 8.7. Although the 30% ash bound aggregate fell short of the commercial aggregate, it was still suitable for X0 applications. Concrete manufactured using 50% ash aggregate was comparable to LECA concrete, and appeared suitable for use in XC1 applications, where concrete containing reinforcing is either maintained in a permanently wet or dry state, but not subjected to the cyclical stresses of wetting and drying. Lytag concrete met XC2, which permits burial in wet soil that is not exposed to wetting and drying cycles. Concrete made from Lytag also met the criteria for freeze-thaw exposure.

Table 8.6: Concrete exposure classes (B.C.A, 2000)

Class Designation	**Exposure Conditions**
XO	Concrete without reinforcement or embedded metal, or concrete with reinforcement or embedded metal in very dry conditions. No freeze/thaw, abrasion or chemical attack.
XC	Corrosion induced by carbonation
XC1	Dry or permanently wet
XC2	Wet, rarely dry
XC3	Moderate humidity or cyclic wet and dry
XS	Corrosion induced by chloride from seawater
XS1	Exposure to airborne salt but not in direct contact with seawater
XS2	Permanently submerged
XS3	Tidal, splash and spray zones
XD	Corrosion induced by chloride other than seawater
XD1	Moderate humidity
XD2	Wet, rarely dry
XD3	Cyclic wet and dry
XF	Freeze/thaw attack
XF1	Moderate water saturation without de-icing agent
XF2	Moderate water saturation with de-icing agent
XF3	High water saturation without de-icing agent
XF4	High water saturation with de-icing agent
XA	Chemical attack

Table 8.7: Exposure classes for the manufactured lightweight concretes

	30% Ash Hydrated	**30% Ash Carbonated**	**50% Ash Hydrated**	**50% Ash Carbonated**	**Lytag**	**LECA**
Compressive Strength Class (BS EN 206)	LC16/18	LC16/18	LC20/22	LC20/22	LC25/28	LC20/22
Exposure Class	X0	X0	XC1	XC1	XC2 / XF2 / XF3	XC1

The concrete produced from the pellets was significantly denser than that produced from Lytag or LECA, and was close to the upper limit value for lightweight concrete (BS EN 206-1). This will limit the applications for such a concrete, given the lower strength compared to structural Lytag concrete.

Despite the beneficial effect of accelerated carbonation curing upon the strength of the aggregate, this did significantly affect the strength of the concrete to promote it to a higher exposure class.

8.4.4 Reclassification of waste

The designation of waste is covered in the Waste Framework Directive. Reclassification of waste as a product fit for commercial use requires a number of criteria to be fulfilled. The product needs to be used for a specific purpose, have a market demand, and must comply with the relevant standards and specification. Equally, the product must no longer present a risk to human health or to the environment.

Whilst conformance to standards can be readily assessed, the release of hazardous substances from commercial products is rarely an issue, and few guidelines exist. Since wastes remain as such until proven otherwise, it is appropriate to base risk assessments upon waste criteria. However, the service environment needs to be carefully considered, and more in-depth risk assessments carried out as appropriate. For this reason, developing a product with a specific end-use limits the risk factor. A report by the Environment Agency into the potential risks of using municipal incinerator ash in concrete construction blocks for domestic buildings concluded that there was no significant health risk (E.A, 2002). The use of waste derived aggregate in, for example, concrete represents a two-fold dilution of the original waste, firstly mixed with filler or binder in the aggregate, and again as the aggregate is mixed with fine aggregate, cement and water in concrete. However, the hazardous properties of different wastes needs to be considered.

8.5 Conclusion

Aggregate was produced by blending quarry fines with an incineration ash derived from paper recycling. A specially designed drum pelletiser, which was developed and discussed in Chapter 7, was used to manufacture the aggregate. The effects of increasing the binder content, and accelerated carbonation curing versus natural carbonation were investigated.

The carbonated aggregates were tested according to British Standard against three commercial lightweight aggregates. Carbonated aggregates had comparable or improved sulfate and choride contents. Bulk densities of the aggregates were within lightweight guidelines, but produced concretes on the maximum limit for lightweight classification. Strength and freeze-thaw durability of the aggregate was enhanced by increasing the binder content and as a result of accelerated carbonation curing. This was likely to be the result of pore closure due to calcium carbonate precipitation and reduced water/cement ratio.

Concretes produced from the aggregate attained strengths comparable to or greater than LECA and Aardelite, but considerably weaker than Lytag which is commonly used to produce structural lightweight concrete. Aggregates with a higher binder content produced concretes which attained a higher exposure classification. These concretes could be exposed to either permanently wet or dry conditions. A companion study explored the use of these aggregates as a horticultural substrate on green roofs. The study concluded that these materials would be perfectly suitable as a growing substrate.

Chapter 9 : Discussion and Conclusions

9.1 Discussion

Wastes that are reactive with carbon dioxide can be treated to reduce hazardous properties, and may be used as cement replacements to bind non-reactive wastes together to produce agglomerated products for use as aggregate.

The reactivity of wastes with carbon dioxide is controlled primarily by the calcium content. However, the mineral form in which this calcium is bound affects the total amount of carbon dioxide which the waste will combine with. Compared to Portland cement, cement dusts and paper incineration ashes were the most reactive with CO_2. Biomass and municipal incineration ashes were moderately reactive, clinical incineration ash and coal ashes were unreactive.

Contaminant fixation was not directly related to carbon dioxide reactivity. Instead, behaviour was dependent upon the contaminants present. Carbonation moderated lead and barium leaching, and had negligible effect upon the other contaminants. Sulfates and chlorides were commonly present in hazardous or in stable non-reactive hazardous levels, and were unaffected by carbonation. The mobility of these contaminants has implications for the end-use of an aggregate product, particularly concerning the affects on sulfate and chloride upon concrete. Metal leaching after carbonation was within stable non-reactive limits, facilitating the re-use of products containing these wastes.

Equally, the value of wastes as cement replacements depended not upon the degree of reactivity and instead upon the mineralogy. Wastes containing lime as the prominent reactive phase have theoretically the greatest reactive potential, yet did not necessarily produce the strongest materials. The presence of calcium silicates was apparently a key requisite for strength development. Hydration of these calcium silicates akin the reactions occurring in Portland cement was equally important. However, the exact mechanisms occurring in these mineralogically complex materials could not be fully explored. The use of reactive wastes as cement replacements would need to consider the mineralogy and hence final strength, together with the levels of contaminants present, based upon the specification of the final end-use of the product.

The process of manufacturing carbonated aggregate needs to optimise both the machinery variables and mix formulation. The latter is largely concerned with the grain size distribution, and blending with a fine or coarse grained material may be necessary to achieve the required degree of packing and interparticle friction to induce pelletising and sufficient final strength. Equally, selecting an optimum rotation speed and mixing time had an important influence upon the product. Upon scaling up the process, the conditions devised in the laboratory setup were directly translatable once the equipment had been modified to closely resemble each other.

Producing a pelletised product which was suitably carbonated to have sufficient strength for immediate use was not achieved. The moisture content differential for efficient pelletising and carbonation, prevented the two from being effectively combined. Attempting to overcome this issue by altering the physical properties of the materials including grain size distribution or through the use of chemicals to induce wetting or plasticising of the mixture were not effective. This can be largely attributed to the need for pore saturation to adhere grains together regardless of the actual moisture content of material, or the size of the grains. This was compounded by the issues of compaction of the material and a reduction in surface area as a result of agglomeration. However, chemical rate enhancers to speed the carbonation of saturated materials are effective. The use of the rate enhancers is constrained by the cost of the chemicals, and that the reaction is still not accelerated sufficiently within the timescale of the pelletising process itself. Prolonged exposure by curing in carbon dioxide after forming the pellets was necessary to achieve the extent of carbonation desired. This makes the use of rate enhancers somewhat extraneous.

The strength of the fresh pellets presented an issue for handling and conveying. Saturated pellets had lower strength than when dried. Attaining full strength development was a combination of curing through hydration and carbonation, and drying. This drying also helped to promote carbonation by removing water blocking the pores of the pellets. A method for hardening the pellets needs to take these factors into account. Similarly, conveying wet pellets was a technical challenge, but one which can be overcome by dusting the pellet surface with a lime-rich waste. Since an appreciable amount of the strength of the pellet is concentrated in the crust, dusting also had the added effect of increasing strength.

Premixing of the materials was a key factor for ensuring the quality of the final product. The use of a mixer with sufficient shear to effectively combine the binder with the other components was critical to achieve a product with the required strength. This can be linked to disproportionate variations in the failure strengths of pellets within the same batch. Similarly, a high energy mixer was also needed to evenly distribute the water throughout the powder, to produce a material with an even grain size which would then grow into similar sized pellets. The control over the measurement and consistency over smaller volumes of material which was possible in the laboratory, was less achievable on site. Developing a product with sufficient binder content or a grain size balance which can be pelletised over a broad range of moisture contents will account for variability in the mix occurring at a larger scale.

The choice of wastes for producing the final product were motivated by the low contaminant release, the ease of manufacture and the cementitious properties of the reactive waste. Considering the wider application of the process, some degree of compromise on these characteristics is likely when dealing with wastes. The use of valuable materials such as cement or natural sand may be necessary to achieve the desired properties. Equally, it may be necessary in employ some kind of pretreatment of the wastes to deal with contaminants which are not affected by carbonation. For these reasons, the use of a carbonated aggregate process may be limited to certain wastes, or that the product is restricted to certain low risk end-uses.

Use of the pelletised product in concrete was explored since it is one of the most common uses for aggregate. The resulting concrete was distinctly heavier and not as strong as structural lightweight concrete. Consequently, the aggregate may be better suited to alternative uses such as medium-weight concrete block production, or as growing medium for green roofs. However, adjustment of the mix formulation may allow the creation of a sufficiently lighter product to compete with commercial lightweight aggregates, and command a premium market price. The use of dense materials such as sand contributed to the weight, and increasing the use of lighter materials, such as ashes, would help to achieve this aim.

Wastes are notoriously variable materials, since they do not conform to any specifications. This variability was noted in the reactivity of different batches of the wastes. In turn this has implication if the wastes are being treated to confirm to certain landfill acceptance criteria. More importantly, if these wastes are used as cement replacements, then the product may have highly variable strength and durability, requiring stringent monitoring of incoming raw materials and product quality control.

9.2 Conclusions

This study examined the use of an accelerated carbonation process for the treatment and re-use of industrial wastes as aggregate. A number of objectives were set to achieve this aim.

- Explore the potential for treating wastes with accelerated carbonation to aid waste management and economic disposal.
- Investigate the pelletising method, and optimize the process.
- Utilise accelerated carbonation to produce an aggregate product from these wastes
- Scale up the process and produce aggregate material for testing
- Test the aggregate to regulatory standard, and consider potential end-uses

Wastes from paper making, cement production, and energy generation from coal are increasingly being re-used. However, a proportion remains that is being sent to landfill. Other wastes such as fly ashes from municipal waste incineration are not being utilised, and are set to become an increasing problem as waste management practices change, such as the adoption of incineration of waste opposed to landfilling.

The pH of wastes was often the reason for their classification as hazardous. The levels of leachable metals and salts were generally within stable non-reactive waste limits. Carbonation constitutes a suitable treatment for reducing pH, and for immobilising lead and barium. The reactivity of a material is related to its mineral composition, and not just to elemental composition.

A low shear pelletising process is suitable for producing pellets from waste. Blending wastes together is often necessary to achieve the required grain size distribution and degree of reactivity to bind the material together.

Carbonation is not affected by pelletising conditions including rotation speed and pelletising time to an extent that it has a bearing upon the early strength of the pelletised material. Moisture content is a key variable which controls the efficiency, but is different for pelletising and carbonation. Forming the pellets and then curing in carbon dioxide is necessary to achieve near total carbonation.

The process can be readily scaled up. A simple drum pelletiser is suitable for pelletising the wastes on a larger scale. The pellets are then placed in a large vessel for curing.

Carbonated aggregates produced in the larger process are comparable in strength and freeze-thaw durability to commercial lightweight aggregate. However, bulk density is higher, and may limit the potential end-uses for the aggregate.

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