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From Carbon Dioxide to Building Materials – Improving Process Efficiency

IEA GREENHOUSE GAS R&D PROGRAMME

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ACKNOWLEDGEMENTS AND CITATIONS

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FROM CO_2 TO BUILDING MATERIALS - IMPROVING PROCESS EFFICIENCY

(IEA/CON/20/271)

IEAGHG commissioned a study to investigate how captured CO_2 can be used in building materials. It also explored the processes that are used to capture this CO_2 and includes case studies where these processes are happening. The work has evaluated CO_2 utilisation in the context of cement and concrete production by looking into the effects of carbonation on material utilisation and the design of a potential carbonation plant. The market analysis and market pull of carbonated building products is also covered.

Key Messages

- Accelerated carbonation products have the potential to be used as aggregates, fillers, reactive fillers, and supplementary cementitious materials (SCM).
- Carbonation is a relatively expensive method of CO_2 utilisation unless there is substantial avoided cost associated with raw material disposal.
- There is a degree of discrepancy between theoretical and experimental uptake rates for different materials. The measured CO_2 uptake is significantly lower than an estimation based solely on composition.
- It is important to consider the inherent trade-offs between each potential use – carbonating materials or use as an SCM.
- In many cases, carbonated materials should be preferentially used as a supplementary cementitious material or otherwise blended in to cement where possible.
- Non-Portland cementitious materials are frequently carbonated and can be used as an additive to cement and contribute to strength development in the final product. Note that the total amount of CO_2 present in the cement should generally not be too high as it can reduce the pH of the cement binder and dilute its cementitious properties.
- Natural carbonation processes will occur which will reduce the additionality of accelerated carbonation.
- Carbonation can act as a waste treatment process, stabilising heavy metals.
- The main driver for carbonation processes is the avoidance of landfill costs where applicable.
- Current market prices suggest that the market for carbonated products is limited and will be closely linked to robust CO_2 pricing mechanisms that recognise and value the mitigation service of carbonation.
- Further research is needed both to understand the potentials of more novel carbonated materials to store CO_2, and their production processes, as well as to understand their material properties.
- There is currently insufficient pull from the construction industry for carbonated or low carbon emission produced products.

Background to the Study

Decarbonising the economy through carbon capture, usage and storage (CCUS) relies not only on viable methods to capture carbon dioxide (CO_2) but also efficient usage and/or storage of that CO_2. In some instances, (e.g. where large transport distances are required, or for countries which do not have large geological storage resources), utilising the captured CO_2, or carbon capture and utilisation (CCU), may be the most effective way to decarbonise rather than transporting to a storage site. CCU also provides additional revenue streams and allays any public perception issues associated with underground storage. Cement is one of the world's most used building materials and is responsible for ~5.6% of global CO_2 emissions. Captured CO_2 can be used to produce materials such as concrete, in aggregate production from carbonated waste materials, produce chemicals such as plastics and fertilisers, or produce synthetic low carbon fuels that can replace fossil fuels to decarbonise transport.

Potential beneficiaries of this study include nation states, especially those without storage resource, and potentially the CCUS industry at large, particularly companies involved in the capture of CO_2 if the research can lead to effective techniques for utilising captured carbon at a competitive price. The construction industry stands to gain credibility if it can use low carbon emission materials especially if they include CO_2 capture.

Scope of Work

The aim of this study was to quantify the CO_2 emissions savings from increasing the process efficiency of carbonation during cement / concrete aggregate production and from the concrete curing process assessed in this study. This is particularly valuable as using CO_2 emissions to create a carbonate/aggregate could help to decarbonise cement production. About 60% of the CO_2 process emissions of cement production are process inherent and thus difficult to avoid. Storing captured CO_2 in building materials is also a more permanent way than is the case for many other CCU pathways, such as fuels or chemicals. Cement has an array of uses and a low-carbon cement market would provide a significant opportunity for the CCUS community. One of the challenges facing the use of any new innovative building material is the necessity of meeting standards that are acceptable to the construction industry. Such materials also need to be produced at reasonable cost, despite their environmental benefits.

Specifically, the study looked into the cement industry, carbonation, material feedstocks for carbonation, and the availability of carbonatable materials and CO_2. The effects of carbonation on material utilisation in building products, the design of a carbonation plant, market analysis, legislation, standards and market pull were also investigated.

Findings of the Study

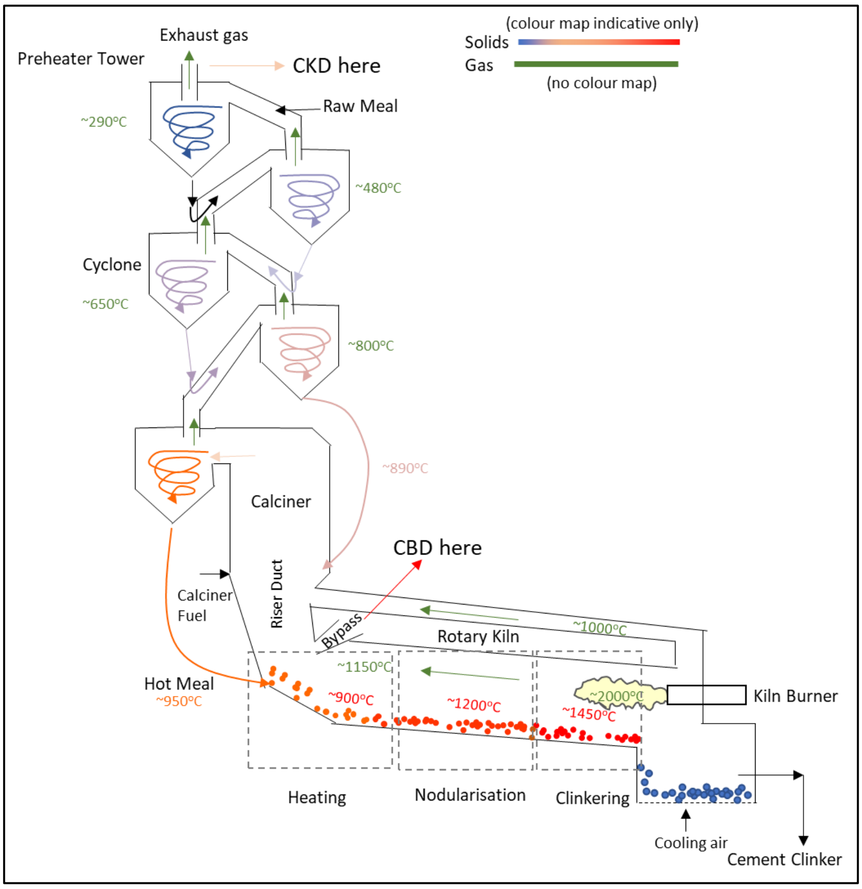

Figure 1. Detailed diagram to show the cement production process, including approximate temperatures (blue to red scale from cold to hot). *(IEAGHG, report number 2022-04, figure 4-3 pg 8)*

For information and reference, the above diagram (Figure 1) illustrates the cement production process.

Carbonation

There are a variety of reactions that can be used to carbonate different types of materials including cementitious materials and this work investigated those processes along with other methods to introduce CO_2 into the system other than as a gaseous reactant. The fundamental reactions can occur over a single stage ('direct carbonation') or multiple stages ('indirect carbonation'). Direct carbonation, or 'gas-solid', is one of the most important carbonation processes for the application of carbonation of a waste material with flue gas, direct contact between a gaseous CO_2-containing stream and the carbonatable material. The constituents of cement binders (e.g. concrete products) can be directly carbonated. Direct carbonation can also take place in the aqueous phase, where carbonatable solids are in contact with water or in a slurry, and the solid-liquid mixture is then contacted with CO_2. Indirect carbonation is also aqueous and similar to the direct carbonation reactions, but the process is conducted over multiple stages and the use of additional substances (for example potassium hydroxide) during the first stage means subsequent removal for economic recovery. Aqueous carbonate solutions can be used as a replacement for water in the 'activation' of solid cementitious materials, however this technology is currently niche and not widely applied in practical construction. Indirect carbonation is outside the scope of this study. Cementitious materials are also being naturally carbonated due to the concentration of CO_2 in the atmosphere, which is relevant for CO_2 uptake in building materials. In practice, carbonation only occurs on the external surfaces of concrete and internally where cracks are present to expose inner areas. Natural carbonation can therefore become a durability issue if there is significant cracking or with the presence of additional aggressive species. More highly porous cement applications like mortars carbonate at a faster rate than less porous (e.g. self-compacting concrete) and those not exposed to atmospheric CO_2 such as foundations.

Carbonation can also take place during curing by the addition of fine limestone as a reactive filler and / or atmospheric CO_2. Some companies are exploring the potential of significant carbonation by the injection of CO_2 into the wet paste before setting or by curing concrete within a sealed chamber containing CO_2. Adding CO_2 into a ready-mix concrete during the batching process acts as a strength accelerator, promoting the formation or carbonated hydrate phases, and enhancing the early mechanical properties of the concrete which reduces the amount of fine limestone needed as a reactive filler. This technology can be expected to lead to consequent modest reductions in CO_2 (~5%). The company pioneering this technology (Carbon Cure) estimate that this leads to a reduction of CO_2 emissions of ~47kg /tonne depending on composition. Another approach is to modify the underlying chemistry of the cement, allowing significantly higher uptake of CO_2. One US-based company has developed a carbonatable calcium silicate clinker-based cement, based on synthetic calcium silicate clinker, and claim their composition allows CO_2 uptake of ~250-300 kg /tonne of clinker during curing. There is also current work to develop a technology to form carbonate precast PC concrete blocks with denser microstructures compared to common PC concrete blocks, resulting in improved mechanical properties and lower porosity.

Material Feedstocks for Carbonation

The study investigates materials that are suitable for carbonation and use as building materials and are categorised as being either Portland-based cementitious materials (PCMs) or non-Portland cementitious materials (NPCMs).

During the production of Portland cement, two major dusts are produced – cement kiln dusts (CKDs) and cement bypass dusts (CBDs), see Figure 1. It is common practice to recycle as much of the dust as possible within the cement production process. This is because significant energy has been used to calcine the dusts, and those that are mainly CaO and $CaCO_3$ require additional limestone to replace them if they leave the process. This internal recycle limits somewhat the potential for a subsequent accelerated carbonation process to produce aggregate to be applied. Concrete slurry waste (CSW) and recycled concrete aggregates (RCAs) are other waste streams that offer opportunities for carbonation. CSW represents an underutilised material with some potential for carbonation to produce building materials with reduced net CO_2 emissions. RCAs show promise as a carbonated building material, particularly since these materials are already being incorporated into concrete.

NPCMs include fly ash (FA), steelmaking slags and other wastes / residues which can act as supplementary cementitious materials (SCMs). Fly ash offers excellent potential for carbonation, as well as being established SCMs for integration within cements, but should only be considered for carbonation where their incorporation into cement is not possible (e.g. due to excessive contamination). They can be used as SCMs as this directly leads to a reduction in clinker ratio, often improving material properties, and thus lowering CO_2 emissions. Steelmaking slags offer excellent potential for carbonation due to their high quantities of CaO and MgO and are an unavoidable by-product of the process. Consequently, they have a more reliable long-term availability compared to fly ash.

The viability of large-scale carbonation processes fundamentally relies on the cost, availability, and geographic location of the carbonatable materials and CO_2. The ideal feedstock is a material with low cost which is generated in close proximity to a concentrated source of CO_2. In many cases waste streams are ideal feedstocks since they can be acquired for minimal cost and are generated in close proximity to point source emitters with access to flue gases containing high concentrations of CO_2. Transporting feedstock materials can incur financial / energetic penalties; research indicates that transport costs would be ~£0.12 /tonne.

The maximum CO_2 uptake capacity that a material can theoretically capture through carbonation was compared for the various materials reviewed including fly ashes, steelmaking slags and other industrial wastes (detailed in tables 6-2, 6-3 and 6-4 in the study). These comparisons showed that there is a general trend that the experimental uptake (tested usually at laboratory scale) was significantly less that the theoretically predicted quantities (as show in Figure 2). This difference is partially explainable by carbonation reactivity issues such as low porosity, large particle sizes or poor dissolution kinetics meaning that the solid embedded CaO sources are not accessible to form carbonate materials. To reflect this contrast, the later modelling done in this report used a relatively low average uptake of CO_2 (50% of the maximum theoretical uptake) into the waste materials.

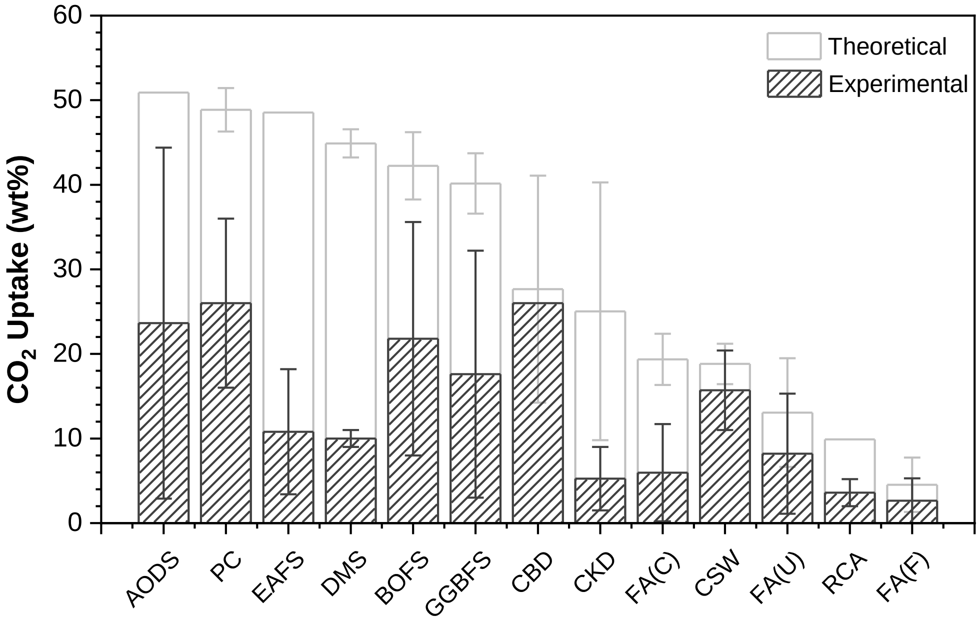

Figure 2. Graph to show the comparison of theoretical and experimental CO_2 uptake capacities. *(IEAGHG, report number 2022-04, figure 6-2 pg 10)*

Effects of Carbonation on Material Utilisation in Building Products

PCMs:

CKD, CBD, and CSW can be used as cement kiln feedstock or as reactive materials in cementitious systems. The study recommends that they are used as cement kiln feedstock where possible, or if not, to use them as SCMs or reactive fillers. The remaining material, which will be small in comparison to the total, can be carbonated. By managing exposure of CKD, CBD, and CSW to carbonation, it is expected that the carbonated output materials will have some potential to stabilise contaminants that may be present in industrial flue gases, and that carbonation can to some degree be considered as a waste treatment process. RCA can be carbonated prior to incorporation into mortar and concrete but using recycled aggregates rather than primary aggregates in structural concrete leads to increased water demand and reduced physical properties so their use in concrete does not necessarily lead to a reduction in greenhouse gas emissions.

NPCMs:

The carbonation process can stabilise trace elements in the matrix of the material. Poorly reactive NPCMs, and NPCMs with relatively high levels of contamination, should be targeted for carbonation. Low reactivity materials, including some types of FA and slag, behave as fillers and are suitable for carbonation. The process results in the formation of calcite and Al-Si gels in addition to inert Al-Si phases. If these gels gain reactivity they may be suitable for use as reactive fillers.

Design of a Carbonation Plant

The study looked into the design of a carbonation plant suitable for processing industrial wastes and simulated the plant processes. The results provided evidence of the technical viability for carbonation processes to be installed at cement plants according to this design scenario, mostly due to the free availability of both carbonatable solids and suitably concentrated CO_2. Furthermore, the relative simplicity of the carbonation process in this design means minimal additional inputs are required that do not impact the operation of the host cement plant. However, although technically feasible, the studied carbonation process cannot achieve meaningful reductions in net CO_2 emissions. The capacity of the carbonation process only represents a nominal fraction of the flue generated by the host cement plant. Even with reasonable CBD conversions, carbonation only results in the capture of ~0.3-0.9% of the direct CO_2 emissions from the cement plant. The value of carbonation lies primarily in its abilities for remediation of hazardous wastes that otherwise incur gate fees for disposal / landfilling.

Costing of the designed plant brought up changes in design that could improve the viability of such a carbonation plant, namely minimising the purchase cost of the rotary reactor. It must be noted that there were negligible costs for raw materials (assuming CBD and flue gas was sourced from the host cement plant without costs) and minimal costs for utilities like water and electricity (which account for ~0.2% and ~5% respectively of the calculated annual production cost).

Market Analysis

The market analysis undertaken was based on the carbonation plant as referred to above, which adopts CBD as the candidate feedstock for the carbonation process. This analysis therefore assumed that other materials can be similarly carbonated.

The relatively high CO_2 uptake potential of CBD, i.e. ~ 20.5 %wt, means that a market price of €64 per tonne (€/t) is sufficient to offset its carbonation cost. However, since the average selling price of clinker is around 75 €/t, carbonated CBD would need to be sold at a 140 €/t to generate the same revenues, making CBD the least profitable material for carbonation. Assuming that fly ashes (FAs) can be recovered from existing stockpiles, a benchmark selling price of 67 €/t is associated with their use as carbonated materials. This is because, stockpiled fly ashes are unlikely to be used as SCMs due to their lower reactivity, hence cement producers would necessarily procure FAs from municipal solid waste

(MSW) or coal combustion plants, at a price of 27 €/t. Steelmaking slags are relatively cheap feedstocks, and benefit from relatively high CO_2 uptakes. Hence, when sold at 80 €/t, carbonated basic oxygen furnaces (BOF) slags are more profitable than as aggregates in road construction. Looking at the trend of CSW, it is clear that its use as carbonated material represents the most profitable route, due to the combined avoidance of landfill and carbon taxes.

Combining the results obtained from marginal abatement cost curves with the market analysis presented above, two important conclusions can be derived. Firstly, FAs and ground granulated blast furnace (GGBF) slag are not only more economically valuable as SCMs but they also offer little CO_2 removal services, as they are either scarce (GGBF) or have low CO_2 uptake (FA class F). Secondly, whilst materials generated through the production of cement-based products such as CBD are abundant, and could represent excellent materials for carbonation, the market price required for the use of CBD as carbonated building product is considerable, i.e. 140 €/t, when compared to its conventional use for clinker production. Conversely, significant economic and mitigation opportunities could derive from the carbonation of CSW, especially in countries that have adopted stringent waste disposal policies, such as the UK. These facts suggest that the value of carbonation relies on its waste remediation potential rather than on its CO_2 mitigation benefits. In particular, costs for CO_2 mitigation of 300 – 600 €/t should be considered relative to the cost of carbon capture and storage, where costs have been estimated to range between around \$40 and \$110 (€33 – €90) for CO_2 capture from cement, per tonne of CO_2 avoided. It is also important to note that not all of the CO_2 in the flue gas will be captured, and that emitters will still need to pay the relevant carbon taxes for any CO_2 not captured, unless the plant is fitted with CCS and the exhaust from the carbonation process is rerouted to a CCS system.

Legislation, Standards and Market Pull

Carbonated aggregates (and the materials that are produced from them) are sold into the same markets as other aggregate materials, and the products produced from them will be specified under the same building codes.

End of waste is an important certification for carbonated materials. The waste has to be converted into a distinct and marketable product, which can be used in exactly the same way as a non-waste virgin material. The processed substance must be able to be used with environmental effects that are no worse than those of a comparative virgin material. Building products utilising carbonated aggregates can readily be included within current ASTM / BS / EN standards and will be sold on a ‘like for like’ basis.

Governments can play an important role in developing and commercialising new technologies and, in particular, those that offer significant benefits to society, such as reduction of emissions. The use of government incentives to preferentially purchase low-carbon products can lead to the development of a market for such products and ultimately assist in reducing incumbent advantage. Government can potentially drive adoption of new materials through standards based on embodied CO_2 providing products meet materials standards.

In 2020 the EU developed a standard / taxonomy for “green” bonds which are being rolled out globally. Draft legislation is currently passing through the EU parliament. These bonds will fund projects which lead to a substantial reduction in CO_2. Currently the carbonation of dusts and or other materials would not qualify but addition of such a process to the regulations would not be an insurmountable task. EU committees are looking at developing criteria which could qualify carbonation such as circular economy by reuse of dusts, recycled aggregates etc. With the international trade in steel slags, and potential for trade of cementitious materials around the world, it is essential to ensure that materials which have been produced with a significantly lower CO_2 footprint do not face unfair external competition from those that are produced without such requirements. Both the EU and the US are considering the importance of policy incentives to enable Net Zero transition which could cover and include use of carbonatable materials.

Conclusions

The report, initially aiming at decarbonising cement production, investigated the carbonation of different materials and their potential for use as media for accelerated carbonation. It was found in many cases (e.g. steel slags and dusts produced during cement manufacture) that these materials should preferentially be used as a supplementary cementitious material or otherwise blended in to cement where this is possible.

Accelerated carbonation products are not widely used but have the potential to be used as aggregates, fillers, reactive fillers, and supplementary cementitious materials, depending on the material carbonated. In some cases, carbonation can significantly improve material properties but has negligible changes or reductions for other cases, therefore there is an active trade-off in accelerated carbonation of materials between use directly for CO_2 storage versus other beneficial uses, which includes substitution of high-CO_2 Portland cement clinker. Carbonation can act as a waste treatment process, stabilising heavy metals, which brings significant and genuine benefits to the valorisation of more unconventional and toxic or contaminated materials, like air pollution control residues. Further research is needed both to understand the potentials of more novel carbonated materials to store CO_2 and their production processes, as well as to understand their material properties.

The main driver for carbonation processes is the avoidance of landfill costs where they are applicable, and unless there is a substantial avoided cost associated with raw material disposal, carbonation is a relatively expensive method of CO_2 utilisation, costing around 300 – 600 €/tonne of CO_2 sequestered. Whilst the market size of aggregates is considerable in Europe, current market prices suggest that the market for carbonated products is limited and will be closely linked to robust CO_2 pricing mechanisms that recognise and value the mitigation service of carbonation. It is also important to note that natural carbonation processes will also occur, over a time span of decades, reducing the additionality of accelerated carbonation.

The study conducted marginal abatement cost curves which showed that around 8.6 Mt of CO_2 could be utilised and stored in carbonated products such as concrete slurry waste, cement bypass dusts and steelmaking slags in Europe at a mitigation cost of approximately 430 €/tonne of CO_2. A higher level of mitigation could be possible but with higher abatement costs. Findings suggest that the value of carbonation relies on the waste remediation potential rather than its mitigation benefits for CO_2.

There is currently insufficient market pull from the construction industry for carbonated or low carbon emission produced products and changing this may require product demonstrations, carbon standards, and increased carbon taxes. Development of the industry will require financing at a large scale, within which green bonds may help.

It will be increasingly important to ensure that cross-border flows of materials such as both products of accelerated carbonation, supplementary cementitious materials such as blast furnace slag and cement, are treated appropriately in terms of carbon border adjustments.

Expert Review

The study was reviewed by four external experts from the industry and research sectors. The experts felt that this analysis was useful, interesting and produced a well-rounded report. Comments received noted that the document excelled in two areas: it is a realistic assessment of the techno-economic viability of various carbonation routes; and provides a design of a plant for carbonation of waste. This has provided a level of rigour to the analysis.

Only minor suggestions were made to edit the report. Greater clarity was needed in some sections, more on the area of legislation and standards, addition of a knowledge gaps section due to the contractors' extensive expertise in this area and more content on the conclusions chapter. All comments were diligently acted upon where possible as per the remit of the work and more was input into those aforementioned sections.

Recommendations

Several important knowledge gaps were recognised in the study which leads to recommendations for further work:

- The long-term performance of carbonated materials (novel aggregates, cements, binders, concretes, etc.) during service is a key area requiring improved understanding.
- Continue careful monitoring and assessment of the long-term effects of CO_2 curing in accelerated carbonation processes moving all the way through to final demolition and disposal from a technical perspective.
- Complementary life cycle environmental assessments of carbonation processes and products are also needed, to provide the quantitative evidence base to evaluate their environmental performance.
- Continued progress in accelerated carbonation to examine the trade-offs between the carbonation extent of materials and their properties with respect to the products produced, and their environmental performance.
- Further analysis of accelerated carbonation is needed. Specifically, improvements to the gas/solid mixing in a carbonator may improve the differences in theoretical versus experimental CO_2 uptake capacities.
- More research is needed to carefully investigate the integration of plants producing multiple outputs.
- The continued production and verification of independent technology assessments examining likely prices for new cement technologies, CO_2 uptakes, and potential markets, will be an important ongoing area of research.
- It would be worthy of future investigation to consider whether the potential use of CO_2 for insulation materials could be more economical.

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This report was prepared by

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1.0 Contents

2.0 Glossary

ACT	Accelerated Carbonation Technology
AFm	Alumino-Ferrite-mono cement hydrate phase
AFt	Alumino-Ferrite-tri cement hydrate phase
AODS	Argon Oxygen Decarburization Slag
APC	Air Pollutant Control
ASTM	American Society for Testing and Materials
BAT	Best Available Technology
BF	Blast Furnace
BFG	Blast Furnace Gas
BOF	Basic Oxygen Furnace
BOFS	Basic Oxygen Furnace Slag
C-(A-)S-H	Calcium aluminate silicate hydrates. Components of set cement.
C_3S, C_2S, C_3A, C_4AF	Different phases in Portland cement clinker
CAPEX	Capital Cost
CBD	Cement Bypass Dust
CBA	Carbon Border Adjustment
CBI	Climate Bonds Initiative
CCS	Carbon Capture and Storage
CEM I / II	Two standardised Portland cement types
CKD	Cement Kiln Dust
C-S-H	Calcium Silicate Hydrate. The key binding phase in hydrated cement.
CSW	Concrete Slurry Waste
DMS	Demetalisation Slag
DPC	Direct Production Cost
D_R	Reactor Diameter
DSC	Differential Scanning Calorimeter
DSR	Direct Separation Reactor
EAFS	Electric Arc Furnace Slag
ECRA	European Cement Research Academy
FA	Fly Ash
FCC	Fixed Capital Cost

F_m	Material Factor for Costing
FTIR	Fourier Transform Infra-Red
GATT	General Agreement on Trades and Tariffs
GGBFS	Ground Granulated Blast Furnace Slag
LC	Labour Cost
LEILAC	Low Emission Intensity Lime and Cement
LOI	Loss on Ignition
L_R	Reactor Length
MC	Maintenance Cost
MS	Mass Spectrometer
M-S-H	Magnesium Silicate Hydrate
MSW	Municipal Solid Waste
Mt	Million Tonnes
NPCM	Non Portland Cementitious Material
n_R	Rotational Speed
OPC / PC	Ordinary Portland Cement / Portland Cement
OPEX	Operating Cost
PCC	Total Physical Plant Cost
RCA	Recycled Concrete Aggregates
RDF	Refuse Derived Fuel
SCM	Supplementary Cementitious Material
SSE	Scottish and Southern Electricity
SSP	Shared Socioeconomic Pathway
t_G	Gas Residence Time
TGA	Thermogravimetric Analyser
TPC	Total Purchase Cost
UCLA	University of California, Los Angeles
u_G	Superficial Velocity of Gas
VOC	Variable Operating Cost
V_S	Volumetric Feed Rate
WCC	Working Capital Cost
β_R	Reactor Angle of Inclination
θ_S	Angle of Repose of Solids

3.0 Executive Summary

Researchers from Imperial College were commissioned to investigate the potential for emissions savings from increasing the process efficiency of carbonation processes during building product production. In certain circumstances (e.g. where large transport distances are required, or where countries do not have geological storage available) it has been proposed to utilise captured CO_2. Utilisation in building products would also alleviate issues relating to public perception of CO_2 storage underground. (IEAGHG, 2021).

The aim of the study was to quantify CO_2 emissions savings from increasing the process efficiency of carbonation during cement / concrete aggregate production and from the following concrete curing process. We consider applications to the cement production process, which accounts for around 7 % of global anthropogenic CO_2 emissions (International Energy Agency and Cement Sustainability Inititative, 2018). Ordinary Portland Cement (the vast majority of cement produced globally) is a material which is produced from a mixture of calcium silicates, which after the addition of aggregates (and hydration) sets to form the hard product which is ubiquitous in modern society. The focus in terms of products has been the production of aggregates, since these are the basic accelerated carbonation product which is produced, and that can then be used in other products, such as concrete blocks. During initial discussions it was decided to bring in to the scope of the project the production and use of supplementary cementitious materials (SCMs). These allow replacement of cement clinker. The distinction is important since a number of materials can be *either* carbonated, *or* used as a SCM, and it is very important to consider the inherent trade-offs between each potential use. It is important to consider that slags and ashes are internationally traded, and can be carbonated or used in different jurisdictions, leading to interesting questions of who should pay / be responsible for CO_2 emissions associated with their subsequent use, and production. This might, for example, be an area where border adjustments based on CO_2 emissions might become increasingly important.

Figure 4-3 (for ease of location, figures are numbered as in the report) shows the cement production process. A number of dusts are produced in addition to the cement clinker product, which is the material that holds cement together and gives concrete its strength. Dusts are produced in two main locations. Firstly, dusts from the exhaust from the preheater tower and from the cement clinker cooler are collectively referred to as Cement Kiln Dust, CKD. Dust from the bypass duct, which is produced to reduce the internal recycle of a number of problematic species, is referred to as Cement Bypass Dust, CBD. These two materials are examples of Portland Cement-based materials, which act similarly to cement clinker and can be used in small part to replace clinker. The dusts are within this report assessed for their potential for carbonation, to reduce the overall emissions of CO_2 from the process. We also discuss potentially more economically and environmentally profitable uses. In general it is preferable to recycle the dusts within the cement works, on CO_2 emission, energy efficiency and cost grounds, where possible. Of course, the balance between different potential uses may change as e.g. the price of emission of CO_2 increases, and this has been assessed in this study.

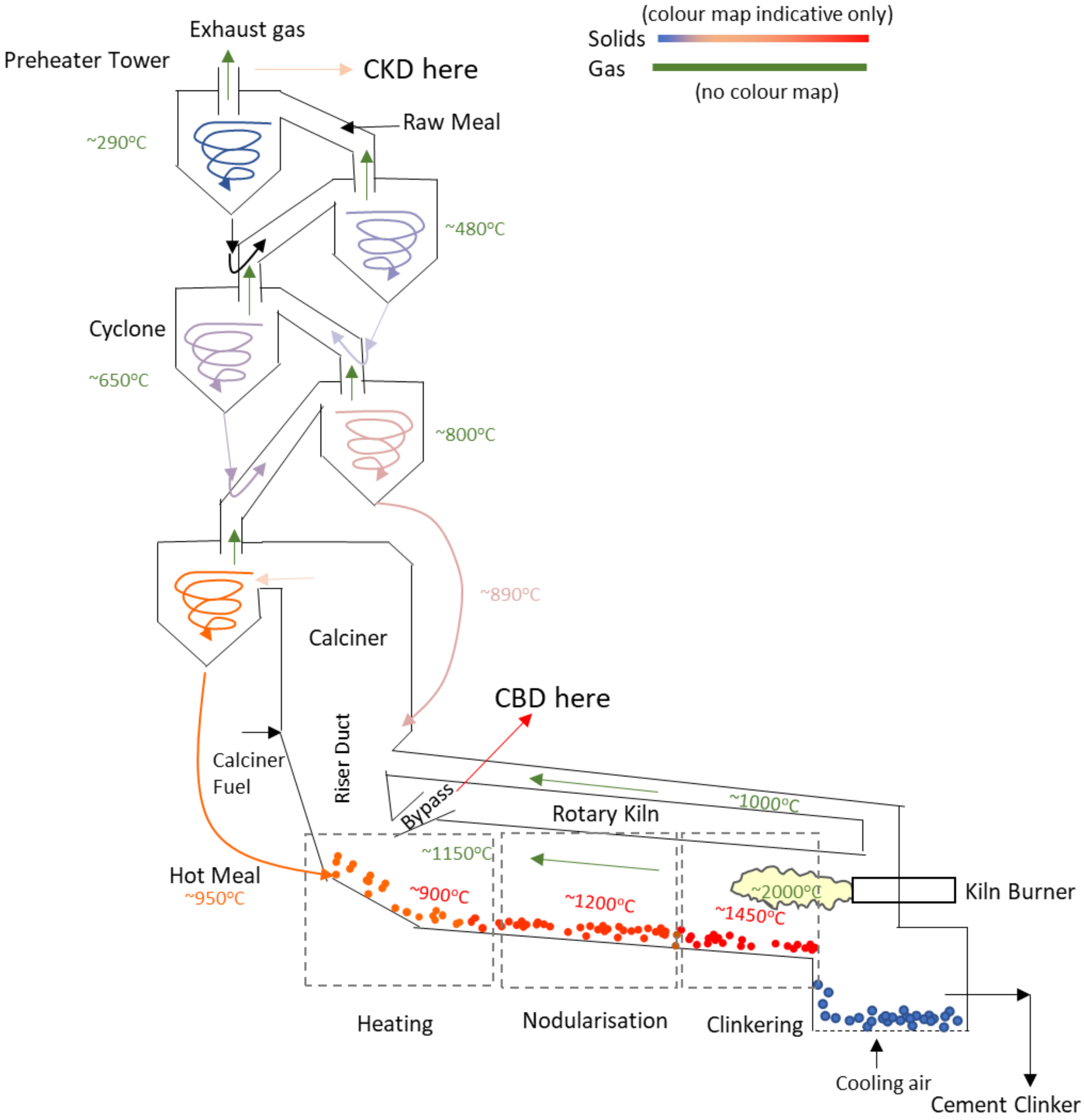

Figure 4-3. Detailed diagram of cement production process, including approximate temperatures (blue to red scale from cold to hot). Data from (Mut, 2014).

After discussing the cement production process, including the production of carbonatable wastes during cement production, the report discusses different carbonation processes and mechanisms. Next, a survey of different carbonatable materials is conducted, and the extent to which they can be carbonated is assessed based on their compositions and a survey of experimental work which has been done in the field. Table 4-2 shows the variety of non-Portland Cementitious Materials (NPCMs) discussed. These are frequently materials that are carbonatable, can be used as an additive to cement, and that contribute to the development of strength in the final cement product, e.g. a concrete structure. It is however important to note that the total amount of CO_2 present in the cement (from all sources, and including CO_2 that is of mineralogical sources, commonly fine limestone) should generally not be too high. This is because it can both reduce the pH of the cement binder, increasing susceptibility of corrosion of steel reinforcement, and dilute its cementitious properties, reducing strength.

This does not preclude the use of carbonated residues as aggregates in concrete, since the particle sizes of aggregate materials are sufficiently high (which leads to low reaction rates) and aggregates are suitably unreactive in general, that they do not significantly affect the properties of the cement binder "gluing" them together.

Table 4-2 Overview of the main NPCMs (actual or potential application). Adapted from (Snellings, 2016).

Material	Chemistry	In Use	General Comments	Reference
Ca-based				
Limestone	$CaCO_3$	Yes	Natural 5% reactive in hydrated PC >5% reactive when added together with reactive Si-Al sources	(Snellings, 2016)
Si-Al-based (Pozzolanic SCMs)				
Fly Ashes (FA)				
FA (Class C)	Si-Al-Ca	Yes	Fewer coal-fired power plants in the future	(Snellings, 2016) (MCCARTHY, et al., 2017)
FA (Class F)	Si-Al	Yes	Fewer coal-fired power plants in the future	(Snellings, 2016) (MCCARTHY, et al., 2017)
Natural pozzolans (*e.g.* volcanic ash)	Si-Al	Yes	Natural, large variety	(Snellings, 2016)
MSWI bottom ashes	Si-Al-Ca	No	Expansive and corrosive components, contamination issues	(Snellings, 2016)
Si-based				
Silica fume	Si	Yes	Expensive, used in high performance concrete	(Snellings, 2016)
Biomass ash	Si	No	Competition with soils amendments	(Snellings, 2016)
Slags				
Blast furnace slag	Ca-Si-Al	Yes	Nearly fully exploited	(Snellings, 2016)
Steel slag	Ca-Si-Fe	No	Hard to grind, variable composition	(Snellings, 2016)
Copper slag	Fe-Si	No	Heavy metal, low reactivity, research needed	(Snellings, 2016)
Other slags	Fe-(Si)-(Ca)	No	Heavy metal, low reactivity, research needed	(Snellings, 2016)
Bauxite residue	Fe-Al-Si	No	Coloured, low reactivity (needs to be processed to turn into a SCM), high alkali content	(Snellings, 2016)
Waste glass	Si-Na-Ca	No	High alkali content, not usually used as a SCM	(Snellings, 2016)
Calcined clay	Si-Al	Yes	Natural, extremely large availability, can have high reactivity	(Snellings, 2016)

It is found that over a wide variety of materials it is reasonable to assume that they achieve around 50 % of the theoretical maximum carbonation within around one hour, when exposed to flue gas including around 20 % CO_2.

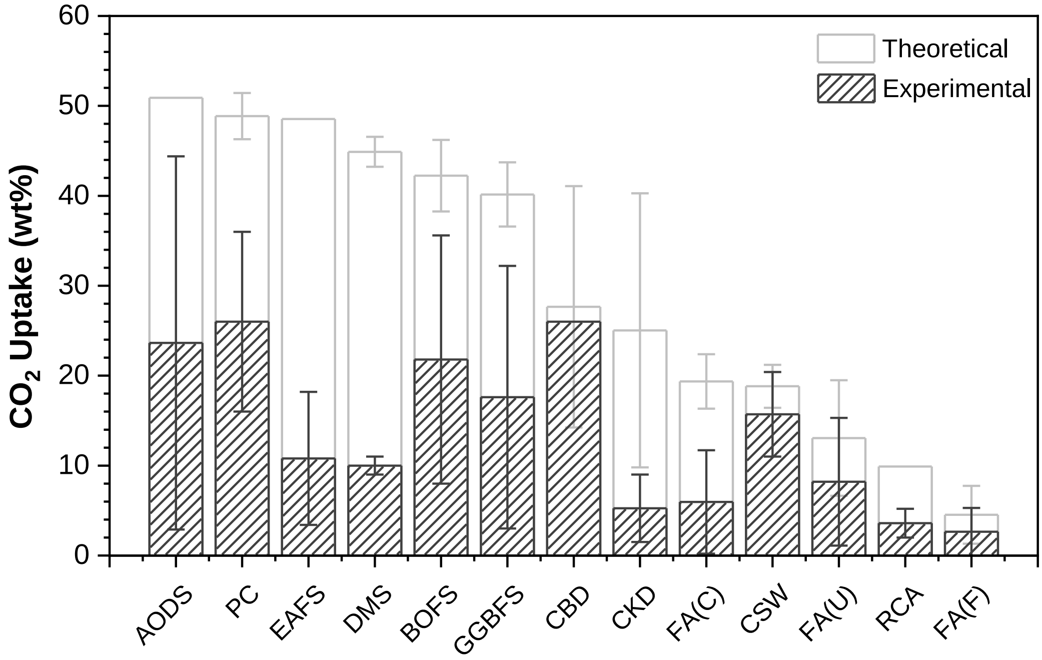

Figure 6-2 Comparison of theoretical and experimental CO_2 uptake capacities. Theoretical uptake calculated as part of this study, whereas experimental uptake was taken from literature. Number of sources used per material varied between n = 1-5. Materials were Argon Oxygen Decarburization Slag (AODS), Portland Cement (PC), Electric Arc Furnace Slag (EAFS), Demetalisation Slag (DMS), Basic Oxygen Furnace Slag (BOFS), Blast Furnace Slag (GGBFS), Cement Bypass Dust (CBD), Cement Kiln Dust (CKD), Fly Ash (FA) (various types), Concrete Slurry Waste (CSW), Recycled Concrete Aggregates (RCA).

Figure 6-2 shows the theoretical CO_2 uptake for a variety of carbonatable materials, based on their composition of CaO, MgO, and some other compounds, compared to the experimentally measured CO_2 uptake from a variety of literature sources. It is clear that the measured CO_2 uptake is significantly lower than an estimation based solely on composition – further work to assess the effects of e.g. particle morphology may assist in elucidating the reasons. It should be acknowledged here that as well as the accelerated carbonation processes examined here, there is a significant uptake of CO_2 by concrete, over a decadal lifetime. It is possible to enhance the rate of this carbonation by a number of methods other than accelerated carbonation, such as crushing and regrinding. It is also possible to enhance the carbonation of cement-based materials by, for example, curing them in a high CO_2 atmosphere.

A reactor to effect the carbonation reaction is designed and costed, and the production costs and value added for a variety of carbonated aggregate materials are assessed. As an example, and depending upon the carbonation extent, the cost of aggregates from the process was to range between £71.5 to £74.2/tonne of carbonated CBD. Doubling the utilization of Refused derived fuel (RDF) would lead to a 30% lower production costs, i.e. between £49.2 to £52/tonne of carbonated CBD, thanks to more CBD being available for carbonation. The model developed was generic and allowed consideration of the costs of production of any of the other materials shown in Figure 6-2. Following the cost analysis, marginal abatement cost curves of different carbonated materials are presented, based on the availability of various carbonatable feedstocks across the UK and Europe.

Figure 10-4 shows that around 8.6 $MtCO_2$ per year could be sequestered in carbonated products in Europe at a mitigation cost of around 430 eur/$ton_{CO2.}$ Adopting feedstock with marginal sequestration potentials such as FAs class C and GGBFs would lead to cost of up to 750 eur/$tonnes_{CO2.}$ In addition, whilst carbonated CBD shows significant mitigation potential, under current cement prices, i.e. ~ 75 eur/tonne, its use for clinker production represent the most profitable option for cement producers. Conversely, the carbonation of waste cementitious materials, i.e. the bottom ashes from MSW (municipal solid waste), is financially viable in the UK and European markets, as this would allow the avoidance of expensive landfill duties. Of course, there is uncertainty around the actual costs, especially considering the effect of project scale-up. In our discussions with industry, we found that where carbonated products could be used on a like-for-like basis (and were within building codes) there were no issues with product acceptance. However, there was also little desire to pay a significant price premium for such materials, currently.

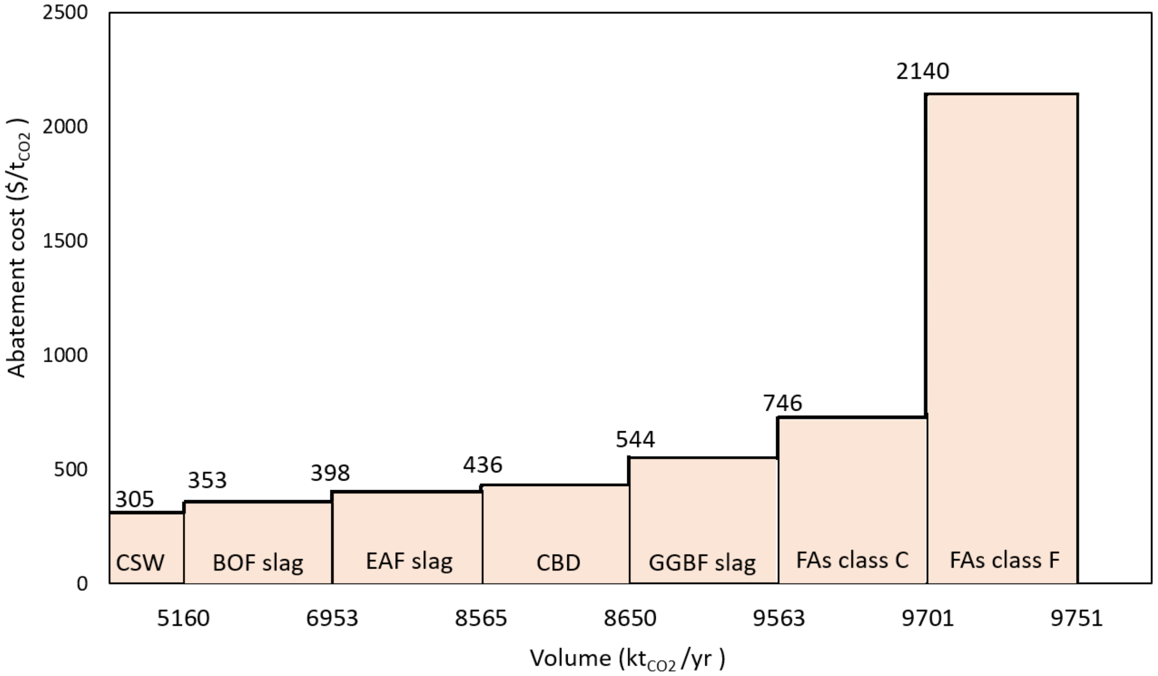

Figure 10-4 Marginal Abatement Cost (MACC) for the production of accelerated carbonated products in EU

It is important to consider that costs for CO_2 mitigation of 300 + euros per tonne compare relatively poorly with $40 and $110 (33 – 90 Euros) for CO_2 capture from cement (Leeson, et al., 2017), per tonne of CO_2 avoided. Where a plant is able to be on a CCS network, this will likely be the preferred option.

3.1 Companies Currently Working in Cement and Concrete Decarbonisation.

There are already some companies working in the field of carbonation of waste materials, and also the use of CO_2 during the curing of cement, which are quite different applications. Within the field of cement production, there are a number of potential applications. Most cement is used to produce ready-mixed concrete - around 48 % in total in the EU (Favier, et al., 2018), and 70 – 75 % in the USA (Curry, 2020). Other applications include Pre-cast concrete (28 % in the EU, split evenly between reinforced and non reinforced applications, 10 % in total in the USA), with the remainder being used for mortars, plasters and other applications. There are undoubtedly other companies working in the field and this should not be taken to be a fully comprehensive review. It is also important to note that the costs etc of products for sale (particularly at significant scale) by the companies below are generally commercially confidential – it is challenging to determine profitability etc, which is one reason that we have conducted an independent analysis in sections 9.0 and 10.0 for the production of aggregates.

O.C.O. Technology is a follow-on company operating under license utilising an original technology developed by the University of Greenwich and initially commercialised by Carbon8 Systems. It has three factories in the UK producing carbonated aggregate materials, mainly from air pollution control residues; these have so far been used in the equivalent of 21 million building blocks. It has recently announced partnerships with companies around the world, including Mitsubishi. Its plants in Avonmouth, Leeds and Suffolk now produce more than 450,000 tonnes of “carbon negative” aggregate a year, though the actual amount of CO_2 locked away will be a small fraction of this (perhaps 10 – 20 wt % of CO_2 will be taken up by the air-pollution control residues). Clients include Grundon Waste management, Viridor and the Ferrybridge multifuel (FM2) power station (SSE). It has now moved into biomass APCr, signing a contract recently with Tilbury Green Power. The carbonation technology that they use is to contact a variety of waste materials with CO_2, producing pellets of carbonated materials (OCO Technologies, 2021) which can then be used as aggregates and to produce building blocks.

Carbon8 Systems is a separate company which has developed accelerated carbonation technology (ACT), and has recently embodied this with the CO_2ntainer (a process for carbonation of materials that is contained within a shipping container) and which has been deployed at a number of locations around the world, including the UK, France, and Canada.

Blue Planet (Blue Planet, n.d.) have developed a process for the production of aggregates via a dissolution / reprecipitation process involving the use of waste / end of life concrete as a source of Ca ions, which are then reacted with CO_2 to produce $CaCO_3$ aggregate material. Their aggregates were included in a small section of 2016 construction work at San Francisco airport.

Carbon Cure. In the field of CO_2 utilisation during concrete curing, the US company Carbon Cure is the leading technology provider. This technology involves the injection of relatively small quantities of CO_2 during delivery of ready-mix concrete (Carboncure, 2017), though was originally developed for the pre-cast market.

Mineral Carbonation International are an Australian company, who are investigating the use of CO_2 to produce aggregate products from alkaline mining waste.

CO_2Concrete is another US-based start-up (a spin-out from UCLA) and is currently developing technology to produce precast blocks with a high degree of initial carbonation.

Solidia has developed a carbonatable calcium silicate clinker-based cement, which uses CO_2 rather than H_2O during the curing process, and so takes up a very large amount of CO_2 per unit mass. It is important to note that this technology does not produce Ordinary Portland Cement, which has been for many years the greatest proportion of cement used, and so may be limited in its range of applications by inertia and a certain degree of (justified) risk aversion in the construction industry. Its current focus is on pre-cast products, cured in a CO_2 chamber (for example, paving) and for which construction industry risk aversion is less of an issue, though as noted above, the non-reinforced precast market is much smaller than the ready-mixed market.

Carbicrete (Carbicrete, n.d.) is another company looking to commercialise an alternative cement product, based on steel slag (as discussed below, steel slag has cementitious properties). Similar to Solidia's product, it utilises CO_2 during the curing process, and produces pre-cast products. The company claims CO_2 negative cement, though this will require emissions produced during the production of the steel slag to be assigned to the steelmaking process.

Vito / Orbix have developed a product (Carbstone) which is also produced from steelmaking slag (in this case, after metal recovery). Again, it utilises CO_2 in the curing process, though the use of an autoclave indicates somewhat high pressures during the production process (Vito, n.d.).

This work focusses mainly on the decarbonisation of existing cement processes, and pays particular attention to the accelerated carbonation of waste materials.

4.0 Overview of Cement Industry

4.1 Cement Production

Typical Cement Process

Around 3.5 billion tonnes of cement are produced a year, with ~63% being manufactured in China (2.2. billion tonnes) and ~9% in India (USGS, 2019). The vast majority of the cement produced is Portland cement (PC), which has undergone considerable development to greatly improving many of its qualities as a binder (*e.g.* setting time, workability, strength) since it was first patented in 1824. The production rate of cement has increased faster than GDP throughout approximately the last century (Kelly & van Oss, 2015). Emissions of CO_2 from cement production are significant, comprising 5-8% of global anthropogenic direct emissions (Cement Sustainability Initiative, 2018). These emissions derive from two main sources during production, with the majority (~60%) from calcination of the main feedstock (Eqn. 4.1), and the remainder (~40%) from fuels used to provide heating for the process (Davis, et al., 2018) (Dean, et al., 2011). The latter also includes indirect emissions from electricity usage within the plant, however this can be offset to some extent by waste heat recovery within the process. A brief summary of cement production is discussed below, accompanied by a diagram including the main processes in Figure 4-1.

$$\mathrm{CaCO_3} \longrightarrow \mathrm{CaO} + \mathrm{CO_2} \qquad \mathbf{4.1}$$

The main feedstock to the cement process (referred to as raw meal) is principally composed of limestone ($CaCO_3$) with minor additions from other materials (*e.g.* clays, sands, additives) to match the desired chemical composition. After grinding in a raw mill, these solids are fed to the top of the preheating tower. In successive cyclonic preheating stages, the feed is heated by direct counter-current contact with the off-gases from the rotary kiln. The resulting increase in temperature causes the limestone constituent to undergo partial calcination (Eqn. 4.1), resulting in the formation of lime (CaO) and releasing CO_2. Additional fuel is often supplied to a precalciner situated at the bottom of the cyclones to assist with the calcination.

The calcined solids then move on to the rotary kiln where the temperature is significantly increased by combustion from a kiln burner, prompting reactions to form a complex solid, referred to as PC clinker, containing a mixture of calcium silicate and aluminate phases. Details on the typical composition of PC clinker are given in Table 4-1. The mixture passes out of the kiln to a grate cooler, where ambient air rapidly cools the clinker whilst simultaneously preheating secondary/tertiary air for the kiln burner. Rapid cooling of the clinker is important since this prevents unwanted phase transitions. The cooled clinker is then mixed with various additives (*e.g.* fillers, minor constituents, or supplementary cementitious materials [SCMs]) before storage in silos and transport off-site.

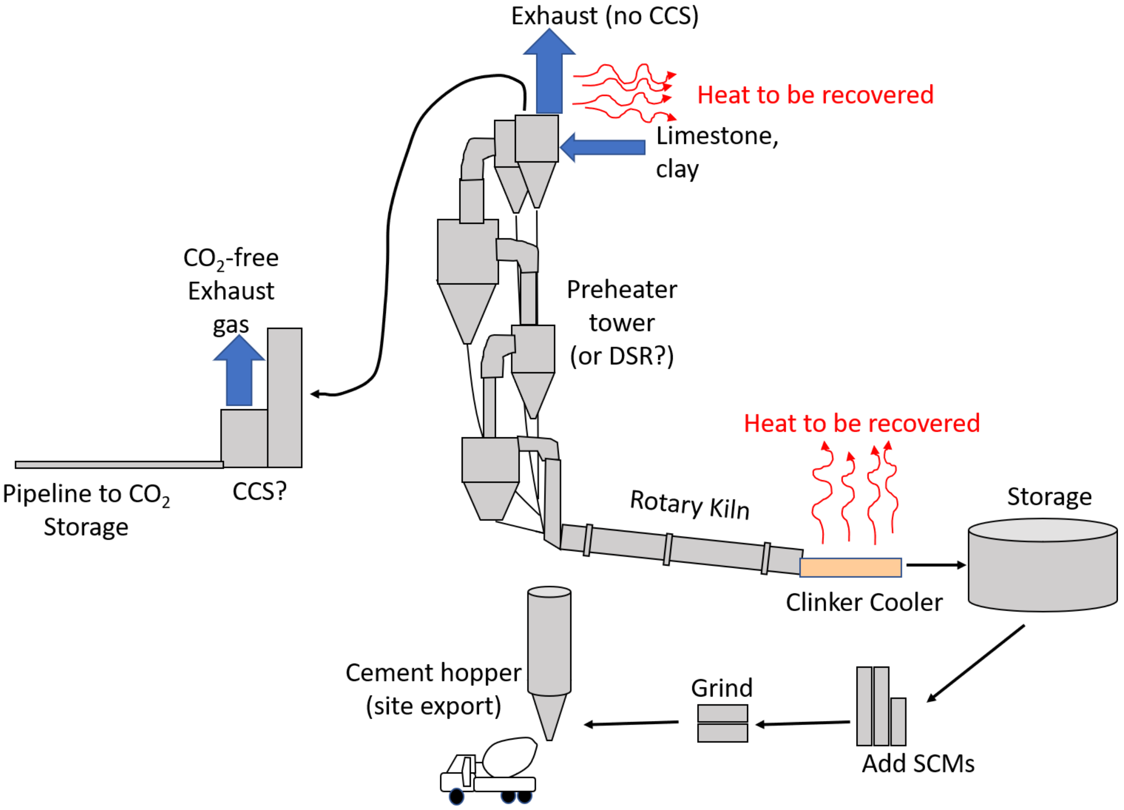

Figure 4-1: Illustrative schematic of the main processes in a typical cement plant. CCS refers to Carbon Capture and Storage, SCMs are supplementary cementitious materials and DSR is a direct separation reactor. Question marks indicate that CCS is not currently core to cement production.

Typical PC Clinker Composition

As shown in Table 4-1, PC clinker is principally composed of the oxide components lime (CaO), silica (SiO_2), alumina (Al_2O_3), iron oxide (Fe_2O_3) and magnesia (MgO), which in cement chemistry notation are denoted as C, S, A, F and M respectively (Sprung, 2008). These components constitute the chemistry of a number of PC clinker phases, including tricalcium silicate (Ca_3SiO_5, or C_3S), dicalcium silicate (Ca_2SiO_4; or C_2S), calcium alumnoferrite ($Ca_2(Al,Fe)_2O_5$, or C_4AF), and tricalcium aluminate ($Ca_3Al_2O_6$, or C_3A), as well as free lime and magnesia (C and M) (Sprung, 2008). The importance of these phases during hydration of PC (*i.e.* during setting/hardening) is discussed below. Other components such as the oxides of potassium (K_2O), sodium (Na_2O), sulphur (SO_3) and phosphorus (P_2O_5) are present in minor amounts in PC clinker (Sprung, 2008), which are undesirable contaminants above a threshold. These contaminants are particularly significant in the context of dusts generated throughout the PC production process, as detailed in section 4.2. Lastly, PC clinker compositions typically contain a minor quantity of loss on ignition (LOI), which represents the mass loss upon heating (often to 900-1000 °C), which for example can be from drying (H_2O) and decomposition of hydroxide (OH) and CO_2 that has accumulated during storage.

Table 4-1: Composition of Portland Cement (PC) clinker (Sprung, 2008).

Chemical Composition (wt%)

Species		CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	P_2O_5	SO_3	Other	LOI
Average		66.5	21.4	5.5	2.7	1.5	0.9	0.1	0.1	0.8	0.1	0.4
Range	Lower	63.8	19.7	3.8	1.3	0.0	0.3	0.0	0.0	0.2	-	0.1
	Upper	70.1	24.3	6.8	4.6	4.5	1.8	0.3	0.3	2.1	-	1.6

Phase Composition (wt%)

Phase		C_3S	C_2S	$C_2(A,F)$	C_3A	Free CaO	Free MgO
Average		63.0	16.0	8.0	11.0	1.0	1.5
Range	Lower	45.0	0.0	4.0	7.0	0.1	0.5
	Upper	80.0	32.0	14.0	15.0	3.0	4.5

Hydration of PC

Once concrete is produced, by mixing cement and aggregates, it hardens and develops its strength over a period of time, as shown in Figure 4-2. It is important that this is not too fast, since the concrete must be able to be moved around, put into position, etc. Different additives and proportions of materials allow this to happen in different ways. This section discusses how this happens.

The hardening of PC paste, which is the binding phase in concrete, is principally caused by hydration of PC with water, which prompts the occurrence of hydraulic reactions (Sprung, 2008). PC clinker is extremely reactive because its production process creates fine particles containing clinker phases (C_3S, C_2S, C_3A, C_4AF) that are unstable in water. These clinker phases rapidly dissolve and lead to precipitation of 'hydrated' phases such as calcium silicate hydrate (C-S-H), as discussed below.

In the absence of calcium sulfate ($CaSO_4$), the C_3A and C_4AF components in PC clinker undergo rapid hydration soon after mixing, preventing practical application. Hence, $CaSO_4$ is essentially always added to PC, which delays reaction and improves the workability of the mixture. This also leads to the formation of ettringite, which is a calcium sulfoalumino hydrate type alumino-ferrite-tri (AFt) phase, as well as the precipitation of alumino-ferrite-mono (AFm) phases (Sprung, 2008). Normally, ~4 wt% $CaSO_4$ is added, most commonly as gypsum ($CaSO_4.2H_2O$) (Naqi & Jang, 2019).

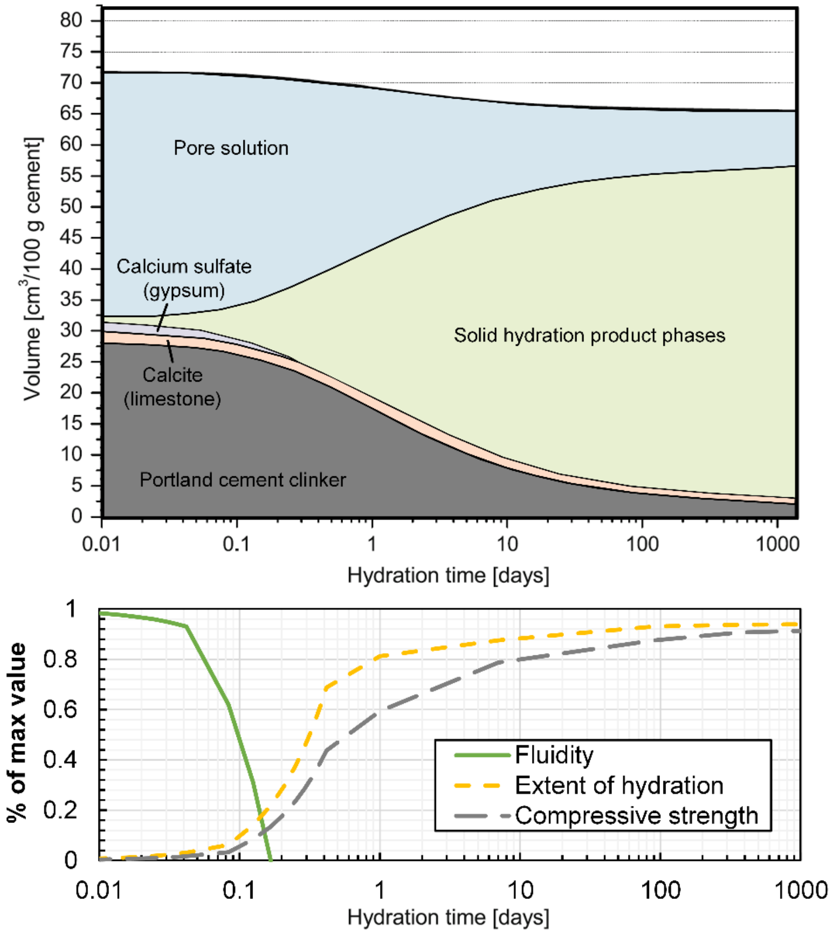

Figure 4-2 Schematic diagram of ordinary PC hydration, and its development of compressive strength and loss of fluidity over time.

The main reactions during setting of PC involve hydration of C_3S and C_2S to eventually cause bulk hardening *via* the precipitation of calcium silicate hydrates ($xCaO.ySiO_2.zH_2O$, or C-S-H) and calcium hydroxide ($Ca(OH)_2$, or CH) (Eqn 4.2-4.3) (Peter, et al., 2008). Hydration of C_3S occurs more rapidly than C_2S, but both reactions continue until completion (most of the C_3S reacts within the first few days, but C_2S reacts appreciably for weeks). Importantly, the reactivity of cement is known to depend on several factors, principally including (i) the particle size, (ii) the stabilities (and thereby dissolution rates) of each of its constituent phases (C_3S, C_2S, etc.), and thus (iii) the types and crystallinities of the phases present. Accordingly, when hydrated, a more finely ground PC will undergo setting/hardening faster than an a coarsely ground PC. The C-S-H phase is the main binding phase in PC paste, mortar, and concrete. These materials are porous, and their porosity contributes greatly to their final strength since such voidages are inherently weaker than solids (Sprung, 2008). Free CaO also reacts during hydration (Eqn 4.4), but does not contribute as significantly to binding properties (Sprung, 2008).

$$2Ca_3SiO_5 + 7H_2O \longrightarrow 3CaO \cdot 2SiO_2.4H_2O + 3Ca(OH)_2 \qquad \Delta H_r = -173\ kJ/mol \qquad \textbf{4.2}$$

$$2Ca_2SiO_4 + 5H_2O \longrightarrow 3CaO \cdot 2SiO_2.4H_2O + Ca(OH)_2 \qquad \Delta H_r = -59\ kJ/mol \qquad \textbf{4.3}$$

$$CaO + H_2O \longrightarrow Ca(OH)_2 \qquad \Delta H_r = -64\ kJ/mol \qquad \textbf{4.4}$$

$$3Ca(OH)_2 + 2SiO_2 \cdot 2H_2O \longrightarrow 3CaO \cdot 2SiO_2.5H_2O \qquad \textbf{4.5}$$

Other additives can undergo hydration reactions and similarly contribute to setting and hardening. These include solid admixtures (*e.g.* gypsum) and supplementary cementitious materials (SCMs). Due to their increasing importance within modern cements, this study will review the carbonation of components in both PC and a range of cementitious materials, as discussed in section 6.0. These exhibit varying reactivity, ranging from fillers (*i.e.* inert materials such as aggregates) and reactive fillers (*i.e.* slightly reactive materials), through to SCMs (*i.e.* significantly reactive materials).

4.2 Generation of Cement Dusts

Two main types of dust are produced in cement production, cement kiln dust and cement bypass dust. Kiln dust is mainly from loss of limestone particles as they are fed to the plant, and is not highly contaminated. It is generally fed back to the kiln in a modern plant. Cement bypass dust is produced in order to purge particular undesirable elements from the plant, preventing them from accumulating in the process, causing blockages. We discuss the details of dust formation below.

A significant quantity of dust is generated during normal operation of a PC plant. The quantity generated differs considerably based on whether the plant is functioning in compound operation (*i.e.* using hot exhaust gases to heat the raw mill) or direct operation (*i.e.* no milling, with exhaust gases vented), which respectively generate dust at a rate of roughly 54-144 and 80-200 kg/tonne of clinker (Schorcht, et al., 2013). In either case, the fine dusts entrained in the gases must be removed before release to the atmosphere, typically by electrostatic precipitators and/or fabric filters. Dust removed by these processes is known as cement kiln dust (CKD) (Figure 4-3, in 'Exhaust gas'), and is composed of partially calcined meal that leaves the process by the preheater cyclones before eventual reintroduction to the process.

The European Cement Research Academy (ECRA) has developed a best practice model that states "almost all dust streams are recycled within the clinker burning process or utilised for the production of cement or cementitious products" (European Cement Research Academy, 2017). In this regard, it appears that there is a significant flaw in academic literature whereby researchers repeat outdated values for dust production in cement plants that contrast current best practice.

Separate from CKD is cement bypass dust (CBD), which is generated at the bypass between the rotary kiln and the riser duct (Figure 4-3, in 'Bypass'). A bypass is required if feed concentrations of compounds based on sulphur (S), chlorine (Cl), potassium (K) and sodium (Na) are too high. These contaminants are volatilised by the high temperatures in the clinkering stage of the rotary kiln (*i.e.* closest to the burner) but condense at the lower temperatures in the cyclone preheater. This produces an internal recirculation of these species which evaporate in the kiln, are transported downstream and condense in the riser pipes and lower cyclones (Mut, 2014). Excessive recirculation of these species leads to liquid products, which reduce the flowability of the raw meal and can cause build-ups on the cyclone walls and riser ducts (*e.g.* ring formation due to sulfospurrite from excess sulphur) (Mut, 2014). If unmanaged, in addition to causing blockages, these species can then leave within the centre of nodules of the clinker product, potentially degrading product quality.

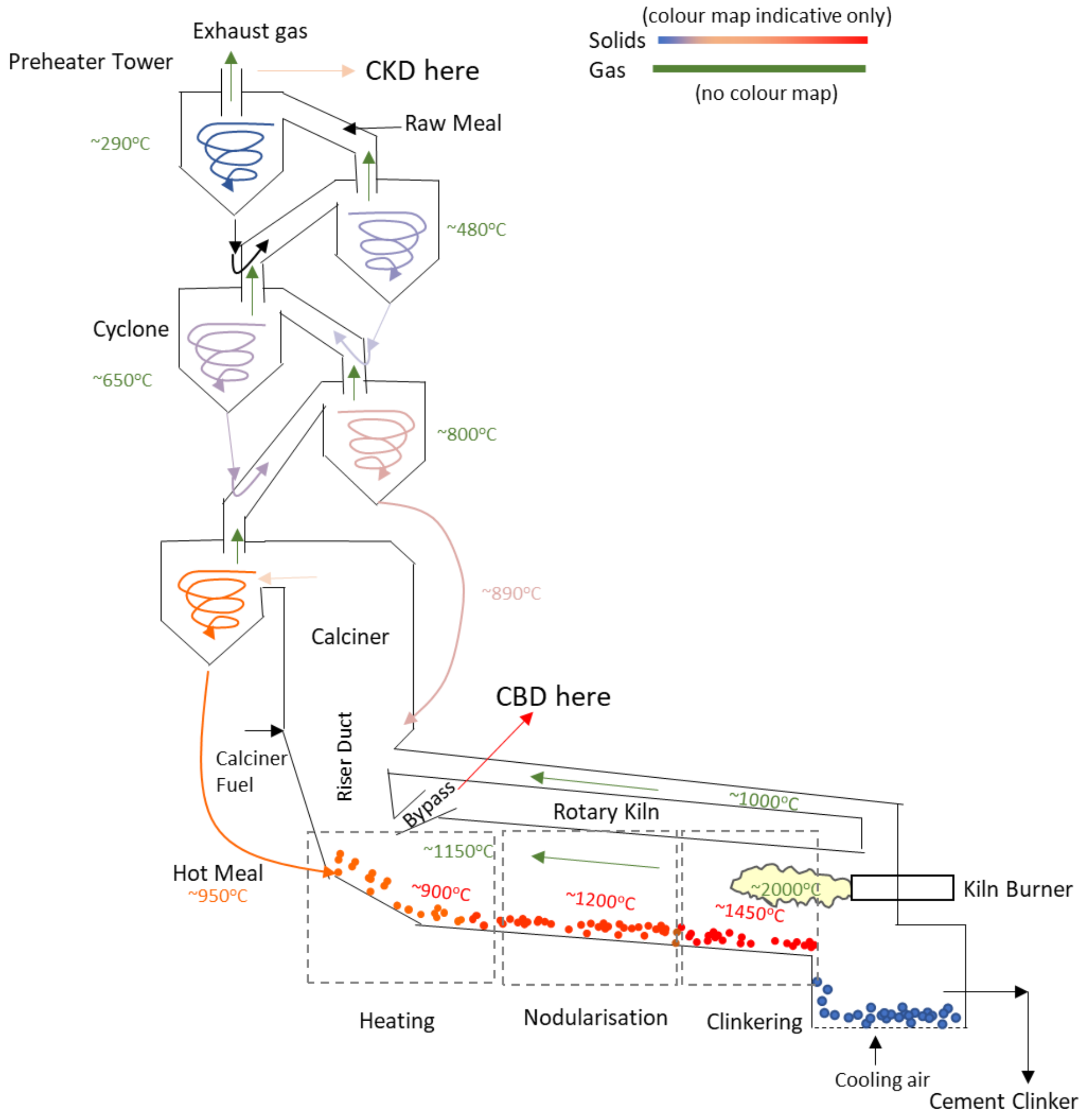

Figure 4-3: Detailed diagram of cement production process, including approximate temperatures (blue to red scale). Data from (Mut, 2014).

Since these compounds are volatile, a convenient solution to prevent such recirculation is to purge a fraction of the contaminated kiln gases at the bypass duct (thereby breaking the recirculation). Under certain circumstances, previous studies have found relatively low bypass rates (~5%) achieved almost complete removal of Cl from the gas phase (90%), though higher bypass rates were required for removal of K and S with similar effectiveness. Nevertheless, a high bypass flow is undesirable due to the reduction in overall energy efficiency for clinker production. Of course, present within the bypass is a moderate amount of CBD consisting of partially calcined meal with free CaO, upon which the Na, K and Cl species condense.

The main transformations which occur for K, Na, Cl and S are illustrated in Figure 4-4. Firstly, the alkalis will react with any chlorine present to form KCl and NaCl before leaving the kiln at the bypass. Remaining alkali will then react with SO_2, with any excess thereafter reacting with CaO to form solid $CaSO_4$ that leaves the kiln alongside the clinker. Nevertheless, an appreciable amount of sulphur introduced in the raw meal will also leave by the exhaust gas (as indicated in Figure 4-3). Following this, residual alkalis will react with CO_2 and H_2O to form alkaline carbonates (*e.g.* Na_2CO_3, K_2CO_3) and hydroxides (*i.e.* NaOH, KOH). Collectively, these alkali salts will leave the kiln either trapped within nodules of clinker or as part of the CBD, with the latter the main non-internally recycled dust stream.

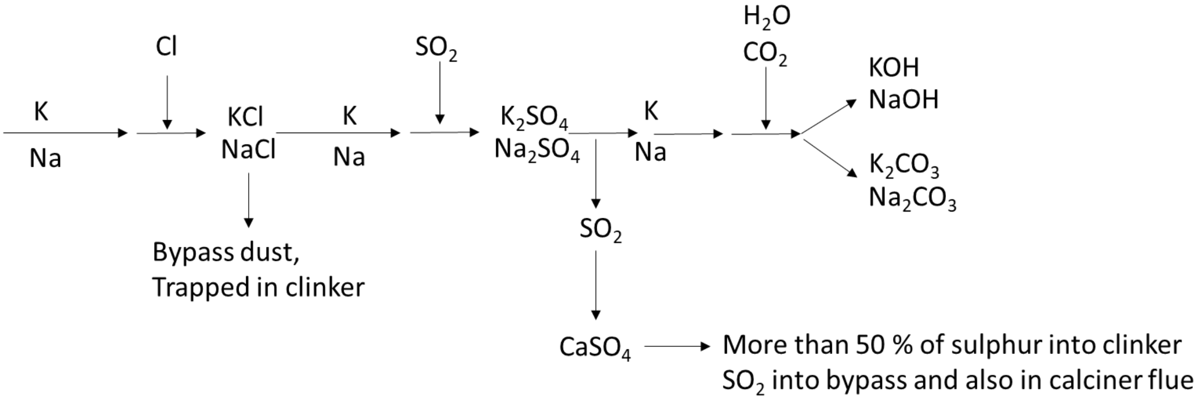

Figure 4-4. Transformations of various elements during the cement production process.

The chlorine in the bypass dust mainly solidifies as fine particles of KCl due to rapid cooling of the gas stream. Investigations into the composition of dust particles of different size fractions found ~80% of the chlorine is present within particles <2 µm (Sutou, et al., 1999), meaning targeted removal of these fine particles (≤2 µm) by cyclonic separation significantly reduces the quantity of CBD generated (*i.e.* larger particles with less chlorine can be returned to the rotary kiln) (Scott, 2007). Recently, other innovations by BHS-Sonthofen allow separation by an indexing belt filter (Bowden, 2017), which has been stated to achieve up to 95% removal of chlorides and substantial return of CBD to the kiln (Bowden, 2017). Tests conducted in collaboration with Holcim gave positive results, with BHS-Sonthofen now offering a technical solution with an annual capacity of 20,000 tonnes. Minimisation of CBD by use of such as system means up to ~3% higher plant throughput, with the washed-out chlorides present as a liquid product for disposal (Bowden, 2017).

4.3 Improvements to the Cement Industry

Alternative Fuels

Historically, coal has been the major fuel used within the cement industry, however rotary kilns can flexibly operate with many different types of fuel. Increasingly, the industry has turned toward higher utilisation of alternative fuels, frequently municipal solid waste (MSW) and refuse-derived fuels (RDFs), produced from a diverse range of industrial wastes (*e.g.* tyres, plastics, textiles, sawdust, *etc.*) (Schorcht, et al., 2013). As mentioned previously, it is important to recognise that a minority (~40%) of emissions in cement production derive from combustion of fuels (Davis, et al., 2018) (Dean, et al., 2011), meaning even complete adoption of 'carbon neutral' fuels would still result in substantial net CO_2 emissions (*i.e.* ~60% from calcination of raw meal). The same reasoning applies to the use of either hydrogen to fuel the process, or electrification of the kiln or calciner (Fennell, et al., 2021).

In fact, it is relatively cost effective for cement producers to accept such RDFs since the high temperatures of the kiln result in complete incineration and the ashes are incorporated into clinker (offering more efficient utilisation than simply landfilling these wastes). All the large multinationals make use of such alternative fuels, accounting for 20%, 24% and 57% of the global fuel usage at LafargeHolcim, Heidelberg Cement, and Cemex (in the UK) respectively (HeidelbergCement, 2020) (Cemex, 2020) (LafargeHolcim, 2020). Increasing uptake of RDFs affects downstream carbonation potential since their combustion consequently increases the rate at which CBD is required to be produced to purge undesirable materials (as discussed in section 7.1).

Nevertheless, because alternative fuels generally have lower calorific values and higher moisture contents, their use increases the overall energy demand of the plant. The energy requirement per kilogram of clinker (kJ/kg) is shown in Figure 4-5 for the current best available technology (BAT) (European Cement Research Academy, 2017), showing the effect of higher utilisation of alternative fuels. Additionally, alternative fuels have implications for specific pieces of equipment, notably the main kiln burner which requires the energy content of the fuel be ~18-22 GJ/tonne of fuel for stable operation. Because a large number of wastes contain organic matter with relatively low calorific value (~10-18 GJ/tonne), it is often necessary to co-fire them with a support fuel with higher energy content. Lower calorific value fuels can be better tolerated in the calciner rather than the kiln.

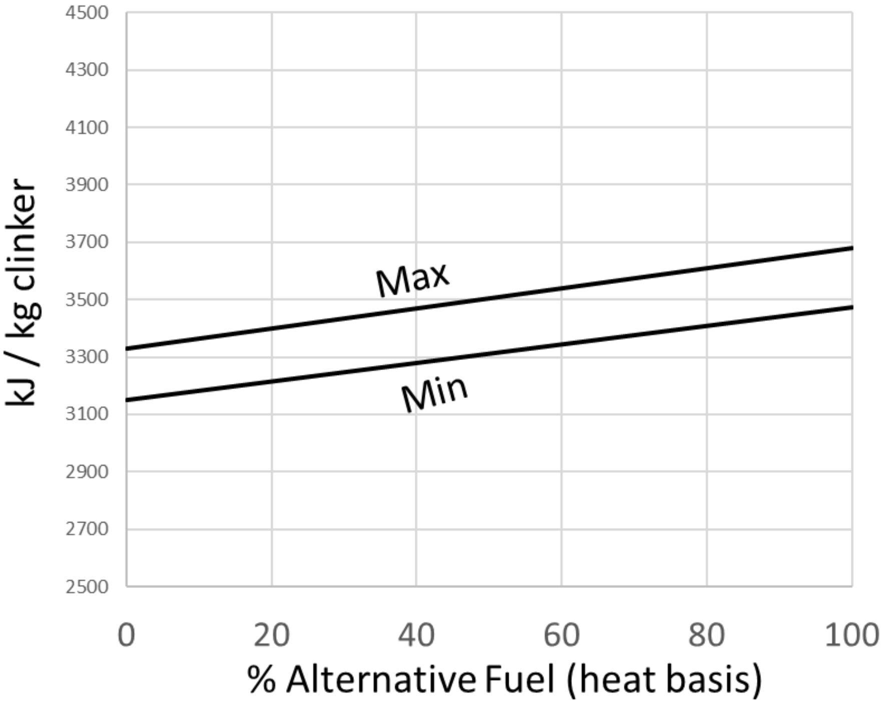

Figure 4-5: BAT energy use per kg of clinker with changes in alternative fuel use. (European Cement Research Academy, 2017).

Process Improvements

Emissions intensity is reported as standard for many global cement companies including LafargeHolcim, Cemex and Heidelberg Cement. These companies respectively have emissions intensities of 0.561, 0.622 and 0.590 tonnes of CO_2 per tonne of cement produced in 2020 (LafargeHolcim, 2020; LafargeHolcim, 2020) (Cemex, 2020) (HeidelbergCement, 2020). The emissions intensity of cement production is currently being driven by the following factors:

Clinker ratio: As detailed previously, PC clinker is associated with significant CO_2 emissions. There has been recent movement toward greater incorporation of additives (*e.g.* fillers, minor constituents, SCMs) that serve to lower the clinker-to-cement ratio (often referred to as the 'clinker ratio'). In this way, a portion of the clinker in cement can be replaced by materials with fewer associated CO_2 emissions (CEMBUREAU, 2021), lowering the net CO_2 associated with the cement. Compared to the clinker ratio of conventional PC with 5 wt% minor constituents (~0.95), current practices produce cements with reduced clinker ratios (~0.74-0.77) (World Business Council for Sustainable Development, 2009) (CEMBUREAU, 2021). A broad range of additives have been studied, however there is particular interest in SCMs, which are typically pozzolanic materials with significant reactivity, as further detailed in section 6.0.

Waste heat recovery: PC production requires high temperatures (~900-1450 °C) to drive the calcination and clinkering reactions, meaning there tends to be high quantities of heat available for recovery. Current heat recovery practice typically involves using process air from the grate coolers as preheated secondary/tertiary air in the burners of the kiln and calciner (or otherwise used for drying raw meal). Nevertheless, the amount of preheated air often exceeds demand elsewhere in the plant. Basic steam cycles to recover waste heat were developed by Japanese companies in the 1980s, with the first system of sizeable capacity (15 MW) being installed by Kawasaki Heavy Industries for Taiheiyo Cement in 1982 (Gibbons, 2013a). Organic Rankine cycles have also been applied on cement plants, with the first demonstration being a 1.1 MW installation in Heidelberg Cements's Lengfurt plant in 1999 (Baatz & Heidt, 2000). Overall, implementing better waste heat recovery processes can be used to increase plant efficiency and reduce emissions of CO_2.

Type of Cement Plant: Several different cement processes that have been developed over recent decades, as seen in Figure 4-6. Globally there is still a considerable amount of installed capacity contributed to by inefficient processes (*i.e.* wet, semi-wet and semi-dry type processes) with older processing equipment (*e.g.* Lepol kilns). However, these are being steadily phased out in favour of more modern and efficient processes, with the current BAT being the dry type process. As can be seen in Figure 4-6, modern plants based on the dry process only require ~3.3 GJ_{th}/tonne of clinker (European Commission, 2010) (Oda, et al., 2012), around twice the thermodynamic limit of ~1.75 GJ_{th}/tonne of clinker (Taylor, 1990).

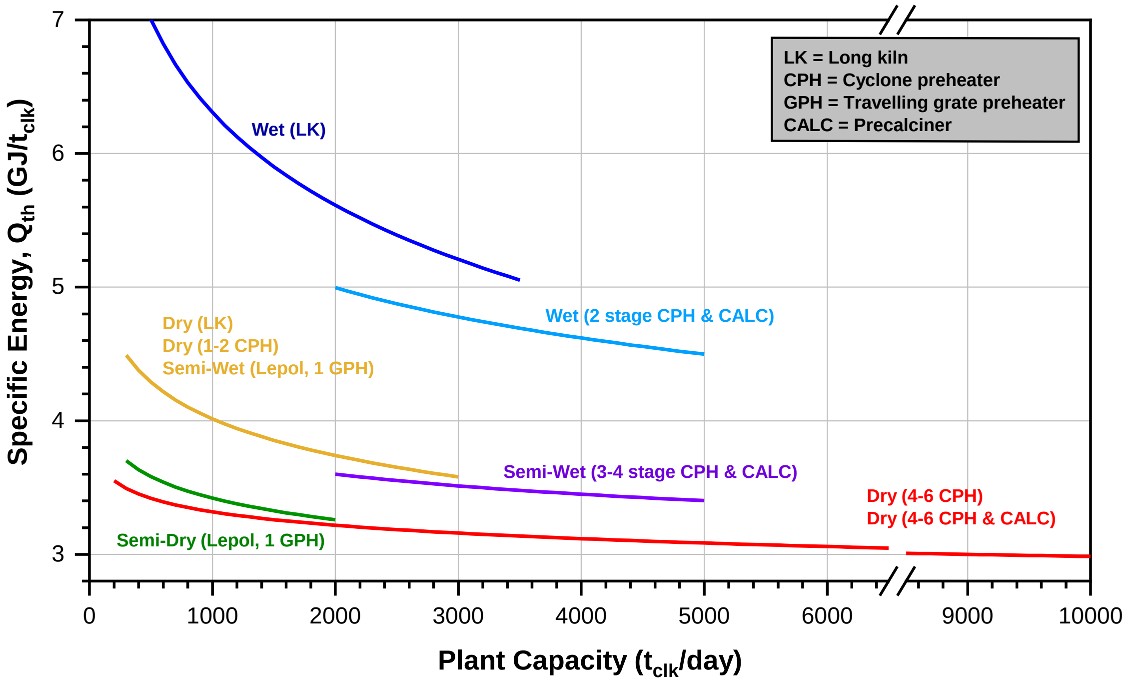

Figure 4-6: Thermal energy consumption of different cement processes. Reconstructed based on data presented by (Oda, et al., 2012)

Carbon Capture and Storage: Carbon Capture and Storage (CCS) may be used to decarbonise cement production in the future, and when combined with fuels with a high biogenic content can potentially offer negative emissions, enhancing the value of the carbonation discussed elsewhere in the report (Fennell, et al., 2021). Although not currently implemented outside of a few test facilities, CCS can play a major role in decarbonising the cement industry, owing to the intrinsic process CO_2 emissions generated by calcination. There are multiple potential processes for capturing CO_2 that offer varying levels of integration with cement plants. There is ongoing innovation in the field as seen by recent development of the direct separation reactor (DSR), which is an efficient alternative to current CCS technologies (Hodgson, et al.,

2018) and is currently being trialled at pilot scale as part of LEILAC II. Importantly, HeidelbergCement has recently received approval and funding from the Norwegian government to add CCS to its Brevik plant to cut around 50 % of the emissions by 2024 (HeidelbergCement, 2020).

Non-Portland cementitious materials (NPCMs)

As well as alternative fuels, various process improvements can be made to cement processes to reduce their net CO_2 emissions. When considering the potential for carbonation of materials, it is important to consider what other possibilities there are for their use, and whether carbonation would detrimentally affect these potential uses.

Non-Portland cementitious materials (NPCMs) are any reactive materials in the context of cementitious systems that modify the properties of the cementitious binder (Pamenter & Myers, 2021). They include reactive fillers and SCMs, including both industrial wastes (*e.g.* steelmaking slags, fly ashes) and natural materials (*e.g.* pozzolans from calcined clay) (Tran & Ghosh, 2020). They are blended with PC according to standard EN 197-1 (EN.197-1, 2011).

Replacing PC clinker with NPCMs can be particularly beneficial if the latter are: i) comprised of fine particles that complement the particle size distribution of cement particles to improve workability at constant water addition, although this requires careful control of the particle size distribution and use of dispersants (*i.e.* superplasticisers) (John, et al., 2018); and/or ii) reactive enough to precipitate binding phases in the order of at least days. NPCMs are usually added in finely divided form to densify the microstructure of cement paste. For example, high strength performance concretes formulations are based on addition of microsilica to PC to optimise the particle size distribution (from nanometre to micrometre sized particles) which leads to the formation of good binding C-S-H phases in the nanoporosity (Neville & Pierre-Claude, 1998). NPCMs are used to reduce the clinker ratio of cement and so reduce its associated CO_2 emissions.

Supplementary cementitious materials (SCMs): SCMs tend to be significantly reactive, but less so than PC clinker, since the latter is engineered via the clinker production process to be highly reactive in the presence of water. This means that high substitution levels of SCMs for PC require the SCMs to be significantly reactive.

Pozzolanic aluminosilicates are arguably the most important class of SCMs. They include granulated blast furnace slag, coal fly ash, and calcined clay. Their partial substitutions of PC clinker are well-known, commonly used, and standardised. The 'pozzolanic' term corresponds to the reaction of the material with calcium hydroxide when it is present in finely divided form and with water. The reaction product is usually C-S-H (Calcium Silicate Hydrate), or C-(A-)S-H (Calcium Aluminate Silicate Hydrates) when aluminium is present in the SCM (Eqn. 4.5) (Sprung, 2008). Since these materials are aluminosilicates, they are more soluble at high pH, and thus the high pH environment of PC binder increases their reactivity.

Regarding fly ashes, only classes F and C are commonly used SCMs. Class F fly ash is derived from burning of anthracite or bituminous coal, and is defined with a specific composition $SiO_2 + Al_2O_3 + Fe_2O_3 \geq 70$ wt%. On the other hand, class C fly ash is obtained from burning of lignite or subbituminous coal, is defined with $SiO_2 + Al_2O_3 + Fe_2O_3 \geq 50$ wt%, and contains a larger amount of lime (CaO) (ASTM.C618-00, 2001) (Thomas, 2007).

Various metallurgical slags are pozzolanic, although only granulated blast furnace slag, a by-product from pig iron production, is standardised and commonly used as a SCM. Granulated blast furnace slag is hydraulic (reacts in the presence of water), and so is one of the most useful SCMs. Metallurgical slags are discussed further in section 5.2.

Calcined clay has recently been recognised to have high potential as a reactive pozzolanic aluminosilicate material. Such clays can have moderate-to-high kaolin clay content (>40 wt% (Scrivener, et al., 2018)). They can be calcined to high reactivity at temperatures ~600-800°C, which is much lower than the corresponding temperatures for production of PC clinker (~900-1450 ^{o}C). Furthermore, these clays are widely available.

Reactive fillers: Reactive fillers are materials that are less reactive than SCMs. Naturally mined limestone (calcium carbonate sedimentary rock) is by far the most widely used reactive filler (and most common NPCM). It is usually ground finely and then added to cement, and reduces costs associated with cement production. It is typically added in PC (CEM I) as a minor constituent, and in CEM II / L or LL regulated by EN 197-1 (EN.197-1, 2011). Such calcium carbonate additions can be beneficial (or at least not detrimental) to the mechanical properties of the final concrete when replacing relatively small amounts of PC clinker (~<10 wt%).

Fine limestone reacts to form carbonated binding phases, principally CO_2-containing AFm phases (Lothenbach, et al., 2008) (Ramezanianpour & Hooton, 2014) (Matschei, et al., 2007) (Zajac, et al., 2014). These phases are beneficial to the early mechanical properties of PC binder.

Analysis of potential: Relevant authorities state that NPCMs could be used to lower the clinker ratio from the current value of ~0.77 to 0.61 by 2050 (World Business Council for Sustainable Development, 2009). Theoretically, further reductions to ~0.5 could be achieved by combining calcined clays and calcium carbonate in calcined clay-limestone-cement (LC^3) (Scrivener, et al., 2018). Addition of SCMs directly affect the properties of the concrete (*e.g.* setting time, workability, strength development), meaning their addition must be previously tested and controlled to ensure no negative effects. Depending on their quantity and composition, SCMs can offer binding properties and further strength through hydraulic and/or pozzolanic reactivity (Tran & Ghosh, 2020).

Evidentially, Hanson have developed a new blend of cement marketed as 'Hanson Eco-Plus', which incorporates a large amount of ground granulated blast furnace slag (GGBFS). The manufacturers offer a variety of different formulations, including one with 50% GGBFS that can be used for structural applications and complies with appropriate standards for concrete (BS 8500:2). There is always the risk that high substitutions may not be favoured by purchasing managers due to perceived quality or longevity issues. The Hanson Eco-plus brochure (Hanson, n.d.) states that 70 % substitution of clinker with GGBS proportionately reduces the CO_2 emissions from 292 to 117 kg / m^3 of cement. It is important that the emissions reductions are not double-counted in such situations – either the steel plant, or the cement plant, can claim the CO_2 reductions, but not both. Importantly, some of these industrial wastes (or by-products) are increasingly unavailable due to the phasing out of coal-fired power generation and national steelmaking (Lehne, et al., 2018). Hence, relying on large quantities of these materials for carbonation would be accompanied with considerable risk, as outlined in section 7.0). Many of the main NPCMs have been summarised in Table 4-2.

Table 4-2: Overview of the main NPCMs (actual or potential application). Adapted from (Snellings, 2016).

Material	Chemistry	In Use	Comments	Reference
Ca-based				
Limestone	$CaCO_3$	Yes	Natural 5% reactive in hydrated PC >5% reactive when added together with reactive Si-Al sources	(Snellings, 2016)
Si-Al-based (Pozzolanic SCMs)				
Fly Ashes (FA)				
FA (Class C)	Si-Al-Ca	Yes	Less coal-fired power plants in the future	(Snellings, 2016) (MCCARTHY, et al., 2017)
FA (Class F)	Si-Al	Yes	Less coal-fired power plants in the future	(Snellings, 2016) (MCCARTHY, et al., 2017)
Natural pozzolans (*e.g.* volcanic ash)	Si-Al	Yes	Natural, large variety	(Snellings, 2016)
MSWI bottom ashes	Si-Al-Ca	No	Expansive and corrosive components, contamination issues	(Snellings, 2016)
Si-based				
Silica fume	Si	Yes	Expensive, used in high performance concrete	(Snellings, 2016)
Biomass ash	Si	No	Competition with soils amendments	(Snellings, 2016)
Slags				
Blast furnace slag	Ca-Si-Al	Yes	Nearly fully exploited	(Snellings, 2016)
Steel slag	Ca-Si-Fe	No	Hard to grind, variable composition	(Snellings, 2016)
Copper slag	Fe-Si	No	Heavy metal, low reactivity, research needed	(Snellings, 2016)
Other slags	Fe-(Si)-(Ca)	No	Heavy metal, low reactivity, research needed	(Snellings, 2016)
Bauxite residue	Fe-Al-Si	No	Coloured, low reactivity (needs to be processed to turn into a SCM), high alkali content	(Snellings, 2016)
Waste glass	Si-Na-Ca	No	High alkali content, not usually used as a SCM	(Snellings, 2016)
Calcined clay	Si-Al	Yes	Natural, extremely large availability, can have high reactivity	(Snellings, 2016)

5.0 Carbonation

This section discusses the fundamental reactions which can be used to carbonate different types of materials, including cementitious materials. It includes other methods to introduce CO_2 into the system other than as a gaseous reactant. It is relevant to both carbonation of waste materials to produce aggregates (as in the Carbon8 Systems process) and the general carbonation of cementitious materials during curing. It does not discuss all possible combinations of cement chemistry (for example, Carbonatable Calcium Silicate cements).

5.1 Fundamental Reactions

There are a variety of carbonation processes reported in literature, with these principally divided between those that occur over a single stage (referred to as Direct Carbonation) and those that occur over multiple stages (so called Indirect Carbonation) (Sanna, et al., 2014). The former can be further categorised into either Gas-Solid or Aqueous processes (whereas Indirect processes are exclusively Aqueous) (Sanna, et al., 2014). These processes are individually summarised in their respective sections herein.

Direct Carbonation (Gas-Solid)

In the following section we discuss the most important carbonation process for practical application of carbonation of a waste material with flue gas, direct contact between a gaseous CO_2-containing stream and the carbonatable material. Further discussion of cement chemistry is found in section 4.1.

The constituents of cement binders (*e.g.* in mortars, concrete products) can be directly carbonated, as explored in section 5.2. Overall, direct carbonation of CaO and MgO respectively produces $CaCO_3$ and $MgCO_3$ (as calcite and magnesite respectively). Hydrated PC clinker typically contains a minor amount of the unreacted clinker phases C_3S, C_2S, and C_3A, and these can thus be neglected in accounting for CO_2 uptake, though they can be carbonated via (Eqns 5.3-5.5) (Sanna, et al., 2014), leading to production of $CaCO_3$ and $MgCO_3$ and additional oxides (*i.e.* SiO_2, Al_2O_3, Fe_2O_3) (Groves, et al., 1990) (Nishikawa, et al., 1992). The reactivity of these components with CO_2 reportedly decreases in the trend $C_3S > C_2S > C_3A > C_4(A,F)$ (Liu, et al., 2020). Again, although these reactions do proceed in the presence of CO_2, their rates are typically too slow for practical use and carbonation of hydrated mixtures is more commonly pursued.

$$\mathrm{CaO + CO_2 \longrightarrow CaCO_3} \quad \Delta \mathrm{H_r} = -179\,\mathrm{kJ/mol} \tag{5.1}$$

$$\mathrm{MgO + CO_2 \longrightarrow MgCO_3} \quad \Delta \mathrm{H_r} = -118\,\mathrm{kJ/mol} \tag{5.2}$$

$$\mathrm{Ca_3SiO_5 + 3CO_2 \longrightarrow 3CaCO_3 + SiO_2} \tag{5.3}$$

$$\mathrm{Ca_2SiO_4 + 2CO_2 \longrightarrow 2CaCO_3 + SiO_2} \tag{5.4}$$

$$\mathrm{Ca_3Al_2O_6 + 3CO_2 \longrightarrow 3CaCO_3 + Al_2O_3} \tag{5.5}$$

Accordingly, most accelerated carbonation processes to carbonate wastes are conducted in the presence of water and/or with hydrated species. For direct gas-solid carbonation a relatively small amount of water is present, typically either as wetted solids or absorbed from humidified CO_2. This allows carbonation to proceed by dissolution of CO_2 in the aqueous solution surrounding cement particles, which is highly basic (pH ≥ 13), and then reaction of dissolved carbonate complexes (*i.e.* CO_2^0, CO_3^{2-}, HCO_3^-, $H_2CO_3^0$) with the products of the aforementioned cement hydration reactions (i.e. those formed in Eqs. 4.2-4.5). This is also contributed to by the presence of alkali metals (*i.e.* K_2O, Na_2O) which similarly raise the basicity. Carbonation of the Ca-bearing solid phases such as $Ca(OH)_2$ and C-S-H precipitates $CaCO_3$. Carbonation of Mg-bearing solid phases such as $Mg(OH)_2$ to produce $MgCO_3$ also occurs (Jang, et al., 2016).

Concerning $CaCO_3$, although carbonation selectively forms the calcite phase, in the presence of water the reaction may lead to precipitation of the vaterite and aragonite phases (Black, et al., 2007). Specifically, carbonation of C-S-H leads to the formation of $CaCO_3$ and silicate gels ($SiO_2.nH_2O$, or S-H) (Morandeau, et al., 2014) (Groves, et al., 1990), however this only generally proceeds after significant removal of the portlandite ($Ca(OH)_2$) phase. Concerning $MgCO_3$, the reaction instead precipitates brucite, but other phases including the nesquehonite, dypingite and/or arinite phases are possible (Vandeperre & Al-Tabbaa, 2007). Aluminate (C_4A, $C_4(A,F)$) (Nishikawa, et al., 1992) and alkali (K_2O, Na_2O) species can also react, with the latter particularly stabilising into salts (*i.e.* NaCl, KCl, K_2SO_4, Na_2SO_4) (Mut, et al., 2015) making them less prominent carbonation targets.

Direct Carbonation (Aqueous)

Different reactions govern direct carbonation in the aqueous phase, wherein carbonatable solids are in contact with water or in a slurry, and the solid-liquid mixture is then contacted with CO_2 (Sanna, et al., 2014). Here, at high pH typical of PC binder, CO_2 dissolves stabilising carbonate ions (CO_3^{2-}) due to the high basicity of the solution (pH ≥ 13), and eventually bicarbonate ions (HCO_3^{-}) if the solution pH decreases sufficiently (pH = ~4-6) (Eqns.5.6-5.7) (Sanna, et al., 2014). This decrease in pH will lead to destabilisation of cementitious phases such as C-S-H, and lead to release of ions such as Ca^{2+} into solution. Aqueous metal ion complexes such as Ca^{2+} and Mg^{2+} can react with dissolved carbonate species and precipitate insoluble $CaCO_3$ and $MgCO_3$ respectively (Eqns. 5.8 - 5.12, where M = an alkali metal such as K or Na, or a bivalent metal such as Ca or Mg), which then react in the aforementioned manner (Sanna, et al., 2014).

$$\mathrm{CO_2}_{(g)} + \mathrm{H_2O}_{(l)} \longrightarrow \mathrm{H_2CO_3}_{(aq)} \longrightarrow \mathrm{HCO_3}^{-}{}_{(aq)} + \mathrm{H}^{+}{}_{(aq)} \qquad \textbf{5.6}$$

$$\mathrm{HCO_3}^{-}{}_{(aq)} + \mathrm{OH}^{-}{}_{(aq)} \longrightarrow \mathrm{CO_3}^{2-}{}_{(aq)} + \mathrm{H_2O}_{(l)} \qquad \textbf{5.7}$$

$$\mathrm{M(OH)_2}_{(s)} \longrightarrow \mathrm{M}^{2+}{}_{(aq)} + 2\mathrm{OH}^{-}{}_{(aq)} \qquad \textbf{5.8}$$

$$\mathrm{M}^{2+}{}_{(\mathrm{aq})} + \mathrm{HCO_3}^{-}{}_{(\mathrm{aq})} \longrightarrow \mathrm{MCO_3}_{(s)} + \mathrm{H}^{+}{}_{(aq)} \qquad \textbf{5.9}$$

$$\mathrm{M}^{+}{}_{(\mathrm{aq})} + \mathrm{HCO_3}^{-}{}_{(\mathrm{aq})} \longrightarrow \mathrm{MHCO_3}_{(s)} \qquad \textbf{5.10}$$

$$\mathrm{M}^{2+}{}_{(\mathrm{aq})} + \mathrm{CO_3}^{2-}{}_{(\mathrm{aq})} \longrightarrow \mathrm{MCO_3}_{(s)} \qquad \textbf{5.11}$$

$$2\mathrm{M}^{+}{}_{(\mathrm{aq})} + \mathrm{CO_3}^{2-}{}_{(\mathrm{aq})} \longrightarrow M_2\mathrm{CO_3}_{(s)} \qquad \textbf{5.12}$$

Carbonation of hydrated cementitious materials involves different chemical reactions to those shown in Eqns. 5.6-5.12). Since these materials contain significant water content unless pre-dried, direct carbonation processes here will involve both solid-gas reactions and dissolution of the CO_2 gas into solution and then solid-liquid reactions. The solid-gas reactions produce $CaCO_3$ and $MgCO_3$ similarly to Eqns. 5.6-5.12 albeit with more complex cementitious solid phases (relative to *e.g.* CaO).

For the latter solid-liquid reactions, carbonation proceeds by reaction of dissolved carbonate complexes (i.e. CO_2^0, CO_3^{2-}, HCO_3^-, $H_2CO_3^0$) in the prevailing high pH pore solution of hydrated PC binder (pH ≥ 13) (Eqns.5.6-5.12) with Ca-bearing solid phases such as $Ca(OH)_2$ and C-S-H to precipitate $CaCO_3$ (Eqns. 5.13-5.14). Although carbonation selectively forms the calcite phase, in the presence of water the reaction may lead to precipitation of the vaterite and aragonite phases (Black, et al., 2007). Specifically, carbonation of C-S-H leads to the formation of $CaCO_3$ and silicate gels ($SiO_2.nH_2O$, or S-H) (Eqns. 5.13-5.14) (Morandeau, et al., 2014) (Groves, et al., 1990), however this only generally proceeds after significant removal of the portlandite ($Ca(OH)_2$) phase.

$$\mathrm{Ca(OH)_2} + \mathrm{CO_2} \longrightarrow \mathrm{CaCO_3} + \mathrm{H_2O} \qquad \textbf{5.13}$$

$$x\mathrm{CaO}\cdot y\mathrm{SiO_2}.z\mathrm{H_2O} + x\mathrm{CO_2} \longrightarrow x\mathrm{CaCO_3} + y(\mathrm{SiO_2}.n\mathrm{H_2O}) + (z - yn)\mathrm{H_2O} \qquad \textbf{5.14}$$

Carbonation of Mg-bearing solid phases in hydrated PC binder such as hydrotalcite (*e.g.* $Mg_4Al_2(OH)_{14}.3H_2O$) can lead to the production of e.g. complex carbonate-bearing solid phases (*e.g.* CO_2-containing hydrotalcite, $Mg_6Al_2(OH)_{16}(CO_3).5H_2O$), hydrated forms of $MgCO_3$, and other components (*e.g.* $Al(OH)_3$), depending on the reaction conditions. These Mg containing phases are typically present in minor amounts in PC binder due to its relatively low Mg content. Non-PC binders such as alkali-activated granulated blast furnace slag, can contain higher quantities of Mg-containing phases due to the higher Mg content in blast furnace slag than PC clinker. However, these are currently niche/used in small quantities globally, and so today provide little opportunity for CO_2 uptake.

Indirect Carbonation

Indirect carbonation is also aqueous and fundamentally similar to the reactions described above, however the process is conducted over multiple stages (Sanna, et al., 2014). Usually this includes an initial stage involving the reaction of CO_2 with an aqueous solution that has high affinity for CO_2 (*e.g.* NaOH, KOH) to form aqueous carbonate species (*i.e.* Na_2CO_3, K_2CO_3). This stream can then be mixed with a source of Ca^{2+}/Mg^{2+} (*e.g.* solid materials) in the same way as the direct process, but now using an aqueous source of CO_2 rather than a gaseous source (Sanna, et al., 2014). Such alkaline solids contribute toward a high pH in solution, and decrease the solubility of $CaCO_3$/$MgCO_3$ causing these species to precipitate, allowing their removal from the slurry (*e.g.* filtration). Nevertheless, the use of additional substances (*e.g.* KOH) during the first stage necessitates subsequent removal for economic recovery. Aqueous carbonate solutions can be used in replacement for water in 'activation' of solid cementitious materials, however this technology is currently niche and not widely applied in practical construction. For these reasons, indirect carbonation is outside the scope of this review.

Natural carbonation of hydrated PC

The preceding sections discuss carbonation of solids via the use of processes and materials to introduce CO_2 into the reacting system. However, cementitious materials are also continually being naturally carbonated due to concentration of CO_2 in the atmosphere. Here we detail this natural carbonation process in more detail, in particular its relevance to material properties, since this is relevant for CO_2 uptake in building materials.

Natural carbonation affects the chemistry of Portland cement binder, but in practice such effects are not necessarily strongly negative. Most studies of direct carbonation of hydrated PC show an initial destabilisation of portlandite and precipitation of calcite, resulting in a decrease in porosity and thus possibly improved compressive strength. At low carbonation extents, this can manifest in the precipitation of a less permeable calcite layer at the surface and actually improve durability, by better protecting the internal concrete from other phenomena such as leaching and/or ingress of aggressive species (*e.g.* Cl). However, high carbonation extents lead to significant destabilisation of the binding C-S-H phase (see section 4.1) and an increase in porosity, which increases permeability and thus reduces durability.

These effects can be seen in Figure 5-1, which shows the thermodynamically stable phases upon progressive carbonation of a hydrated PC wherein 90% of its PC clinker has reacted with water (which is typically reached by ~1 year of hydration). As hydrated PC carbonates, the portlandite present in the system is preferentially destabilised leading to precipitation of calcite. Other phases such as C-S-H and ettringite destabilise later. Experimental carbonation studies report confirm these modelling results, that calcite and amorphous aluminosilicate gel stabilises at extreme carbonation exposure (Zajac, et al., 2020).

In practice, carbonation only occurs on the external surface(s) of concrete, and here the surface becomes covered by dense layers of calcite. However, carbonation does often occur internally if cracks are present to expose inner parts of the concrete cover. Thus carbonation in itself is not usually a major durability concern on its own, but rather becomes one when it is combined with significant cracking and presence of additional aggressive species, most notably Cl, which is a steel corrosion-inducing agent. Hence there is uptake of CO_2 over the lifetime of a concrete structure (Xi, et al., 2016), which occurs from external surface(s) of cement approximately following an inverse square relationship over time (Hills, et al., 2015). More highly porous applications of cement (*e.g.* mortars) carbonate at a faster rate than less porous applications (e.g. self-compacting concrete) and those not exposed to atmospheric CO_2 (*e.g.* foundation*s*).

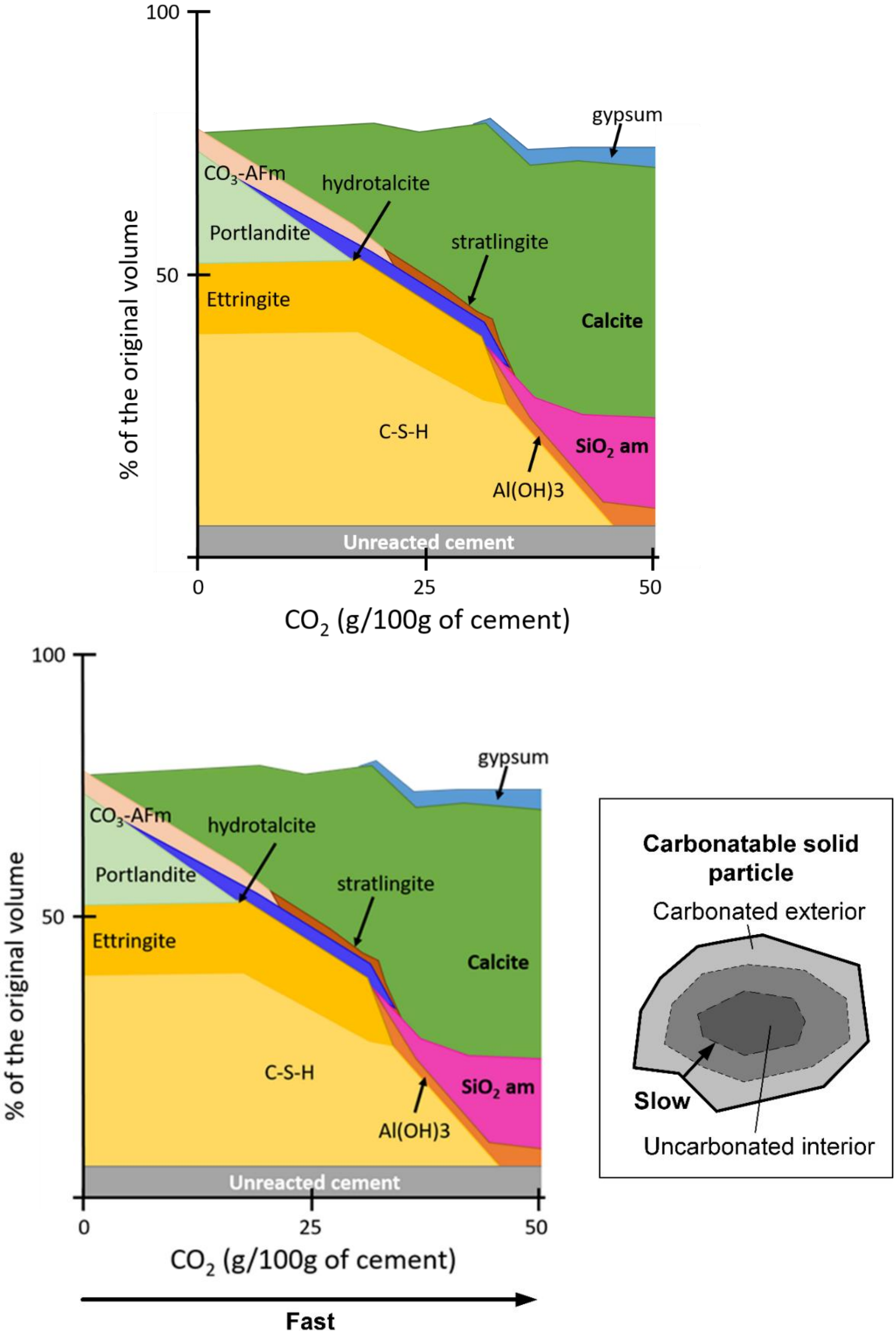

Figure 5-1: Schematic of representative changes in the phase assemblage during carbonation of a white PC w/b = 0.5 and degree of hydration 90%. The undamaged cement paste is shown on the left-hand side, moving to the right as more CO_2 reacts with the hydrates. Adapted from (Greve-Dierfeld, et al., 2020).

5.2 Carbonation during Curing

Setting and hardening of cement can also involve CO_2, although usually this is *via* either: (i) addition of fine limestone as a reactive filler (*e.g.* in CEM II/LL) and/or (ii) atmospheric CO_2 at ambient conditions, though the concentration of CO_2 is typically too low to significantly affect the curing process. However, if curing is performed in environments with high CO_2 concentrations, carbonation can be significant, leading to moderate amounts of carbonation during curing. This is most often achieved by injection of CO_2 into the wet paste before setting, or by curing concrete within a sealed chamber containing CO_2.

Such possibilities are being explored by a number of different companies, with several offering proprietary technologies for curing with accelerated carbonation. For instance, Carbon Cure offers a technology that was initially only available for the pre-cast market, but has been developed toward injection of CO_2 into ready-mix concrete during the batching process (Carboncure, 2017), including at the customer's own site. The technology is available at scale with more than 760,000 m^3 treated. From a technical perspective, this technology acts as a strength accelerator, since the gaseous CO_2 dissolves and reacts rapidly with the PC clinker phases, promoting the formation of carbonated hydrate phases and enhancing the early mechanical properties of the concrete (Monkman, et al., 2016) (Monkman & MacDonald, 2017). Adding CO_2 in this way reduces the amount of fine limestone that may be added as a reactive filler, to limit the overall content of CO_2 in the system so as to not lead to deleterious effects on material properties. By increasing the early strength development, this technology allows use of less PC clinker for a given application and thus can be expected to lead to consequent modest reductions in CO_2 ($\sim$5 %) (Majcher, 2015). The company has observed no adverse effects upon addition of Al-Si-based SCMs or for any other admixtures (CarbonCure, n.d.), but we note that its use requires the overall CO_2 content in the concrete to be managed. The company asserts this technology leads to a reduction in CO_2 emissions of $\sim$15 kg/m^3 of cement laid, which corresponds to $\sim$47 kg/tonne (depending on composition) (CarbonCure, n.d.). Further details are available from CarbonCure (Monkman, 2017).

A somewhat different approach is to modify the underlying chemistry of the cement, allowing significantly higher uptake of CO_2. This is an approach championed by the US-based company Solidia Technologies who have developed a carbonatable calcium silicate clinker based cement, based on synthetic calcium silicate clinker. Solidia claim their composition allows CO_2 uptake of $\sim$250-300 kg/tonne of clinker during curing (DeChristofaro, et al., 2017). Other advantages include the lower kiln temperature required to form the calcium silicate clinker, and the lower fraction of limestone in the raw meal (from 70 to 45 wt%) which collectively lower the fuel requirement by $\sim$30%. Overall, the total reduction equates to $\sim$30% of the CO_2 emissions, suggesting an intensity of around 570 kg/tonne of clinker (ZKG International Staff, 2014). There have been recent improvements to ensure more homogenous setting (ZKG International Staff, 2014), and the mixtures can accommodate additives (*e.g.* fillers, SCMs). This technology is clearly well suited to pre-cast applications, where curing chambers could be modified to allow a high CO_2 atmosphere. It is notable that LafargeHolcim are involved in the efforts to commercialise the process, which increases the likelihood of more rapid commercial deployment. Further work to commercialise the technology is ongoing, with a recent presentation (Meyer, et al., 2018) discussing the development of a 4th pilot plant, with ongoing trials of the long-term durability of materials produced using the Solidia cement, including more than 50 trials worldwide, and a European Technical Assessment "ongoing" as of 2018.

Another US-based start-up, CO_2Concrete, a spin-off from UCLA, currently at demonstration scale, is developing technology to form carbonate precast PC concrete blocks with denser microstructures compared to common PC concrete blocks, resulting in improved mechanical properties and lower porosity. Based on personal communication with the company (Sant, 2020), they are developing a process to control the extent of carbonation so that only the outer layer of the precast component is carbonated, to allow for the potential to produce steel reinforced precast concrete blocks, where the inner layer of the concrete is uncarbonated. This is important since completely carbonated precast blocks can only be used for unreinforced applications, because the pH of the concrete cover is too low to create passivating corrosion conditions. The market for precast blocks is currently relatively minor in Europe (~28% of concrete demand, though clearly a large overall amount), although can be expected to grow in the future alongside greater use of modular and digital construction (Favier, et al., 2018).

6.0 Material Feedstocks for Carbonation

This section details materials identified during the review that are suitable for carbonation and use as building materials (i.e. to produce aggregates via accelerated carbonation). For the purposes of discussion, these have been categorised as being either Portland-based cementitious materials (PCMs) or non-Portland cementitious materials (NPCMs) (with this section also including miscellaneous other wastes/residues). A ternary diagram summarising the composition of these materials is presented in Figure 6-1. In this figure, each material is normalised to the cumulative content of the main cementitious oxides (*i.e.* CaO, MgO, Al_2O_3, Fe_2O_3, and SiO_2), which typically accounted for the majority of the composition (typically ∼80-95 wt%). Although this shifts the compositions of the materials by neglecting other minor species, it allows convenient comparison of the major components of most interest in building materials, since these are the main cementitious components.

Firstly, a discussion will be made of each of the potentially carbonatable materials in turn, including their potential for other uses which may preclude carbonation. After this discussion, the theoretical uptake of CO_2 will be discussed for each material, with subsequent consideration of the practically achievable CO_2 uptake. This section in general only discusses the properties of the materials, it does not aim to comprehensively discuss the quantities available, markets, etc, which are discussed in detail in sections 7.0 and 10.0 respectively.

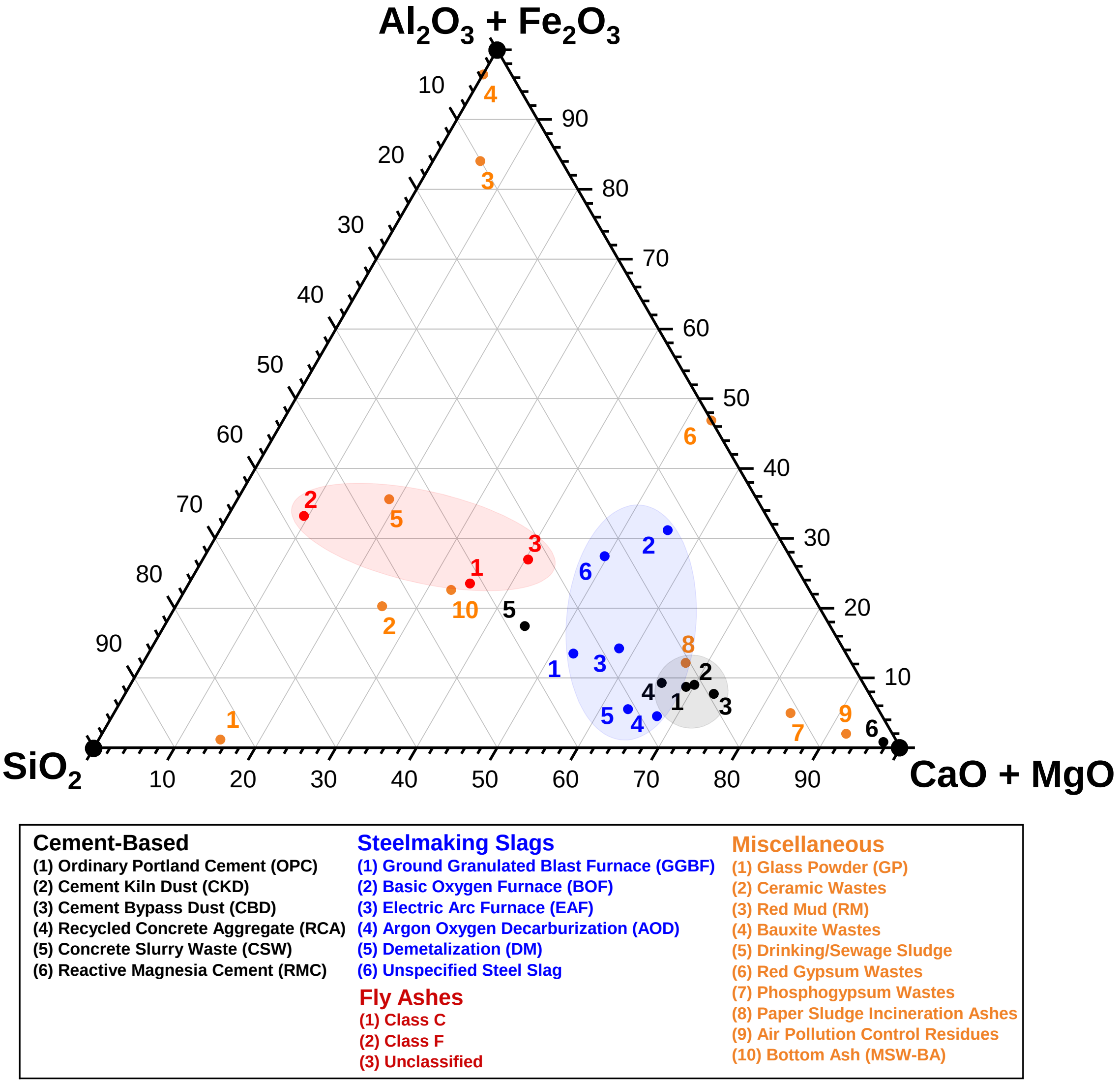

Figure 6-1: Ternary diagram showing the composition of materials reviewed in this study, with their contents expressed as (CaO + MgO), (Al_2O_3 + Fe_2O_3) and SiO_2. The composition for each material was normalised to the cumulative content of these species, which typically constituted 80-95 wt%.

6.1 Portland Cement-based Materials (PCMs)

As discussed in section 4.2, two major dusts are produced during the production of Portland Cement. These come from different parts of the process, and have different compositions. It is common practice to recycle as much of the dust as possible within the cement production process. This is because significant energy has been used to calcine the dusts, and those that are mainly CaO and $CaCO_3$ require additional limestone to replace them if they leave the process. This internal recycle limits somewhat the potential for a subsequent accelerated carbonation process to produce aggregate to be applied, as detailed below. Other materials suitable for carbonation, including construction wastes, are also discussed below.

Cement Kiln Dusts (CKDs)

Cement kiln dust (CKD) is generated during the production of cement, and consists of small particles of partially calcined meal that become entrained in the exhaust gases rising through the preheater cyclones. These are removed (*e.g.* filter, cyclone, electrostatic precipitation) from the gas stream and are typically fed back into the process to supplement the raw meal and/or clinker (Schorcht, et al., 2013). Accordingly, the average composition of CKD Table 6-1) approximates that of PC, with broadly similar values for the major oxides such as CaO (~53.7 wt%), SiO_2 (~13.0 wt%), Al_2O_3 (~4.2 wt%) and Fe_2O_3 (~2.2 wt%). Nonetheless, the quantity of contaminants in CKD is appreciably higher, with the values for K_2O (~2.9 wt%), Na_2O (~1.1 wt%), and SO_3 (~5.4 wt%) significantly exceeding the corresponding amounts in PC. Another difference is the higher Loss on Ignition (LOI) (~18.6 wt%) which suggests a higher quantity of uncalcined $CaCO_3$ and water. Phase compositions of CKD demonstrate a low degree of clinkering since they do not get heated to the high temperatures prevailing in the kiln, with the predominant phases lime and calcite (Abdel-Gawwad, et al., 2019) and a relatively low amount of free CaO (~9.4 wt%) available for carbonation. As detailed previously, CKD was produced in higher quantities but improvements in modern cement plants means the vast majority is now reintroduced into the process alongside the raw meal feed (offering little value/opportunity for carbonation technologies).

Cement Bypass Dusts (CBDs)

Cement bypass dust (CBD) is generated during the purging of undesirable contaminants from the process (namely K, Na, Cl and S) through a bypass located in the riser of the calciner. In the literature, the terms CKD and CBD are often mistakenly used interchangeably leading to some uncertainty about the materials studied by a given author. Regardless, the composition of CBD is generally between that of PC and CKD Table 6-1), with intermediate values for CaO (~50.4 wt%), SiO_2 (~10.9 wt%), Al_2O_3 (~3.3 wt%) and Fe_2O_3 (~2.6 wt%). The corresponding values for K_2O (~11.2 wt%), Na_2O (~1.6 wt%), SO_3 (~7.0 wt%) and Cl (~9.9 wt%) in CBD are significantly higher than these values in CKD, due to the concentrations of these species in the bypass. Similar contamination values for chlorine have been reported in literature (~7.5-21.9 wt% reported by (Lanzerstorfer, 2016)) and during our interviews with industry who reported an absolute maximum of 10 wt% Cl in CBD at a plant operated by Vicat (but typically much lower depending on type of waste fuels) (Carey (Carbon8), 2020) (Barnes-Davin (Vicat), 2020). There is also generally a much higher proportion of free lime (~38.0 wt%) available in CBD, which is in agreement with interviewed industrial operators who suggested an average free CaO content ranging between 10-40 wt% (Discussion, 2020). Similar to CKD, improvements in modern cement plants have reduced the generation of CBD. Rapid cooling of the bypass condenses small particles of contaminants (*e.g.* KCl, NaCl, K_2SO_4, Na_2SO_4, $CaSO_4$, *etc.*) which can be more efficiently removed, allowing a greater proportion of the entrained solids to be returned to the process (Bowden, 2017).

Concrete Slurry Waste (CSW)

Another waste stream is that of concrete slurry waste (CSW), which is often generated from ready-mixed concrete. At batching plants, cement is mixed with sand, water and aggregates to form fresh concrete, which is then loaded into trucks and delivered to construction sites (Kaliyavaradhan, et al., 2020). This process frequently results in excess fresh concrete that cannot be fully utilised at the construction site and must be returned to the batch plant (*e.g.* incorrect formulation, poor workmanship, ordered surplus, logistical issues, *etc.*) (Xuan, et al., 2018). At the plant, this excess mixture can be sprayed before setting to recover the aggregates for reuse in subsequent batches, with the washings containing cement and sand forming a slurry. The solids can be removed from this slurry by initial sedimentation followed by filtration *via* a filter press to form a loose cake referred to as CSW (Xuan, et al., 2018). As seen in Table 6-1 the composition of the cake is similar to PC but contains elevated amounts of SiO_2 (~32.6 wt%), Al_2O_3 (~8.6 wt%) and Fe_2O_3 (~6.3 wt%) consistent with the materials included during mixing (*e.g.* sand, aggregates, fly ashes, slags). In addition to these there is a substantial quantity of CaO (~37.0 wt%) and minor amounts of MgO (~1.5 wt%) that could be utilised for carbonation (with these mostly present as $Ca(OH)_2$ and $Mg(OH)_2$ due to extensive hydration during washing). At present, CSW is widely considered a hazardous waste due to its alkalinity ($pH \geq 11.5$) (including in UK, Spain, and Japan) and is only processed into low value materials (*e.g.* road base, recycled aggregates, fillers, soil stabilisers) or landfilled after sufficient treatment(s) (Xuan, et al., 2016). Based on the above, CSW represents an underutilised material with some potential for carbonation to produce building materials with reduced net CO_2 emissions.

Recycled Concrete Aggregates (RCAs)

Further opportunities are offered by end-of-life materials such as recycled concrete aggregates (RCA), which can be recovered from demolition wastes and separated into fine (≤ 3 mm) and coarse (~3-20 mm) fractions. These can then replace natural aggregates (*e.g.* sand, gravel, crushed rock) in subsequent construction (Xuan, et al., 2016). However, the replacement of primary aggregates by recycled aggregates in structural concrete is limited due to the latter's inherent content of cement paste (hydrated and partially carbonated) and/or unhydrated Portland cement clinker. This is for multiple reasons: (i) workability is decreased, meaning increased water addition into RA-containing concrete and/or additional superplasticisers are needed; and (ii) since recycled aggregates have lower compressive strengths than primary aggregates (Bravo, et al., 2015) (Xiao, et al., 2012), their use in concrete does not necessarily lead to a reduction in life cycle greenhouse gas emissions.

The majority of authors in literature study materials formulated (from cement, water and aggregates) to resemble RCA, rather than actual field-sampled RCAs. This practise is presumably due to the low material costs, sourcing convenience and repeatability. Studies of actual RCA from a construction waste recycling plant (Hong Kong) show distinct compositions of CaO (~17.9 wt%), SiO_2 (~57.4 wt%), Al_2O_3 (~9.6 wt%) and K_2O (~3.4 wt%) (Xuan, et al., 2016). As with CSW, this was considered due to the inclusion of sand and aggregates within the cement mixture, which become physically incorporated and alter the composition of RCA from PC. The field-sampled RCA also exhibited somewhat increased LOI (~5.6 wt%) (Xuan, et al., 2016), which suggested a degree of carbonation to $CaCO_3$, hydration to $Ca(OH)_2$ and absorbed water.

Overall, RCAs show considerable promise as a carbonated building material, particularly since these materials are already being incorporated into concrete. However, unlike for previously discussed materials (*i.e.* CKD, CBD, CSW) which are dusts, the opportunities for RCA need to considered against the potential processing costs for comminution (*e.g.* crushing, grinding, milling) and grading.

Table 6-1. Composition and fraction of Carbonatable CaO in a variety of Portland Cement-Based Materials.

Source	Composition, X (wt%)											
	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	P_2O_5	SO_3	Cl	LOI	'Carbonatable' CaO[c]
Portland Cement (PC)												
(Pu, et al., 2021)	63.6	19.3	3.8	3.1	1.5	0.7	-	-	-	-	2.5	-
(Chinzorigt, et al., 2020)	60.1	22.0	6.6	2.8	3.3	-	-	-	2.1	-	2.6	55.3
(Carevic, et al., 2019)	60.4	21.0	5.3	2.4	2.4	0.7	0.2	-	3.6	-	3.5	53.4
(Xuan, et al., 2016)	64.5	19.6	3.8	3.1	1.5	0.7		-	5.4	-	1.1	59.3
(Kurda, et al., 2019)	63.5	19.5	5.0	3.3	1.3	0.6	0.2	-	3.3	0.0	-	-
(Zhan, et al., 2016)	63.2	19.6	7.3	3.3	2.1	0.3	0.1	-	2.0	-	2.3	58.9
(Mi, et al., 2021)	64.7	21.6	4.3	3.1	1.3	0.8	0.2	0.1	2.6	-	-	-
(Wang, et al., 2018)	65.7	19.0	4.8	-	1.4	0.8	0.2	0.1	-	-	2.5	-
(Siriruang, et al., 2016)	65.5	18.9	5.5	3.3	1.2	0.3	0.2	-	2.9	-	0.0	63.5
(Meng, et al., 2019)	64.7	21.8	4.6	3.6	2.8	-	-	-	-	-	2.6	-
(Thomas, et al., 2013)	69.6	18.6	3.1	2.7	1.2	0.5	-	-	3.2	-	-	-
(Nedeljkovic, et al., 2018)[b]	62.2	19.6	4.8	3.0	1.8	0.6	0.4	0.2	1.4	-	2.8	57.7
(He, et al., 2019)	65.6	21.5	5.9	3.8	1.6	0.8	-	-	-	-	0.7	-
(Zajac, et al., 2020)	65.9	21.7	5.8	2.5	1.9	1.1	0.2	0.1	0.6	-	0.1	65.4
(Mo, et al., 2017)	64.7	19.4	4.4	3.0	0.9	0.5	0.2		2.2	-	2.4	60.1
Average	**64.3**	**20.2**	**5.0**	**3.1**	**1.7**	**0.6**	**0.2**	**0.1**	**2.7**	**0.0**	**1.9**	**59.2**
Standard Deviation	**2.2**	**1.2**	**1.1**	**0.4**	**0.6**	**0.2**	**0.1**	**0.0**	**1.2**	**0.0**	**1.1**	**3.7**
Cement Kiln Dust (CKD)												
(Gunning, et al., 2010)	46.2	16.4	4.6	2.9	1.5	3.9	0.5	0.1	22.3	-	-	-
(Khater, 2019)	51.9	8.3	2.8	2.1	0.6	3.4	2.6	0.1	2.1	6.1	19.6	25.5
(Sharma & Goyal, 2018)	39.4	15.0	3.2	2.3	1.8	3.1	1.4	-	5.7	3.8	19.0	11.2
(Siriwardena, et al., 2015)	37.1	11.7	2.2	2.9	0.9	7.2	0.9	-	7.7	0.6	29.1	0.0
(Siriwardena, et al., 2015)	61.2	14.6	4.5	2.1	3.8	3.5	0.8	-	10.6	-	23.4	24.0
(Bagheri, et al., 2020)	44.9	11.7	3.3	2.4	0.8	0.5	0.3	-	0.0	-	36.0	0.0
(Al-Rezaiqi, et al., 2018)	66.6	12.5	10.4	3.1	1.5	0.1	0.5	-		1.1	5.0	60.2
(Abdel-Ghani, et al., 2018)	53.3	9.5	2.5	2.6	1.7	3.1	1.8	0.2	4.4	4.6	15.1	31.0
(Najim, et al., 2014)	60.5	18.9	4.1	4.3	1.9	1.5	1.2	-	2.0	0.4	17.5	36.8
(Baghriche, et al., 2020)	58.1	14.3	7.1	5.7	9.2	0.4	0.7	0.6	1.3	-	-	-
(Saleh, et al., 2020)	55.2	11.4	3.5	2.3	1.1	4.2	-	-	6.3	4.2	-	-
(Amadi & Osu, 2018)	67.7	11.5	3.1	3.6	-	1.1	-	-	0.8	-	8.7	56.1
(Heikal, et al., 2020)	56.1	13.5	3.3	2.9	1.7	5.9	1.8	-	1.7	-	13.0	38.3
Average	**53.7**	**13.0**	**4.2**	**3.0**	**2.2**	**2.9**	**1.1**	**0.2**	**5.4**	**3.0**	**18.6**	**28.3**
Standard Deviation	**9.2**	**2.7**	**2.2**	**1.0**	**2.3**	**2.1**	**0.7**	**0.2**	**5.9**	**2.1**	**8.7**	**19.7**
Cement Bypass Dust (CBD)												
(Gunning, et al., 2010)	66.3	17.8	4.4	2.7	1.1	1.7	0.3	0.1	4.6	-	-	-
(Kalina, et al., 2018)	45.7	11.9	4.2	2.4	0.9	16.9	0.4	-	7.2	10.1	-	-
(Abdel-Gawwad, et al., 2020)	53.0	6.5	2.1	3.1	0.9	4.2	2.9	0.2	10.6	9.7	6.5	37.3
(Sultan, et al., 2018)	51.6	9.9	2.3	2.0	2.3	4.3	1.7	-	7.5	7.7	10.1	33.5
(Hanein, et al., 2020) [a]	54.9	15.2	4.1	2.4	2.9	11.7	0.6	-	2.3	6.0	-	-
(Czapik, et al., 2020) [a]	52.2	15.4	3.4	1.8	1.3	6.0	0.3	-	1.7	3.5	14.4	32.7
(Araizi, et al., 2016)	68.0	7.7	2.8	2.6	0.8	4.8	-	0.1	9.3	3.0	0.4	61.0
(Stevulova, et al., 2021)	7.1	1.9	0.5	0.4	0.0	42.8	5.4	0.0	11.1	33.7	0.5	0.0
(Abdel-Gawwad, et al., 2019)	52.9	7.3	2.4	3.3	0.6	5.2	1.0	-	14.4	5.5	7.3	33.5
(Kadhim, et al., 2020)	52.4	15.0	6.8	4.9	-	14.2	-	-	1.3	-	-	-
Average	**50.4**	**10.9**	**3.3**	**2.6**	**1.2**	**11.2**	**1.6**	**0.1**	**7.0**	**9.9**	**6.5**	**33.0**
Standard Deviation	**15.8**	**4.8**	**1.6**	**1.1**	**0.8**	**11.5**	**1.7**	**0.0**	**4.2**	**9.3**	**5.0**	**17.8**
Concrete Slurry Waste (CSW)												
(Kaliyavaradhan, et al., 2020)	52.8	27.3	8.8	3.8	3.1	0.7	-	-	2.4	-	-	- [d]
(Xuan, et al., 2016)	35.5	32.5	8.3	6.8	1.2	1.6	-	-	3.1	-	10.0	-
(Xuan, et al., 2016)	35.8	31.2	8.0	6.4	1.1	1.5	-	-	2.9	-	12.2	-
(Xuan, et al., 2016)	36.9	32.8	8.2	6.7	1.9	1.6	-	-	2.7	-	8.6	-
(Xuan, et al., 2016)	35.3	33.6	8.7	6.9	1.7	1.7	-	-	3.0	-	8.6	-
(Xuan, et al., 2016)	32.4	35.2	9.2	6.8	1.4	1.8	-	-	2.8	-	9.9	-
(Xuan, et al., 2016)	33.7	34.5	9.1	6.0	1.1	1.9	-	-	2.8	-	10.4	-
(Xuan, et al., 2016)	37.5	33.2	9.0	6.3	1.4	1.7	-	-	2.4	-	8.0	-
(Xuan, et al., 2016)	32.8	33.7	9.1	6.7	1.5	1.6	-	-	3.7	-	10.4	-
(Xuan, et al., 2016)	37.4	32.5	8.5	6.7	1.3	1.6	-	-	2.7	-	9.0	-
(Xuan, et al., 2016)	36.8	32.2	8.3	6.6	1.3	1.5	-	-	3.4	-	9.3	-
Average	**37.0**	**32.6**	**8.6**	**6.3**	**1.5**	**1.6**	**-**	**-**	**2.9**	**-**	**9.6**	**-**
Standard Deviation	**5.3**	**2.0**	**0.4**	**0.8**	**0.5**	**0.3**	**-**	**-**	**0.4**	**-**	**1.2**	**-**

[a] Calculated based on elemental composition assuming complete formation of the above oxidised species

[b] Reported S content as total, converted with assumption of complete formation of SO_3

[c] 'Carbonatable' CaO content calculated from Eqn. 6.3

[d] Calculations not performed due to extensive hydration of CaO to $Ca(OH)_2$

Non-Portland Cementitious Materials (NPCMs)

There are a large number of other materials available for carbonation; these can (to a greater or lesser extent) replace cement clinker as a SCM. As discussed in section 6.1, where a material (in that case cement kiln dust) can act as a SCM, it should be used in this manner, rather than being a candidate for accelerated carbonation.

Fly Ash

Fly ashes (FAs) are light solids that become entrained in exhaust gases during combustion of solid fuels such as coals, biomass, and municipal solid wastes (MSW). These ashes are removed from the flue (*e.g.* filtration, cyclone, electrostatic precipitation) before release to atmosphere, generating wastes that can be ideally suited as SCMs in cements. Current international standards (ASTM C618) identify three classes of FA according to their chemical composition and material properties (namely Class C, F and N) (ASTM C618-19). Materials reviewed in this work have been classed by composition and are summarised in Table 6-2.

Class C FA is principally characterised by high CaO content (≥18 wt%), and are typically generated from the combustion of lower grades of coal (*e.g.* lignite) (ASTM C618-19). Examination of Table 4-1 shows these FAs have large quantities of CaO (∼27.8 wt%) and MgO (∼4.0 wt%) meaning they offer considerable potential for carbonation, whilst also having adequate amounts of SiO_2 (∼37.9 wt%), Al_2O_3 (∼15.6 wt%) and Fe_2O_3 (∼5.8 wt%) to serve as SCMs. Contrastingly, FAs of Class F are typically produced by combustion of high grades of coal (*e.g.* anthracite, bituminous) which leads to characteristically low CaO contents (<18 wt%) (ASTM C618-19). Indeed, Table 6-2 shows significantly reduced potential for carbonation of these FAs due to reduced CaO (∼7.1 wt%) and MgO (∼1.7 wt%), however they still serve as effective SCMs due to their higher amounts of SiO_2 (∼53.9 wt%), Al_2O_3 (∼23.9 wt%) and Fe_2O_3 (∼7.3 wt%).

In order to comply with the international standards for addition into cementitious materials, the contaminants for FAs of both Class C and F must be within reasonable limits (explicitly SO_3 ≤ 5 wt%) (ASTM C618-19). This explains the unclassified FAs in Table 6-2, which can exhibit excessive contamination by K_2O (∼2.8 wt%), Na_2O (∼5.7 wt%), SO_3 (∼7.6 wt%) and Cl (∼7.1 wt%), meaning they fail to meet the criteria for Class C or F despite high amounts of CaO (∼23.7 wt%) and MgO (∼4.8 wt%). The majority of the Unclassified FAs in Table 6-2 resulted from combustion of lignite coal or MSW.

Overall, FAs offer excellent potential for carbonation, as well as being established SCMs for integration within cements (designated CEM II). Class C FA offers the highest potential for carbonation due to its high CaO and MgO content. It can be sourced relatively easily from combustion of MSW. In contrast, Class F has lower CaO and MgO content, and is produced from combustion of hard coals, which are gradually being phased out in many countries globally (BEIS, 2017). A concern with FAs derived from MSW are their higher levels of contaminants which often excludes them from being classified as Class C or F. However, they are still suitable for carbonation.

Carbonating these FAs will alter their phase composition, which may stabilise the contaminants in low solubility solid phases. However, these phase transitions are not yet well studied, and thus it is currently unclear to what extent FAs of different compositions should be carbonated to optimise the stabilisation of these contaminants, as a waste treatment technology. In any case, **it is clear that FAs that can be used as SCMs should be used for that purpose rather than carbonated**, since this directly leads to a reduction in clinker ratio, often better material properties, and thus lower CO_2 emissions. Carbonation of FAs should thus only be considered where their incorporation into cement is not possible (*e.g.* due to excessive contamination). Section 7.2 discusses the trade-off in economic terms.

Steelmaking Slags

Various slags are generated during steelmaking processes such as in blast furnaces (BF), basic oxygen furnaces (BOF), electric arc furnaces (EAF). They can be used as carbonatable materials, while only the Blast Furnace Slag (BFS) is used as an SCM. In most of these processes, the metal ores are melted at high temperature with the gangue (*e.g.* silicates, aluminates) and flux materials (*e.g.* CaO) forming a slag phase that removes impurities from the metallic product. If rapidly cooled by quenching, slags form glassy cementitious materials that are established SCMs due to their good reactivity and composition. This section will mainly focus on ground granulated blast furnace slag (GGBFS) and basic-oxygen furnace slag (BOFS), since these are the most important steelmaking slags, and since steelmaking slags are the most important of all metallurgical slags globally for use in cementitious materials.

Slags from ironmaking in the BF often undergo additional processing (*i.e.* grinding, rapid cooling) to improve the physical properties of the material and so produce GGBFS. Due to the presence of gangue and flux, this material contains a significant amount of CaO (~44.1 wt%) and MgO (~6.1 wt%), meaning almost half the content by mass can be available for carbonation. Furthermore, the other major components are also present and can contribute to cement as SCMs, with particularly high amounts of SiO_2 (~32.2 wt%) and Al_2O_3 (~12.3 wt%). Contrastingly, there is comparatively little Fe_2O_3 (~0.52 wt%), due to the intended separation of the metallic product.

Additionally, contamination of the aforementioned compounds is reduced compared to many other materials, meaning few detrimental effects when mixed in cement. Slags produced during steelmaking generate BOFS with practically identical amounts of CaO (~43.8 wt%) and MgO (~7.0 wt%), but with differences in composition for the other major oxides. The amounts of SiO_2 (~12.1 wt%) and Al_2O_3 (~2.9 wt%) are significantly reduced likely due to their removal in the BF, whereas considerably more Fe_2O_3 is purged as BOFS (~25.6 wt%) for removal of contaminants from the steel product. Other types of steelmaking slags such as those listed in Table 6-3 offer roughly the same compositions to those discussed for GGBFS or BOFS.

Here it is important to distinguish rapidly cooled slags, which comprise reactive glassy phases, from slowly (air) cooled slags, which comprise crystalline phases, since the reactivity of the latter material is poor. Thus rapidly cooled slags can be used as SCMs whereas slowly cooled slags can be used as fillers (i.e. aggregate). Similarly to FA, the reactive glassy slags that are rapidly cooled should be used as SCMs to replace PC clinker and not carbonated, whereas the poorly reactive crystalline air cooled slags are suitable for carbonation prior to subsequent use.

Generally all steelmaking slags offer excellent potential for carbonation due to their high quantities of CaO and MgO. Furthermore, slags are an unavoidable by-product of steelmaking, meaning their long-term availability is more reliable compared to FAs (which are increasingly scarce in some regions due to reduced use of solid fuels). The amount of steel slag available is likely to decrease in the future, as the industry transitions towards low carbon direct reduction pathways, and higher scrap recycling rates.

Table 6-2 Review of the compositions of Fly Ashes (FA) studied in Literature

Source	Composition, X (wt%)											
	CaO	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**MgO**	**K_2O**	**Na_2O**	**P_2O_5**	**SO_3**	**Cl**	**LOI**	**'Carbonatable' CaO[c]**
Fly Ash (Class C)												
(Gunning, et al., 2010)	32.1	32.4	15.8	3.4	3.4	0.8	1.8	2.9	3.6	-	-	-
(Ukwattage, et al., 2015)	18.5	54.0	9.5	3.0	5.5	1.2	2.1	-	2.5	-	-	-
(Chang, et al., 2011)	38.8	34.9	15.8	2.0	5.6	-	-	-	0.5	-	-	-
(Siriwardena, et al., 2015)	22.8	38.6	19.2	5.7	4.5	0.6	1.8	-	2.5	-	0.6	20.3
(Siriruang, et al., 2016)	19.3	34.5	19.8	15.0	1.9	2.3	1.1	-	4.1	-	0.5	15.8
(Cwik, et al., 2018)	35.3	33.1	13.8	5.7	3.2	1.0	1.3	0.4	5.0	-	-	-
Average	**27.8**	**37.9**	**15.6**	**5.8**	**4.0**	**1.2**	**1.6**	**1.6**	**3.0**	**-**	**0.5**	**18.0**
Standard Deviation	**7.9**	**7.5**	**3.4**	**4.3**	**1.3**	**0.6**	**0.4**	**1.3**	**1.4**	**-**	**0.1**	**2.2**
Fly Ash (Class F)												
(Dung, et al., 2020)	1.2	58.6	30.4	4.7	0.8	3.5	-	-	0.6	-	0.6	0.0
(Gunning, et al., 2010)	1.3	55.6	23.0	13.8	1.0	2.7	0.5	0.5	0.1	-	-	-
(Muriithi, et al., 2013)	9.2	51.2	26.0	2.4	2.4	0.8	0.5	0.7	0.4	-	-	-
(Wu, et al., 2018)	3.4	52.2	22.2	13.5	0.9	2.6	-	0.1	2.2	0.0	1.0	0.6
(Carevic, et al., 2019)	7.6	58.2	20.2	5.3	2.0	1.5	0.5	0.0	2.2	-	2.1	3.4
(Mastali, et al., 2018)	1.0	60.8	22.7	7.6	2.2	2.7	1.5	-	-	-	-	-
(Kurda, et al., 2019)	3.6	57.8	20.9	7.4	1.0	1.7	1.0	-	0.6	-	3.8	0.0
(Wang, et al., 2019)	15.6	52.2	20.1	-	2.6	-	1.9	-	-	-	-	-
(Liu, et al., 2020)	15.4	46.0	20.2	9.4	1.9	1.4	3.9	-	1.8	-	-	-
(Wang, et al., 2019)	15.6	52.2	20.1	3.1	2.7	-	1.9	-	-	-	-	-
(Teixeira, et al., 2019)	3.3	54.1	26.4	6.1	1.6	1.6	0.5	0.8	1.0	-	2.7	0.0
(Huseien, et al., 2019)	5.2	57.2	28.8	3.7	1.5	0.9	0.1	-	0.1	-	0.1	5.0
(Nedeljkovic, et al., 2018)[b]	4.8	56.8	23.8	7.2	1.5	1.6	0.8	0.5	0.3	-	1.2	3.1
(Younsi, et al., 2011)	5.2	55.3	25.2	6.4	-	-	-	-	0.5	-	-	-
(Ji, et al., 2017)	16.4	42.8	19.2	9.1	1.2	1.5	1.7	-	1.9	-	-	-
(Siriruang, et al., 2016)	16.5	35.7	20.4	15.5	2.0	2.4	1.2	-	4.3	-	0.5	12.9
(Boumaaza, et al., 2020)	5.1	83.5	-	-	-	1.7	1.4	0.0	0.6	-	5.0	0.0
(Mo, et al., 2017)	3.3	48.1	30.2	4.6	2.4	1.2	0.7	-	0.7	-	8.8	0.0
(Zajac, et al., 2020)	5.4	52.3	24.9	6.6	1.7	1.6	0.6	0.9	0.3	-	4.3	0.0
(Mo, et al., 2015)	3.3	48.1	30.2	4.6	2.4	1.2	0.7	-	0.7	-	8.8	0.0
Average	**7.1**	**53.9**	**23.9**	**7.3**	**1.8**	**1.8**	**1.1**	**0.4**	**1.1**	**0.0**	**3.3**	**2.1**
Standard Deviation	**5.4**	**9.0**	**3.7**	**3.6**	**0.6**	**0.7**	**0.9**	**0.3**	**1.1**	**0.0**	**2.9**	**3.6**
Fly Ash (Unclassified)												
(Praneeth, et al., 2020)	17.6	39.9	28.2	4.4	1.2	0.7	0.9	0.9	5.1	-	-	-
(Ukwattage, et al., 2013)[a]	35.3	12.2	4.0	24.0	11.7	-	-	-	8.9	-	-	-
(Viet, et al., 2020)	33.1	8.3	4.5	3.7	1.6	5.7	8.6	-	15.5	11.5	-	-
(Viet, et al., 2020)	31.6	7.7	2.0	4.4	1.2	6.1	13.8	-	6.3	20.0	-	-
(Ashraf, et al., 2019)[b]	18.3	10.1	4.1	2.2	1.6	6.5	8.8	1.4	10.9	6.2	20.2	0.0
(Ashraf, et al., 2019)[b]	20.3	18.3	14.5	2.3	6.7	2.2	12.7	3.5	2.0	3.5	18.4	0.0
(Ukwattage, et al., 2015)	12.5	36.0	2.0	16.0	10.7	0.4	4.2	-	12.0	-	-	-
(Ukwattage, et al., 2015)	24.8	13.0	2.1	23.0	13.0	0.4	9.0	-	12.8	-	-	-
(Teixeira, et al., 2019)	27.4	36.0	8.3	4.1	3.6	4.9	0.9	3.2	3.2	0.6	6.3	17.1
(Mazzella, et al., 2016)	32.0	27.3	8.8	6.5	1.9	0.8	0.9	-	2.1	0.9	-	-
(Dananjayan, et al., 2016)	6.7	41.8	18.4	9.2	2.2	1.1	1.4	0.4	3.3	-	14.0	0.0
(Siriruang, et al., 2016)	25.0	26.6	13.6	18.3	2.3	1.8	1.8	-	8.5	-	0.5	18.4
Average	**23.7**	**23.1**	**9.2**	**9.8**	**4.8**	**2.8**	**5.7**	**1.9**	**7.5**	**7.1**	**11.9**	**7.1**
Standard Deviation	**8.5**	**12.5**	**7.8**	**7.9**	**4.3**	**2.4**	**4.8**	**1.2**	**4.4**	**6.8**	**7.4**	**8.7**

[a] Calculated based on elemental composition assuming complete formation of the above oxidised species

[b] Reported S content as total, converted with assumption of complete formation of SO_3

[c] 'Carbonatable' CaO content calculated from Eqn. 6.3

Table 6-3: Review of the compositions of various Steelmaking Slags studied in Literature

Source	**Composition, X (wt%)**											
	CaO	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**MgO**	**K_2O**	**Na_2O**	**P_2O_5**	**SO_3**	**Cl**	**LOI**	**'Carbonatable' CaO[d]**
Basic Oxygen Furnace Slag (BOFS)												
(Jiang & Ling, 2020)	42.1	16.5	3.5	21.7	6.7	-	-	-	-	-	-	-
(Zhang, et al., 2020)	42.0	15.5	3.0	22.5	8.7	-	-	-	-	-	-	-
(Chang, et al., 2012)	38.8	11.7	3.9	32.8	10.4	0.1	0.0	-	-	-	-	-
(Chang, et al., 2012)	51.1	11.2	1.6	24.0	4.2	-	-	-	-	-	-	-
(Chang, et al., 2012)	42.4	12.0	3.0	26.7	9.2	-	-	-	-	-	-	-
(Pan, et al., 2016)	51.1	11.2	1.2	24.0	4.2	-	-	-	0.4	-	-	50.8
(Pan, et al., 2016)	48.2	8.6	-	26.0	-	-	-	-	-	-	-	-
(Librandi, et al., 2019)[a],[b]	51.0	15.0	3.1	20.0	3.5	-	2.0	1.8	0.2	-	-	50.9
(Chang, et al., 2013)	46.5	10.1	1.0	30.2	6.5	0.0		3.2	0.1	-	-	46.4
(Librandi, et al., 2017)	29.7	8.4	4.0	25.6	7.3	0.2	0.2	-	-	-	-	-
(Librandi, et al., 2017)	44.7	12.6	3.3	22.0	9.6	0.3	0.2	-	-	-	-	-
(Chang, et al., 2018)	47.6	14.8	3.4	21.7	6.6	-	-	1.5	0.3	-	-	47.4
(Chang, et al., 2013)	41.2	10.6	2.2	24.4	9.2	0.0	0.0	2.9	0.1	-	-	41.1
(Li, et al., 2018)	36.7	11.8	4.4	36.1	4.5	0.0	0.1	-	0.4	-	-	36.4
Average	**43.8**	**12.1**	**2.9**	**25.6**	**7.0**	**0.1**	**0.4**	**2.4**	**0.2**	**-**	**-**	**45.5**
Standard Deviation	**5.9**	**2.4**	**1.0**	**4.4**	**2.2**	**0.1**	**0.7**	**0.7**	**0.1**	**-**	**-**	**5.2**
Ground Granulated Blast Furnace Slag (GGBFS)												
(Dung, et al., 2020)	45.3	27.2	12.6	0.3	6.9	3.3	-	-	3.9	-	0.9	41.4
(Mo & Panesar, 2013)	37.9	37.2	8.7	0.4	11.4	0.4	0.4	-	2.7	-	0.8	35.0
(Ukwattage, et al., 2017)	42.5	31.9	13.0	0.3	4.8	0.4	-	-	4.0	-	-	39.7
(Wang, et al., 2019)	42.0	33.0	12.0	1.0	6.0	-	-	-	-	-	-	-
(Zhao, et al., 2020)	34.3	35.7	16.5	0.5	9.4	-	-	-	1.7	-	-	33.1
(Huseien, et al., 2019)	51.8	30.8	10.9	0.6	4.6	0.4	0.5	-	0.1	-	0.2	51.5
(Mun & Cho, 2013)	47.2	31.1	13.8	0.4	3.3	0.5	0.2	-	-	-	-	-
(Kim, et al., 2019)	51.7	30.5	11.1	0.6	2.6	-	-	-	-	-	-	-
Average	**44.1**	**32.2**	**12.3**	**0.5**	**6.1**	**1.0**	**0.4**	**-**	**2.5**	**-**	**0.7**	**40.1**
Standard Deviation	**5.8**	**3.0**	**2.1**	**0.2**	**2.8**	**1.2**	**0.1**	**-**	**1.5**	**-**	**0.3**	**6.4**
Argon Oxygen Decarburization Slag (AODS)												
(Salman, et al., 2014)	54.5	34.1	1.1	0.3	8.0	-	-	-	-	-	-	-
(Baciocchi, et al., 2015)	56.4	30.3	1.3	-	2.4	-	-	-	-	-	-	-
(Wang, et al., 2020)	65.8	24.2	1.7	-	-	-	-	0.0	-	-	-	-
(Moon & Choi, 2018)	54.3	17.7	6.4	3.0	9.2	0.2	0.1	-	0.4	-	1.7	51.9
Average	**57.8**	**26.6**	**2.6**	**1.7**	**6.5**	**0.2**	**0.1**	**0.0**	**0.4**	**-**	**1.7**	**51.9**
Standard Deviation	**4.7**	**6.2**	**2.2**	**1.4**	**3.0**	**0.0**	**0.0**	**0.0**	**0.0**	**-**	**0.0**	**0.0**
Electric Arc Furnace Slag (EAFS)												
(Librandi, et al., 2019)[a],[b]	45.0	36.0	3.8	0.6	12.0		0.4	0.2	0.3	-	-	44.8
(Mahoutian & Shao, 2016)	39.1	12.5	6.9	19.5	10.6	0.0	0.0	0.4	-	-	-	-
(Baciocchi, et al., 2015)	49.3	28.1	3.9	4.6	4.1	0.0	0.5	-	-	-	-	-
Average	**44.4**	**25.5**	**4.8**	**8.2**	**8.9**	**0.0**	**0.3**	**0.3**	**0.3**	**-**	**-**	**44.8**
Standard Deviation	**4.2**	**9.8**	**1.4**	**8.1**	**3.4**	**0.0**	**0.2**	**0.1**	**0.0**	**-**	**-**	**0.0**
Demetalization Slag (DMS)												
(Nielsen, et al., 2020) [b]	44.5	29.7	3.9	2.3	10.9	0.2	0.7	0.6	0.4	-	1.0	42.9
(Nielsen, et al., 2020) [b]	47.5	26.5	3.0	0.7	10.5	0.2	0.7	0.6	0.9	-	6.3	38.8
(Nielsen, et al., 2020) [b]	47.2	27.6	3.4	1.5	10.8	0.2	0.7	0.6	0.9	-	3.0	42.7
Average	**46.4**	**27.9**	**3.4**	**1.5**	**10.7**	**0.2**	**0.7**	**0.6**	**0.7**	**-**	**3.4**	**41.5**
Standard Deviation	**1.3**	**1.3**	**0.3**	**0.7**	**0.2**	**0.0**	**0.0**	**0.0**	**0.2**	**-**	**2.2**	**1.9**
Unspecified Steel Slag												
(Chang, et al., 2019)	47.1	14.6	3.7	22.0	7.3	-	-	-	0.3	-	-	46.9
(Hou, et al., 2021)	39.5	17.9	5.7	23.0	1.7	-	-	-	0.5	-	2.9	35.5
(Shen, et al., 2020)[c]	42.2	12.8	3.2	25.9	9.2	-	-	1.5	-	-	-	-
(Humbert, et al., 2019)	30.2	14.2	12.0	29.5	5.6	-	-	-	-	-	-	-
(Humbert, et al., 2019)	30.9	13.7	10.7	28.3	4.7	-	-	-	-	-	-	-
(Chang, et al., 2011)	42.4	33.9	14.4	0.4	6.4	-	-	-	0.5	-	-	42.0
(Chang, et al., 2011)	38.8	34.9	15.8	2.0	5.6	-	-	-	0.5	-	-	38.4
(Mo, et al., 2016)	42.4	11.0	1.6	27.4	7.2	-	-	2.1	0.1	-	-	42.3
(Boumaaza, et al., 2020)	43.7	37.4	10.8	0.5	6.5	0.4	0.5	-	0.1	-	1.5	41.7
Average	**39.7**	**21.2**	**8.6**	**17.7**	**6.0**	**0.4**	**0.5**	**1.8**	**0.3**	**-**	**2.2**	**41.1**
Standard Deviation	**5.4**	**10.3**	**4.9**	**12.0**	**1.9**	**0.0**	**0.0**	**0.3**	**0.2**	**-**	**0.7**	**3.5**

[a] Reported Fe content as wustite (FeO) instead of Fe_2O_3

[b] Reported S content as total, converted with assumption of complete formation of SO_3

[c] Reported Fe content as Fe_2O_3 (7.8 wt%) and FeO (18.12 wt%)

[d] 'Carbonatable' CaO content calculated from Eqn. 6.3

Other Wastes/Residues

There are a range of other wastes that offer differing potential for carbonation, as reviewed in Table 6-4. Due to their high variability and generally lower availability compared to FA and steelmaking slags, these will not be discussed in detail. Opportunities for carbonation are offered by paper sludge incineration ash (PSIA), which possess high amounts of CaO (∼60.5 wt%) and MgO (∼2.2 wt%). Its relatively low level of other components, mainly SO_3 (∼3.6 wt%), means it is likely suitable for incorporation into cementitious materials. This is not necessarily the case for many other wastes in Table 6-4, which despite exhibiting high CaO and MgO content, are often poorly suited as additions into cementitious materials due to relatively high concentrations of other oxides. Some examples include air pollution control (APC) residues (as are used within the OCO technology processes (OCO Technologies, 2021)), incineration bottom ash (MSW-BA) (as is currently being trialled by Carbon8 systems in collaboration with AVR Duiven (Carey (Carbon8), 2020)), and phosphogypsum or red gypsum wastes (PG/RG), which despite exhibiting between ∼25-47 wt% CaO are limited by high Cl (∼12.9 wt%), SO_3 (∼7.8 wt%) and P_2O_5 (∼50.9 wt%) respectively. This issue of contamination also needs to be considered in utilising other materials such as glass powder, bauxite wastes and wastewater sludge ash, although these materials have been used in cementitious materials (e.g. glass powder can be used as an aggregate, and bauxite residue can be processed and then used as a SCM). In general, while these materials may be processed into SCMs, in their current form they are more suitable for carbonation, use as aggregate, or in the case of high P_2O_5 content, for land spreading (since P is a key nutrient).

Table 6-4 Review of the compositions of other Industrial Wastes studied in Literature

Source	Composition, X (wt%)											
	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	P_2O_5	SO_3	Cl	LOI	'Carbonatable' CaO[c]
Fly Ash (Class C)												
(Gunning, et al., 2010)	32.1	32.4	15.8	3.4	3.4	0.8	1.8	2.9	3.6	-	-	-
(Ukwattage, et al., 2015)	18.5	54.0	9.5	3.0	5.5	1.2	2.1	-	2.5	-	-	-
(Chang, et al., 2011)	38.8	34.9	15.8	2.0	5.6	-	-	-	0.5	-	-	-
(Siriwardena, et al., 2015)	22.8	38.6	19.2	5.7	4.5	0.6	1.8	-	2.5	-	0.6	20.3
(Siriruang, et al., 2016)	19.3	34.5	19.8	15.0	1.9	2.3	1.1	-	4.1	-	0.5	15.8
(Cwik, et al., 2018)	35.3	33.1	13.8	5.7	3.2	1.0	1.3	0.4	5.0	-	-	-
Average	**27.8**	**37.9**	**15.6**	**5.8**	**4.0**	**1.2**	**1.6**	**1.6**	**3.0**	**-**	**0.5**	**18.0**
Standard Deviation	**7.9**	**7.5**	**3.4**	**4.3**	**1.3**	**0.6**	**0.4**	**1.3**	**1.4**	**-**	**0.1**	**2.2**
Fly Ash (Class F)												
(Dung, et al., 2020)	1.2	58.6	30.4	4.7	0.8	3.5	-	-	0.6	-	0.6	0.0
(Gunning, et al., 2010)	1.3	55.6	23.0	13.8	1.0	2.7	0.5	0.5	0.1	-	-	-
(Muriithi, et al., 2013)	9.2	51.2	26.0	2.4	2.4	0.8	0.5	0.7	0.4	-	-	-
(Wu, et al., 2018)	3.4	52.2	22.2	13.5	0.9	2.6	-	0.1	2.2	0.0	1.0	0.6
(Carevic, et al., 2019)	7.6	58.2	20.2	5.3	2.0	1.5	0.5	0.0	2.2	-	2.1	3.4
(Mastali, et al., 2018)	1.0	60.8	22.7	7.6	2.2	2.7	1.5	-	-	-	-	-
(Kurda, et al., 2019)	3.6	57.8	20.9	7.4	1.0	1.7	1.0	-	0.6	-	3.8	0.0
(Wang, et al., 2019)	15.6	52.2	20.1	-	2.6	-	1.9	-	-	-	-	-
(Liu, et al., 2020)	15.4	46.0	20.2	9.4	1.9	1.4	3.9	-	1.8	-	-	-
(Wang, et al., 2019)	15.6	52.2	20.1	3.1	2.7	-	1.9	-	-	-	-	-
(Teixeira, et al., 2019)	3.3	54.1	26.4	6.1	1.6	1.6	0.5	0.8	1.0	-	2.7	0.0
(Huseien, et al., 2019)	5.2	57.2	28.8	3.7	1.5	0.9	0.1	-	0.1	-	0.1	5.0
(Nedeljkovic, et al., 2018)[b]	4.8	56.8	23.8	7.2	1.5	1.6	0.8	0.5	0.3	-	1.2	3.1
(Younsi, et al., 2011)	5.2	55.3	25.2	6.4	-	-	-	-	0.5	-	-	-
(Ji, et al., 2017)	16.4	42.8	19.2	9.1	1.2	1.5	1.7	-	1.9	-	-	-
(Siriruang, et al., 2016)	16.5	35.7	20.4	15.5	2.0	2.4	1.2	-	4.3	-	0.5	12.9
(Boumaaza, et al., 2020)	5.1	83.5	-	-	-	1.7	1.4	0.0	0.6	-	5.0	0.0
(Mo, et al., 2017)	3.3	48.1	30.2	4.6	2.4	1.2	0.7	-	0.7	-	8.8	0.0
(Zajac, et al., 2020)	5.4	52.3	24.9	6.6	1.7	1.6	0.6	0.9	0.3	-	4.3	0.0
(Mo, et al., 2015)	3.3	48.1	30.2	4.6	2.4	1.2	0.7	-	0.7	-	8.8	0.0
Average	**7.1**	**53.9**	**23.9**	**7.3**	**1.8**	**1.8**	**1.1**	**0.4**	**1.1**	**0.0**	**3.3**	**2.1**
Standard Deviation	**5.4**	**9.0**	**3.7**	**3.6**	**0.6**	**0.7**	**0.9**	**0.3**	**1.1**	**0.0**	**2.9**	**3.6**
Fly Ash (Unclassified)												
(Praneeth, et al., 2020)	17.6	39.9	28.2	4.4	1.2	0.7	0.9	0.9	5.1	-	-	-
(Ukwattage, et al., 2013)[a]	35.3	12.2	4.0	24.0	11.7	-	-	-	8.9	-	-	-
(Viet, et al., 2020)	33.1	8.3	4.5	3.7	1.6	5.7	8.6	-	15.5	11.5	-	-
(Viet, et al., 2020)	31.6	7.7	2.0	4.4	1.2	6.1	13.8	-	6.3	20.0	-	-
(Ashraf, et al., 2019)[b]	18.3	10.1	4.1	2.2	1.6	6.5	8.8	1.4	10.9	6.2	20.2	0.0
(Ashraf, et al., 2019)[b]	20.3	18.3	14.5	2.3	6.7	2.2	12.7	3.5	2.0	3.5	18.4	0.0
(Ukwattage, et al., 2015)	12.5	36.0	2.0	16.0	10.7	0.4	4.2	-	12.0	-	-	-
(Ukwattage, et al., 2015)	24.8	13.0	2.1	23.0	13.0	0.4	9.0	-	12.8	-	-	-
(Teixeira, et al., 2019)	27.4	36.0	8.3	4.1	3.6	4.9	0.9	3.2	3.2	0.6	6.3	17.1
(Mazzella, et al., 2016)	32.0	27.3	8.8	6.5	1.9	0.8	0.9	-	2.1	0.9	-	-
(Dananjayan, et al., 2016)	6.7	41.8	18.4	9.2	2.2	1.1	1.4	0.4	3.3	-	14.0	0.0
(Siriruang, et al., 2016)	25.0	26.6	13.6	18.3	2.3	1.8	1.8	-	8.5	-	0.5	18.4
Average	**23.7**	**23.1**	**9.2**	**9.8**	**4.8**	**2.8**	**5.7**	**1.9**	**7.5**	**7.1**	**11.9**	**7.1**
Standard Deviation	**8.5**	**12.5**	**7.8**	**7.9**	**4.3**	**2.4**	**4.8**	**1.2**	**4.4**	**6.8**	**7.4**	**8.7**

[a] Calculated based on elemental composition assuming complete formation of the above oxidised species

[b] Reported S content as total, converted with assumption of complete formation of SO_3

[c] 'Carbonatable' CaO content calculated from Eqn. 6.3.

6.2 Calculation of CO_2 Uptake

The maximum CO_2 uptake capacity (wt%) that a given material can theoretically capture through carbonation has long been studied, and is often calculated using modified versions of the equation proposed by Steinour (Eqn. 6.1-6.2). This predicts the theoretical maximum uptake capacity of a given material by considering the composition of several key species (also wt%). Of course, reaction kinetics also play a role in a real system, this is discussed below. As expected, elevated quantities of carbonatable metal oxides (*i.e.* CaO, MgO, Na_2O and K_2O) positively affect the calculated uptake, according to each species molecular mass (M_i) and stoichiometry (assuming formation of $CaCO_3$, $MgCO_3$, Na_2CO_3 and K_2CO_3 respectively). The quantity of $CaCO_3$ already present within the material is accounted for in Eqn. 6.1, which accordingly reduces the predicted uptake. Other species negatively affect the maximum uptake by stabilising salts from otherwise carbonatable metal oxides, with Eqn. 6.1 showing the detrimental effects of SO_3 and Cl in forming $CaSO_4$ and KCl respectively. Application of the respective molar masses means Eqn. 6.1 is approximated by Eqn. 6.2.

$$\begin{aligned}\mathrm{CO_2\ Uptake\ (wt\%)} &\\ &= \frac{\mathrm{M_{CO_2}}}{\mathrm{M_{CaO}}}\left(\mathrm{CaO} - \frac{\mathrm{M_{CaO}}}{\mathrm{M_{CaCO_3}}}\mathrm{CaCO_3} - \frac{\mathrm{M_{CaO}}}{\mathrm{M_{SO_3}}}\mathrm{SO_3}\right) + \frac{\mathrm{M_{CO_2}}}{\mathrm{M_{MgO}}}\mathrm{MgO} + \cdots \\ &\quad \cdots + \frac{\mathrm{M_{CO_2}}}{\mathrm{M_{Na_2O}}}\mathrm{Na_2O} + \frac{\mathrm{M_{CO_2}}}{\mathrm{M_{R_2O}}}\left(\mathrm{K_2O} - \frac{\mathrm{M_{K_2O}}}{2\mathrm{M_{Cl}}}\mathrm{KCl}\right)\end{aligned} \qquad \mathbf{6.1}$$

$$\begin{aligned}\mathrm{CO_2\ Uptake\ (wt\%)} &\\ &\approx 0.785(\mathrm{CaO} - 0.56\mathrm{CaCO_3} - 0.7\mathrm{SO_3}) + 1.09\mathrm{MgO} + 0.71\mathrm{Na_2O} + \cdots \\ &\quad \cdots + 0.468(\mathrm{K_2O} - 0.632\mathrm{KCl})\end{aligned} \qquad \mathbf{6.2}$$

The amount of $CaCO_3$ within a material is not routinely reported in literature. Hence, this study used a modified equation (Eqn. 6.3) that inferred the quantity of $CaCO_3$ using the values for LOI (*i.e.* assuming LOI was entirely due to CO_2 from calcination of $CaCO_3$). This assumption is conservative since it neglects other species lost during LOI testing (*e.g.* moisture, hydroxyls, volatiles, *etc.*), meaning the predicted quantity of $CaCO_3$ will be overestimated (and therefore the maximum CO_2 uptake will be underestimated). This assumption was deemed justifiable for most fresh, properly stored materials (*i.e.* preventing ambient hydration and/or carbonation from artificially elevating the LOI), however storage methods are rarely reported in literature. This assumption could not be justified for CSW due to extensive hydration of CaO, meaning calculations were not performed. For comparison against the 'total' CaO of each material, Table 6-2 to Table 6-4 show the calculated quantity of 'carbonatable' CaO (*i.e.* CaO not bound as $CaCO_3$ or $CaSO_4$, given by the first bracketed term of Eqn. 6.3). Priority was given to materials with reported values for both LOI and SO_3, however if only one value was available then the missing value was assumed zero to enable calculation.

A further difference with regards to the maximum theoretical uptake was that this study considered the formation of NaCl from Na_2O, which was neglected in Eqns. 6.1-6.2. Such species have been reported in literature (*e.g.* a halite phase in CBD reported by (Khater, 2019)) and are entirely consistent with Figure 4-4 (Mut, 2014). Furthermore, many of the materials reviewed in this study have large quantities of Na_2O, particularly those in Table 6-4. The order of calculation was as-presented in Eqn. 3.3-3.4, with reaction between Na_2O and excess chlorine (Cl′) above that consumed by K_2O. In summary, this study quantified the theoretical maximum CO_2 uptake capacity of the reviewed materials using Eqn. 3.3-3.4.

$$\begin{aligned} &\mathrm{CO_2\ Uptake\ (wt\%)} \\ &\quad = \frac{\mathrm{M_{CO_2}}}{\mathrm{M_{CaO}}}\left(\mathrm{CaO} - \frac{\mathrm{M_{CaO}}}{\mathrm{M_{CO_2}}}\mathrm{LOI} - \frac{\mathrm{M_{CaO}}}{\mathrm{M_{SO_3}}}\mathrm{SO_3}\right) + \frac{\mathrm{M_{CO_2}}}{\mathrm{M_{MgO}}}\mathrm{MgO} + \cdots \\ &\qquad \cdots + \frac{\mathrm{M_{CO_2}}}{\mathrm{M_{K_2O}}}\left(\mathrm{K_2O} - \frac{\mathrm{M_{K_2O}}}{2\mathrm{M_{Cl}}}\mathrm{Cl}\right) \\ &\quad + \frac{\mathrm{M_{CO_2}}}{\mathrm{M_{Na_2O}}}\left(\mathrm{Na_2O} - \frac{\mathrm{M_{Na_2O}}}{2\mathrm{M_{Cl'}}}\mathrm{Cl'}\right) \end{aligned} \tag{6.3}$$

$$\begin{aligned} \mathrm{CO_2\ Uptake\ (wt\%)} &\approx 0.785(\mathrm{CaO} - 1.27\mathrm{LOI} - 0.7\mathrm{SO_3}) + 1.09\mathrm{MgO} + \cdots \\ &\cdots + 0.468(\mathrm{K_2O} - 1.33\mathrm{Cl}) + 0.71(\mathrm{Na_2O} - 0.874\mathrm{Cl'}) \end{aligned} \tag{6.4}$$

Importantly, the uptake capacity actually demonstrated by a given material in a reasonable carbonation time often differs significantly from the theoretically predicted value, meaning that experimental validation is needed. Discrepancies between model and experimental values depend on both material factors (*e.g.* precise composition, nature of contaminants, particle sizes, *etc.*) as well as the process factors (*e.g.* heat/mass transfer, reactor design, reaction conditions, *etc.*) during carbonation. The actual CO_2 uptake capacity can be calculated by a number of methods based on the analytical technique used (*e.g.* TGA, DSC, MS, FTIR), however most methods fundamentally express the same quantity, as shown in Eqn. 6.5.

$$\mathrm{CO_2\ Uptake\ (wt\%)} = \left(\frac{\text{Mass of Captured } \mathrm{CO_2}}{\text{Mass of Dried Solids before Carbonation}}\right) \times 100 \tag{6.5}$$

For the materials reviewed in Table 6-2 to Table 6-4, the theoretical and experimental CO_2 uptake capacities can be compared to establish representative values for these materials. Definitive comparisons between studies are complicated by the individual conditions that each study employed, however general characteristics and trends can be identified. These have been summarised in Table 6-5, which considers the maximum CO_2 uptake experimentally demonstrated regardless of reaction and process conditions. It should be noted that these studies are mainly conducted at the laboratory scale, and that larger scale research such as the ongoing work being done by Carbon8 Systems to prove viability at pilot scale (for example using their CO₂ntainer) is necessary for many possible materials. In general, it can be seen that the experimental uptake of many materials lies far below their theoretically predicted quantities, with the data in also illustrated in Figure 6-2. For Figure 6-2, the experimentally demonstrated uptakes were compared to the theoretical value (as predicted by Eqn. 6.4), which acts as an upper estimate for potential carbonation. Conversely, Figure 6-2 shows the adjusted values with the theoretical uptake calculated from estimated free CaO contents in the materials. It is important to note that the difference between the theoretical CO_2 uptake and the experimentally CO_2 calculated is partially due to carbonation reactivity issues. These issues include the possibility that the solid CaO sources (and MgO,

Na_2O, *etc.*) are not accessible to form carbonate minerals either due to low porosity (formation of carbonate layers), large particle sizes, and/or poor dissolution kinetics (particularly in the case of MgO).

An academic review is shown in Table 6-7 and Figure 6-3 for comparison, which is broadly in agreement with results from this study. Comparison of the average theoretical values from this study against those in Table 6-7 (Renforth, 2019) showed close agreement (± 10%) for the majority of materials. Although there were higher deviations (± 30%) for FAs and EAFS, these were nonetheless within the range of values reported. The experimental uptake values were in similar agreement albeit with higher variability. The future potential for carbonation of these wastes has been illustrated in Figure 6-3 according to several shared socioeconomic pathways (SSPs), as defined by (Riahi, et al., 2017). A brief summary of each SSP has been provided in Table 6-6 to contextualise the results shown in Figure 6-3, however for full context the reader is referred to (Riahi, et al., 2017).

In later modelling (section 9.0), we have chosen a relatively low average uptake of CO_2 into the waste materials (50 % of the maximum theoretical uptake). Of course, further analysis of accelerated carbonation, including specifically improvements to the gas/solid mixing in the carbonator may improve this somewhat; this is clearly an area for further research.

Table 6-5: Comparison of theoretical and actual CO_2 uptake capacities for a selection of materials in this review, namely cement-based materials, fly ashes and steelmaking slags

Material	CO_2 Uptake Capacity (wt%)		Other Components	References
	Theoretical	Actual		
Portland Cement-Based Materials (PCMs)				
Portland Cement (PC)	48.9.0 ± 2.6	36.0-17.2	-	(Nedeljkovic, et al., 2018)
		33.4	30% FA	(Boumaaza, et al., 2020)
		32.2-30.0	40% GGBFS	(Mo & Panesar, 2013)
		∼29.0	-	(Gunning, et al., 2010)
		∼28.0	-	(Pu, et al., 2021)
		∼27-16	-	(Zhan, et al., 2016)
Cement Kiln Dust (CKD)	35.0 ± 15.2	∼9.0	-	(Gunning, et al., 2010)
		4.0-1.5	-	(Siriwardena, et al., 2015)
Cement Bypass Dust (CBD)	27.7 ± 13.4	∼26.0	-	(Gunning, et al., 2010)
Concrete Slurry Waste (CSW)	18.8 ± 2.4	20.4	-	(Kaliyavaradhan, et al., 2020)
		11.0	-	(Xuan, et al., 2016)
Recycled Concrete Aggregates (RCA)	9.9	5.2-2.0		(Xuan, et al., 2016)
Non-Portland Cementitious Materials (NPCMs)				
Fly Ash (FA), Class C	19.4 ± 3.0	11.7	-	(Cwik, et al., 2018)
		∼7.0	-	(Gunning, et al., 2010)
		∼4.0	-	(Chang, et al., 2011)
		3.7	-	(Siriruang, et al., 2016)
		2.1	-	(Ukwattage, et al., 2015)
		0.5-0.2	-	(Siriwardena, et al., 2015)
Fly Ash (FA), Class F	4.5 ± 3.2	5.3-0.7	-	(Nedeljkovic, et al., 2018)
		1.8-1.7	-	(Wang, et al., 2019)
		1.3	-	(Siriruang, et al., 2016)
		∼0.0	-	(Gunning, et al., 2010)
Fly Ash (FA), Unclassified	13.1 ± 6.4	15.3	-	(Mazzella, et al., 2016)
		8.8	-	(Praneeth, et al., 2020)
		8.1-0.3	-	(Viet, et al., 2020)
		7.8-3.3	-	(Ashraf, et al., 2019)
		4.8	-	(Dananjayan, et al., 2016)
		3.0	-	(Siriruang, et al., 2016)
		2.7-1.1	-	(Ukwattage, et al., 2015)
Blast Furnace Slag (GGBFS)	40.2 ± 3.6	32.2-30.0	60% PC	(Mo & Panesar, 2013)
		∼16.0	50% RMC	(Kim, et al., 2019)
		14.4-11.9	-	(Nedeljkovic, et al., 2018)
		7.9-3.0	-	(Ukwattage, et al., 2017)
Basic Oxygen Furnace Slag (BOFS)	42.2 ± 4.0	∼35.6-31.4	-	(Chang, et al., 2012)[a]
		∼31.0-23.0	-	(Pan, et al., 2016)
		∼27.0-8.0	-	(Chang, et al., 2013)
		∼24.5-15.6	-	(Pan, et al., 2016)[a]
		∼21.0-11.0	-	(Librandi, et al., 2019)
		17.3	-	(Chang, et al., 2018)
		15.7-7.4	-	(Jiang & Ling, 2020)
		∼9.0-8.0	-	(Zhang, et al., 2020)
Electric Arc Furnace Slag (EAFS)	48.5	18.2	-	(Baciocchi, et al., 2015)
		∼13-6	-	(Librandi, et al., 2019)
		4.6-3.4	-	(Mahoutian & Shao, 2016)
Argon Oxygen Decarburization Slag (AODS)	50.9	44.4-31.9	30% PC	(Moon & Choi, 2018)
		30.7	-	(Baciocchi, et al., 2015)
		8.1-2.9	-	(Salman, et al., 2014)
Demetalisation Slag (DMS)	44.9 ± 1.7	∼9-11	-	(Nielsen, et al., 2020)

[a] Calculated based on the reported carbonation efficiency, material composition and theoretical uptake capacity
∼ = Estimated capacity based on graphical results or otherwise inferred from reported data

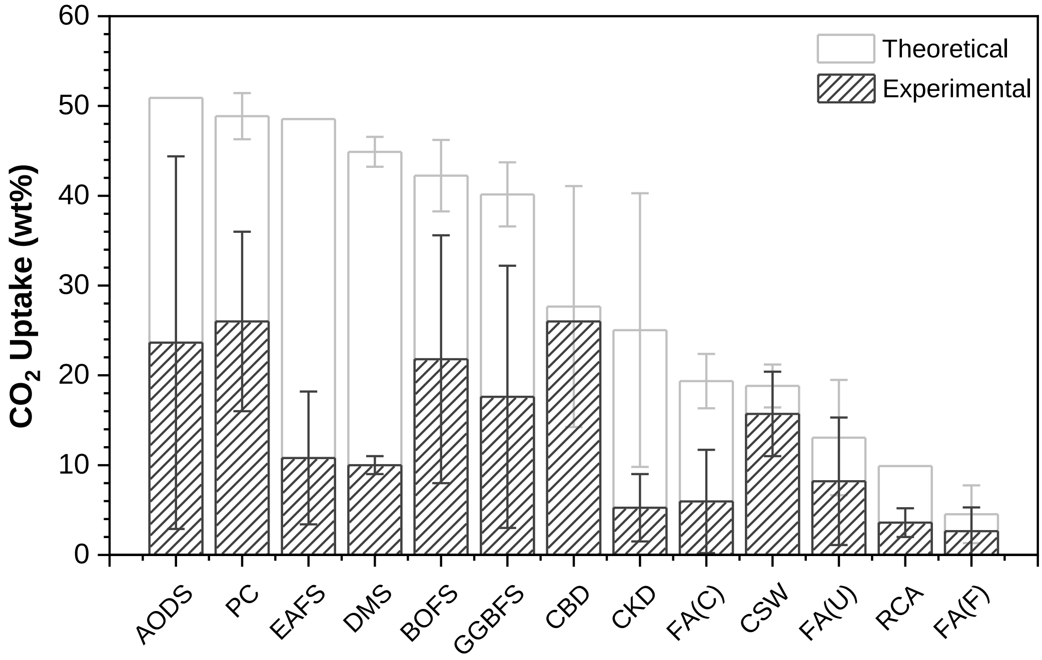

Figure 6-2 Comparison of theoretical and experimental CO$_2$ uptake capacities. Theoretical uptake calculated as part of this study, whereas experimental uptake was taken from literature. Number of sources used per material varied between n = 1-5. Materials were Argon Oxygen Decarburization Slag (AODS), Portland Cement (PC), Electric Arc Furnace Slag (EAFS), Demetalisation Slag (DMS), Basic Oxygen Furnace Slag (BOFS), Blast Furnace Slag (GGBFS), Cement Bypass Dust (CBD), Cement Kiln Dust (CKD), Fly Ash (FA) (various types), Concrete Slurry Waste (CSW), Recycled Concrete Aggregates (RCA).

Table 6-6: Description of Shared Socioeconomic Pathways (SSPs) in Figure 6-3

Pathway		Challenge to:		Summary Description[a]
		Mitigation	Adaption	
SSP1	Sustainability (Taking the Green Road)	Low	Low	“The world shifts gradually but pervasively toward a more sustainable path, emphasising more inclusive development that respects perceived environmental boundaries.”
SSP2	Following Historical Trends (Middle of the Road)	Medium	Medium	“The world follows a path in which social, economic and technological trends do not shift markedly from historical patterns. Development and income growth proceeds unevenly, with some countries making quite good progress.”
SSP3	Regional Rivalry (A Rocky Road)	High	High	“A resurgent nationalism, concerns about competitiveness and security, and regional conflicts push countries to increasingly focus on domestic (or at most, regional) issues.”
SSP4	Inequality (A Road Divided)	Low	High	“Highly unequal investments in human capital, combined with increasing disparities in economic opportunity and political power, lead to increasing inequalities and stratification both across and within countries.”
SSP5	Fossil-Fuelled Development (Taking the highway)	High	Low	“This world places increasing faith in competitive markets, innovation and participatory societies to produce rapid technological progress and development of human capital as the path to sustainable development.”

[a] Summary description: Full descriptions of SSPs given by (Riahi, et al., 2017).

Table 6-7: Carbonation of a selection of alkaline materials illustrating their CO_2 emissions intensity during production, uptake capacity during carbonation, and additional mitigation by reuse/recycling of the carbonated products (Renforth, 2019).

Material	Production Intensity (kg CO_2/t)		CO_2 Uptake Potential (wt%)		Additional Mitigation [a] (kg CO_2/t)
	2010	2050	Theoretical	Experimental	
Portland Cement-based Materials (PCMs)					
Portland Cement (PC)	800	400-200[e]	51.0	30.0	-
Cement Kiln Dust (CKD)	6,900	3,500-1,700	33.0 ± 1.2	26.0 – 8.2	∼0, into rotary kiln
Recycled Concrete Aggregates (RCA)[b]	-	-	11.0-7.7	-	≤5, as Aggregate
Free Lime	1,000	200	77.7 ± 1.3	-	-
Non-Portland Cementitious Materials (NPCMs)					
Fly Ash, Class C [c]	20,000	2,600-2,000[e]	14.6 ± 2.8	26.4 - 23.0	
Fly Ash, Class F [d]	20,000	2,600-2,000[e]	3.6 ± 0.6	3.0 - 2.0	∼100, in typical cements
Blast Furnace Slag (BFS)	12,000	4,300-2,700	41.3 ± 1.3	23.0 - 9.0	∼700, in special cements
Basic Oxygen Furnace Slag (BOFS)	12,000	4,300-2,700	40.2 ± 1.7	54.0 - 5.0	≤5, as aggregate
Electric Arc Furnace Slag (EAFS)	12,000	4,300-2,700	36.8 ± 1.0	30.0	

[a] Mitigated CO_2 achieved by recycling/reuse of the carbonated material (offsetting use of other materials)

[b] Referred to as “Construction & Demolition Waste” in the original source

[c] Referred to as “Lignite Ash” in the original source

[d] Referred to as “Hard Coal Ash” in the original source

[e] Under certain forecasts, reduced values for PC (200-100), steelmaking slags (1080-286) and fly ashes (2600-2000)

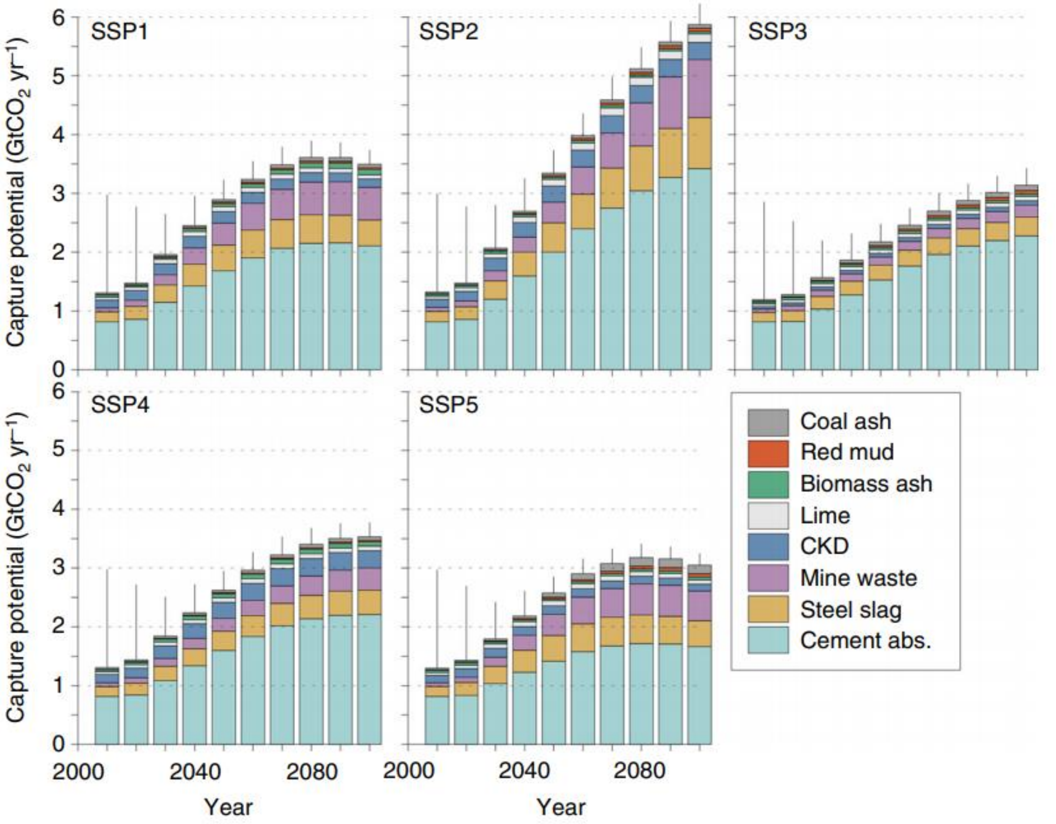

Figure 6-3: Estimated global CO_2 uptake potential by carbonation of alkaline materials from 2010 to 2100 for several baseline shared socioeconomic pathways (SSPs), details of which are available in the original source (Renforth, 2019).

7.0 Availability of carbonatable materials and CO_2

In addition to their specific uptake performances, the viability of large-scale carbonation processes fundamentally relies on the cost, availability, and geographic location of the carbonatable materials. The ideal feedstock is a material with low cost and which is generated in close proximity to a concentrated source of CO_2. Hence, in many cases waste streams are ideal feedstocks since they can be acquired for minimal cost, and are generated in close proximity to point source emitters (*e.g.* power plants, steelworks, cement plants, *etc.*) with access to flue gases containing high concentrations of CO_2. This avoids the financial and energetic penalties associated with transporting feedstock materials over large distances. A rough calculation using the figures from (Huseien, et al., 2019) indicates that transport costs would be around £ 0.12 per tonne, per km. Furthermore, such industrial sites already produce these wastes which (in many cases) incur fees for hazardous waste disposal, so carbonation could command a premium as a waste treatment process whilst also generating value-added building materials.

An illustrative example is shown in Figure 7-1, which highlights the geographic distribution of cement dusts, fly ashes and steelmaking slags in the USA, alongside point source emitters of

CO_2 (Kirchofer, et al., 2013). Similar analyses have been conducted for Västra Götaland (Sweden) concerning concrete curing that also considers the concentration of the available CO_2 (Patricio, et al., 2017), see Figure 7-2. These examples highlight how geographical variability affects the viability of a given carbonation process, in terms of both the carbonatable feedstock (*e.g.* scarcity of steelmaking slags in western USA in Figure 7-1) and sufficiently pure CO_2 (*e.g.* relative lack of 75-100% CO_2 adjacent to curing locations in Figure 7-2). This study is clearly most appropriate for the production of a product such as Carbicrete which requires both steel making slag and a concentrated source of CO_2, rather than an accelerated carbonation system. Of course, as discussed previously, a large proportion of the steelmaking slags may more sensibly be used as an SCM rather than being carbonated. The following section provides a brief overview for the availability of the main wastes identified in section 6.0, after briefly considering flue gas concentrations and suitability as a source for CO_2 to carbonate wastes.

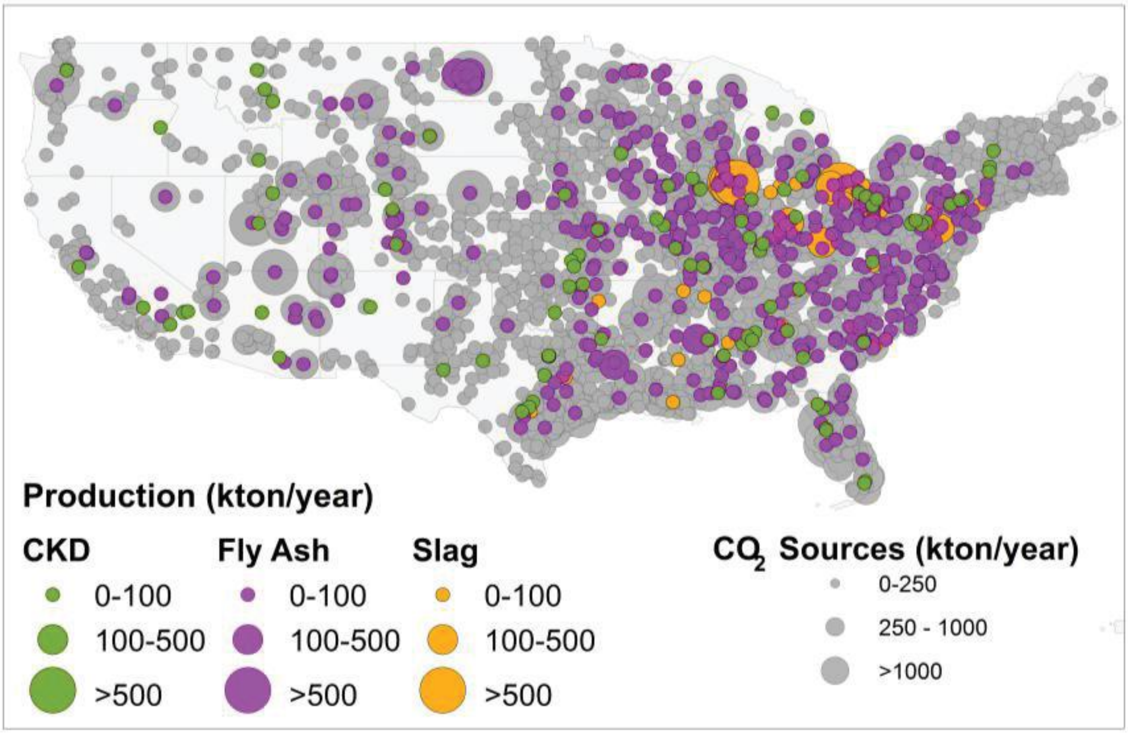

Figure 7-1: Geographical variability in the generation of cement kiln dust (CKD), fly ash (FA) and steelmaking slags, alongside the corresponding availability of point source emitters of CO_2 in USA in 2010 (Kirchofer, et al., 2013).

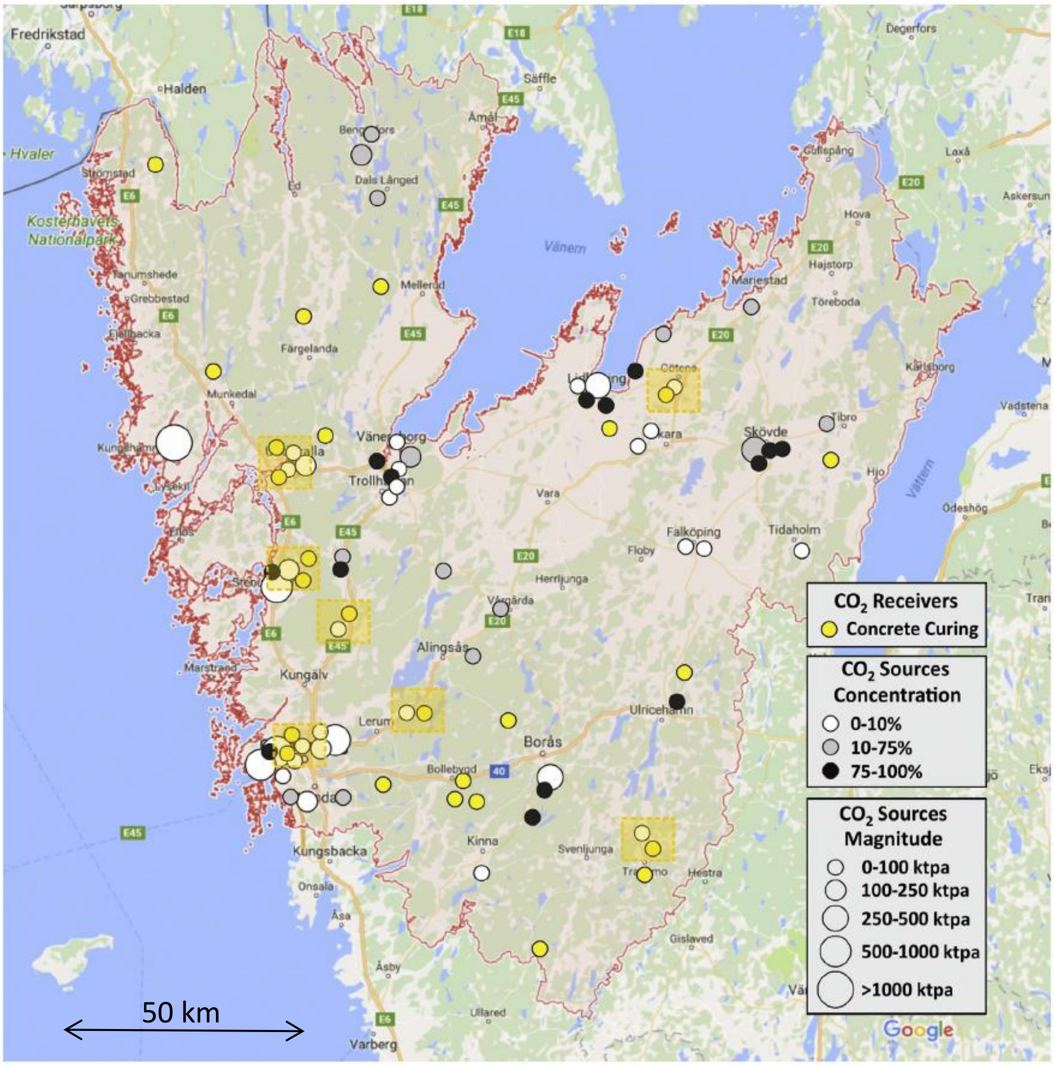

Figure 7-2: Geographical distribution of point source emitters of CO_2 with concentrations 0-10%, 10-75% and 75-100% compared to concrete curing locations in the Västra Götaland region of Sweden (Patricio, et al., 2017).

7.1 Industrial Sources of CO_2 and their Composition

Emissions of CO2 arise from dispersed sources such as passenger vehicles as well as point sources such as coal-fired thermal power plants. We focus on the latter here since they are most relevant to CO2 capture and utilisation for building materials. The main point sources globally are summarised in Table 7-1.

Table 7-1: Origin, amount, and concentration of significant point sources of global CO_2 emissions ca. 2016. Data are from (Naims, 2016).

Sector	Source	CO_2 emissions ($Mt\ CO_2\ year^{-1}$)	CO_2 concentration (vol%)
Power generation	Coal-fired	9,031	12-15
Power generation	Natural gas-fired	2,288	3-10
Industry	Cement production	2,000	14-33
Industry	Iron and steel production	1,000	15
Industry	Refinery products, production and consumption	850	3-13
Power generation	Petroleum-fired	765	3-8
Industry	Ethylene production	260	12
Industry	Ammonia production	150	100
Power generation	Biomass-fired	73	3-8
Industry	Hydrogen production	54	70-90
Industry	Natural gas production	50	5-70
Industry	Waste incineration	60	20
Industry	Fermentation of biomass	18	100
Industry	Aluminium production	8	<1

Table 7-2 summarises the compositions of the main point source emissions. The most common impurities are gaseous N_2, O_2, H_2O, although key iron and steelmaking gas streams contain significant gaseous CO, H_2, and CH_4 content. In a typical integrated steel mill these gas streams are commonly recycled internally or used to generate electricity in a turbine, due to their non-negligible calorific values. This notably results in the blast furnace gas (BFG, the origin of most iron and steelmaking CO_2 emissions (Orth et al., 2007)) being eventually emitted at several points in the process, e.g., the power plant stack. Pollution control technologies such as flue gas desulphurisation are routinely used to reduce SO_x, particulate matter, and NO_x emissions to relatively low values (Srivastava et al., 2005). We focus on the high concentration impurities here since they are most likely to affect properties of building materials produced from them.

There are regulated limit values on the amounts of pollutants that can be emitted to the air from industrial processes, meaning that pollutant emissions are actively managed (e.g. through use of flue gas scrubbing technologies (Nalbandian, 2012)), and relatively low concentrations in the flue gases that represent the main point sources of CO_2 can be expected (Table 7-2). In PC production, flue gas is less concentrated in heavy metals than PC clinker (Arfala, et al., 2018): their concentrations in flue gas need to comply with local emission limits (e.g. 0.03 mg Nm^{-3} Hg in Germany (Edwards, 2014)); therefore they are controlled to typically have Hg, Cd+Tl, and total heavy metal concentrations of 0.001-0.03 mg Nm^{-3}, 0.01-0.04 mg Nm^{-3}, and 0.05-0.8 mg Nm^{-3} respectively. OPC typically has concentrations of <0.001-0.039 mg kg^{-1} for Hg, 0.03-1.12 mg kg^{-1} for Cd, 0.01-2.68 mg kg^{-1} for Tl, and total heavy metal concentrations of >100 mg kg^{-1}, and these elements are generally considered to be immobilised (chemically bound) in properly cured cementitious materials (Horsley, et al., 2016) (Gineys, et al., 2010). This demonstrates that there is little risk of utilising flue gas from cement plants, and especially not when used in cementitious materials such as concrete, which is a well-known stabilisation and solidification material (and thus an effective method for encapsulating trace metal pollutants).

7.2 Portland Cement-based Wastes

Potentially carbonatable wastes are generated throughout the entire life-cycle of cement-based materials, from during their production (*i.e.* CKD, CBD), through excess during use (*i.e.* CSW), to recycling of end-of-life products (*i.e.* RCA).

Cement Kiln Dust

The most recent research estimates the generation of CKD at ~54-144 kg/tonne of clinker under compound operation (or ~80-200 kg/tonne under direct operation) (Schorcht, et al., 2013), which is generally reduced from ~150-200 kg/tonne in recent decades (EPA, 1993). Furthermore, improved on-site utilisation of CKD (~50%) as recycled cement meal (the term for the totality of dry, non-fuel, feedstocks fed to the process when combined) or NPCM has further reduced availability compared to previous years where 60-80% was sent to landfill (EPA, 1993). With global cement production at 4.1 Gt/y in 2019 (IEA, 2020) this suggests CKD availability is ~210-420 Mt/y, assuming reasonable values for clinker ratio (74%), dust generation (140 kg/tonne), and on-site utilisation (0-50%). This rough estimate is validated by the calculated production rate of clinker (~3.0 Gt/y) in good agreement with the same value reported in literature for 2019 (3.7 G/y) (Statista, 2020).

Aside from current production, some countries have significant stockpiles of CKD that could be reclaimed. This chiefly includes the USA, which since the 1980s has historic stockpiles that cumulatively exceed 100 Mt (Sreekrishnavilasam, et al., 2006), with further additions of 4.3 Mt/y (Button, 2003). These stockpiled CKDs can be used for carbonation if they have not been carbonated during stockpiling, but they are unlikely to be suitable SCMs since their reactivity will reduce upon sustained exposure to moisture. They may be mined and used as kiln feed, or applied in various non-construction uses (*e.g.* land spreading, soil stabilisation, de-icing, *etc.*), as discussed subsequently. On the other hand, and as mentioned above, fresh CKD is mainly recycled as a kiln feed, but can also be used as a SCM since it has not yet been exposed to significant moisture (Hanein, et al., 2020).

Table 7-2: Compositions of the main point sources of CO_2 emissions. Compositions of the blast furnace gas (BFG) steam and emissions released at its related downstream point sources are shown. A hyphen ('-') indicates a null entry rather than a zero value.

Source	CO_2	N_2	O_2	H_2O	CO	H_2	Reference
Power Generation							
Coal-fired	10-11	61-76	4-5	20-23	-	-	(Artanto, et al., 2012)
Coal-fired	13.58	72.86	3.54	8.18	-	-	(Arachchige &
Natural gas-fired	4	76	12	8	-	-	(Arachchige &
Natural gas-fired	4.97	74.28	9.73	11.02	-	-	(Scholes, et al., 2016)
Industry							
Cement production	17.2 [a]	70.9 [a]	11.9 [a]	- [a]	- [a]	- [a]	(Bosoaga, 2009) [a]
Cement production	18.9	60.6	7.7	12.8	-	-	(National Energy
Cement production	22-31	65-71	3-7	4	-	-	(Price, et al., 2011)
Iron and steel production, BFG	17-25	50-55	-	-	20-28	1-5	(Carpenter, 2012)
Iron and steel production, BFG	16-26	44-58	-	-	1-8	19-27	(Caillat, 2017)
Iron and steel production, BFG	22	50	-	5	20	5	(Wiley, et al., 2011)
Iron and steel production, BFG, power plant stack	23	68	1	8	-	-	(Wiley, et al., 2011)
Iron and steel production, BFG, coke oven gas	27	67	1	5	-	-	(Wiley, et al., 2011)
Iron and steel production, BFG, blast furnace stoves	21	68	1	10	-	-	(Wiley, et al., 2011)
Iron and steel production, BFG, sinter plant stack	8	70	-	21	1	-	(Wiley, et al., 2011)
Iron and steel production, BFG, basic oxygen	15	13	-	2	70	-	(Wiley, et al., 2011)
Iron and steel production, BFG, hot strip mill stack	7	70	2	21	-	-	(Wiley, et al., 2011)
Iron and steel production, BFG, plate mill stack	7	70	2	21	-	-	(Wiley, et al., 2011)
Iron and steel production, BFG, lime kiln stack	7	70	2	21	-	-	(Wiley, et al., 2011)
Iron and steel production, BFG, electric arc furnace	40	56	3	1	-	-	(Wiley, et al., 2011)

[a] (Bosoga et al., 2009) did not analyse moisture (H_2O) content

Cement Bypass Dust

The scenario is somewhat different for CBDs, where the scale of production is much smaller, estimated at around 15-20 times lower than that for CKD (Hanein, et al., 2020). Based on the previous range for CKD (∼54-200 kg/tonne) (Schorcht, et al., 2013), we expect the production of CBD to be around ∼3-13 kg/tonne. This range agrees with values from three independent industrial sources (∼7-8 kg/tonne) (Mineral Products Association, 2020) (Barnes-Davin (Vicat), 2020) (European Cement Research Academy, 2017), and is similar in magnitude to recent academic literature (20 kg/tonne) (Hanein, et al., 2020). Nevertheless, increasing combustion of refuse-derived fuels (RDFs) seems likely to increase global production of CBD due to elevated amounts of contaminants, which must be purged to prevent re-entry into the kiln (Schorcht, et al., 2013). Assuming that doubled consumption of RDF also results in doubling the generation of CBD suggests ∼6-26 kg/tonne of clinker, equating to a global production of ∼18-79 Mt/y that may be used in a market other than on-site use in cement plants. With the same assumptions given above for CKD, this implies ∼10-40 Mt/y of CBD is available for use globally. Specifically concerning the EU, clinker production is around 120 Mt/y (Eurostat, 2019) which corresponds to an EU market size for CBD of ∼426 kt/y. The country-level breakdown has been shown in Figure 7-3, highlighting how Germany, Spain, Italy and Poland are the largest producers, accounting for roughly 60% of EU CBD production in 2019.

CBD contains significant CaO, offering cementitious properties and demonstrating suitability for carbonation (Czapik, et al., 2020). Hence CBD has the potential for utilisation as a SCM (given sufficiently low contamination, particularly for chlorine). This is current practice in some industrial plants, as highlighted during an interview (Barnes-Davin (Vicat), 2020). It was stated that around 50% of the CBD is used as a SCM (i.e. added in as a clinker replacement) of the cement (<5 wt%), with chloride concentration in the final product limited to 0.1% for concrete containing reinforcing (Barnes-Davin (Vicat), 2020). This is corroborated with the ECRA's BAT model which also conservatively assumes 50% of the CBD produced is used as SCM (European Cement Research Academy, 2017). A discussion with an industrial researcher indicated that because in the UK marine aggregates are used in a significantly greater quantity than in the remainder of the EU, cement is more likely to be sold at a 0.05% Cl standard, not 0.1%, since this allows more headroom for Cl (which is naturally present in such aggregates). The generally elevated amounts of Cl in CBDs (9.9 wt% in Table 6-1 hence pushes them toward non-construction uses (*e.g.* land spreading, soil stabilisation, de-icing, *etc.*) rather than use as a SCM in cement (as discussed below).

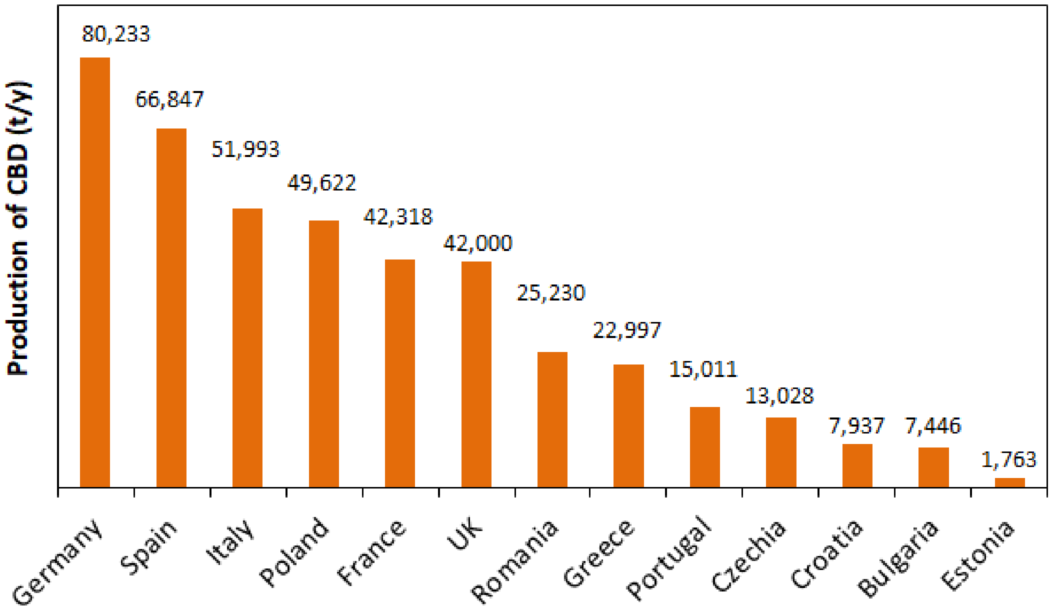

Figure 7-3: Annual CBD production in the EU (Country level clinker production level from Eurostat, 2019)

Alternative Uses of CKD and CBD

Our interview with the Mineral Products Association (MPA) highlighted existing potential uses for both CKD/CBD as liming agents for land spreading (Mineral Products Association, 2020). An assessment of the suitability of CKD/CBD for this purpose was conducted by Amec Foster Wheeler for the UK Department of Environment, Food, and Rural Affairs (DEFRA) (Amec Foster Wheeler, 2015). It was found that land spreading of CKD had potential to enrichment of hazardous substances including antimony, cadmium, chromium, copper, lead, thallium, zinc, molybdenum, silver, vanadium, nickel, barium, selenium, mercury, cobalt, and dioxins/furans (Amec Foster Wheeler, 2015). It should be noted some of these concerns were on the basis of incomplete reporting data, not necessarily because they were expected (Amec Foster Wheeler, 2015). For CBD, the hazards of land spreading principally included cadmium, lead, thallium, selenium and possibly barium. The position of the MPA is that kiln operators desiring to use CKD/CBD for agricultural applications ensure controls that prevent toxic trace elements from entering the kiln, however such controls are country-specific. Such controls may limit the types and thus overall amounts of alternative fuels used. It would thus be necessary to carefully manage alternative fuel use in the cement kiln with respect to these controls. In some countries (*e.g.* the UK), it is also necessary to test the properties of CKD/CBD to ensure that its use is in agreement with any risk assessments made as part of the permitting process (Environment Agency, 2013). Overall, there does not appear to be a large market for carbonation of CBD, as evidenced by larger operators like Cemex who have stated that 95% of wastes are reused in the process, and that “cement kiln bypass dust is used for soil or road stabilization, fertilizer or as a deicing agent for roads in the winter” (Cemex, 2020).

Nevertheless, during land spreading, it is expected that CKD/CBD would readily carbonate due to their physical properties (*i.e.* fine powder) and the weathering conditions (*i.e.* rain, moisture and atmospheric CO_2). Due to their composition, carbonation of CKD/CBD is expected to mainly produce $CaCO_3$ as well as additional mineral phases such as poorly crystalline silicate phases, Friedel’s ($Ca_4Al_2Cl_2(OH)_{12}.4H_2O$) and/or Kuzel’s

($Ca_4Al_2Cl(SO_4)_{0.5}(OH)_{12}.6H_2O$) salts. The conditions will also likely result in the partial dissolution of several soluble elements (*e.g.* alkalis, Cl, Cd, Se, *etc.*). It is likely that some (but not all) of the contaminants will become entrapped in the stabilised solid mineral phases if they remain at relatively high pH (*e.g.* >10), since phases such as C-A-S-H and AFm contain both cationic and anionic components in their atomic structures (Appello, 2021). At neutral and lower pH their solubilities will change and hence so too will the stabilisation of contaminants (in solid phases). Hence it may be advantageous for land spreading applications to mix CBD with other materials to stabilise these contaminants in solid phases. Further research should be carried out to understand this point.

Comparative Value of Carbonation and Recycling of CKD to the Process

Wherever possible the best practise is to return fresh CKD/CBD to the process since it is more valuable when transformed into clinker or cement. A basic analysis can demonstrate this. Assume approximately 12 kg of CBD is available for subsequent carbonation, and that carbonation takes up 50 wt% CO_2 (at the very upper limit of the range theoretically predicted by Eqn. 6.3). From this, ~0.006 t CO_2/t clinker could be sequestered. The UK produces in the region of 9 Mt/y of cement (~7.8 Mt/y of clinker), meaning there is only ~45,000 t/y of CO_2 which could be utilized if all CBD in the UK was utilised for CO_2 capture. In markets where CBD can be used within the cement, this will be the preferred route. For the optimal case, assuming a CO_2 cost of around €30/t, the removal of ~45,000 t/y of CO_2 would be associated with €1.35 million per annum. Whereas, if CBD is used in cement as a SCM it effectively replaces PC clinker, which has a nominal value for PC clinker of around €75/tonne (as suggested by an industry contact). Thus, utilization of all the UK's CBD in cement would result in savings of around € 6.75 million by reducing the amount of clinker required.

This calculation can be performed more generally to assess the carbonation of any given material. For the carbonation of a general material a, with mass fractions of the original material $x_{dis,a}$, $x_{clinker}$ and $x_{product}$ going for disposal, to substitute for PC clinker, and as the produced product, the cost of disposal of the material is $V_{dis} = \dot{m}_a c_{dis,a} x_{dis,a}$ where $c_{dis,a}$ is the cost of disposal of a, and $\dot{m}_a$is the mass flowrate of a. For PC clinker replacement, the value created by this ($V_{clinker}$) is $\dot{m}_a c_{clinker} x_{clinker}$ where $c_{clinker}$ is the cost of clinker. Where carbonation means that a material can be sold into a market, the value of the material produced ($V_{product}$) is $\dot{m}_a\left(1 + x_{CO2,a}\right)c_{product}x_{product}$ where $x_{CO2,a}$ is the mass of CO_2 which can be taken up per unit mass of a, $c_{product}$ is the cost per unit mass of the product. Finally, the value of the CO_2 taken up is $\dot{m}_a x_{CO2,a} c_{CO2} x_{product}$ where c_{CO2} is the disposal cost of the CO_2. This allows the overall value generated by the carbonation process to be calculated (Eqn. 7.1).

$$V_{overall} = \dot{m}_a c_{dis,a} x_{dis,a} + \dot{m}_a c_{clinker} x_{clinker} + \dot{m}_a\left(1 + x_{CO2,a}\right) c_{product} x_{product} + \dot{m}_a x_{CO2,a} c_{CO2} x_{product} \qquad \textbf{7.1}$$

Other Portland Cement-based Wastes

Wastes are also generated during the preparation and use of fresh mortar/concrete. The fraction of processed concrete that is wasted varies between countries, as seen by the values for Italy (1.4%), Japan (1.5%), Hong Kong (1.5%), Europe (2.5%), USA (6.0%) and Brazil (9.0%) (Xuan, et al., 2018). In practical terms this can mean ~300 kg/truck of fresh concrete is returned to batch plants as waste (Paolini & Khurana, 1998). Reasons for such high variability include the prevalence of customer over-ordering, lack of communication between the customer and the batching plant (The Constructor, n.d.). Presumably because of the logistical challenges involved in just-in-time delivery, there is a correlation with the level of development of a country (Contreras, et al., 2016). Washing recovers the coarse aggregates for future batches and generates substantial quantities of CSW, estimated at ~0.8% of the total processed concrete (Xuan, et al., 2016). This can be evaluated from the aforementioned production of cement and conservatively assumed concrete formulations (10-25% cement) (Kropp, 2008), which would tentatively suggest the availability of CSW at ~130-320 Mt/y. This value is an upper estimate since fresh CSW is known to contain significant amounts of water (~62-113 wt% of CSW) (Kaliyavaradhan, et al., 2020) (Xuan, et al., 2016). Indeed CSW is mostly composed of hydrated cement products (*i.e.* $Ca(OH)_2$ and C-S-H), which can easily undergo carbonation. Hence, CSW can be processed (e.g. by filtration, drying, carbonation) into uncarbonated or carbonated building materials, and in concrete/mortar these will likely be (possibly reactive) fillers due to their fine particle sizes.

Concerning construction and demolition waste (CDW), the most recent comprehensive study indicates that global CDW approached ~3 Gt/y in 2012, with many studies since then strongly evidencing continued increases to the present day (Ginga, et al., 2020). The largest producers of CDW are China, India and USA (with nonetheless significant generation in parts of Europe, Japan and South Korea) (Akhtar & Sarmah, 2018). Although a significant proportion of CDW is PC-based concrete (~67% in USA), it also constitutes a diverse range of other construction materials (*e.g.* masonry, bricks, asphalt, *etc.*) (Akhtar & Sarmah, 2018). These materials are often recycled into low value applications (*e.g.* structural fills, backfills, embankments, *etc*.) or otherwise disposed (Akhtar & Sarmah, 2018). The recycling rate is variable with some countries recycling a high proportion of wastes (*e.g.* 95-98% in USA, Canada, Japan, South Korea, many EU countries) (EC-europa, 2011) and others without significant recycling programs (*e.g*. Mexico, South Africa, and a few EU countries (EC-europa, 2011) (Akhtar & Sarmah, 2018). Hence there is room to increase recovery of CDW into RCA, and carbonation of these materials. Their availability is generally high since construction waste is generated at large scales at the regional/national levels. Some countries have stricter requirements on RCAs meaning CDW is currently not widely recycled into this material (Akhtar & Sarmah, 2018), but the authors expect this to change in the future due to the already demonstrated widespread success of using RCA in non-structural applications.

7.3 Non-Portland Cementitious Wastes

As the predominant sources of cementitious wastes, this section focusses on FA and steelmaking slags. Currently, the majority of FA is used in construction, either as SCMs (*e.g.* cement, concrete, bricks and tiles) or directly as structural fills, embankments, roadbase (Yao, et al., 2015). Global production of FA is in the region of 450-750 Mt/y (Gollakota, et al., 2019) (Izquierdo & Querol, 2012), which is in general agreement with ~360-1450 Mt/y conservatively estimated from coal consumption in 2020 (*i.e.* 7243 Mt/y of coal with an assumed ash content of 5-20 wt%) (IEA, 2020). For comparison, global capacity for incineration of MSW has been evaluated at just 260 Mt/y (Lu, et al., 2017), which with the same assumed ash content only predicts around 13-52 Mt/y of FA. Hence, without extensive investment into biomass-derived fuels and/or MSW incineration into the long-term, the supply of FA is for all practical purposes reliant on coal.

The majority of FA is produced in India, China and USA due to a combination of large coal reserves, extensive coal-fired power generation and significant presence of other heavy industries. In particular, China and India demonstrate relatively low utilisation of FA (~38-45%) (Gollakota, et al., 2019), with large quantities of unused material exported globally to regions with insufficient local production. These tend to be regions with comparatively little coal-fired power generation (*e.g.* Middle East, UK) and/or where locally generated FAs are entirely utilised (*e.g.* 85-100% utilisation in Germany, France, Denmark, Italy, Netherlands, Japan) (Gollakota, et al., 2019). However, there are a number of challenges associated with importing FAs, including the insecurity of supply and the relatively high transport cost due to the low bulk density (~860 kg/m^3) compared to other waste materials (*e.g.* steelmaking slags are ~2400 kg/m^3) (BEIS, 2017). This can result in significantly increased prices for FA (*e.g.* prices for FA increased 85-100% in the UK from 2012-2016, coinciding with phasing out of national coal-fired power plants (BEIS, 2017)) as well as higher associated CO_2 emissions due to transportation.

Otherwise, many countries (*e.g.* UK, Germany, France) have stockpiles of FA that could be beneficiated for utilisation (BEIS, 2017). Concerning the UK, official figures by the UK Quality Ash Association (UKQAA) estimate the total quantity of stockpiled FA at ~50 Mt within the UK (BEIS, 2017). During interview with SonoAsh (developers of technology for beneficiation of FA at industrial scale), interviewees expressed their position that this value was greatly underestimated, with the true quantity at ~450 Mt of stockpiled FA in the UK. These are distributed across the UK in locations currently/historically associated with coal, with these varying between ~20-50 Mt of stockpiled FA (at each impoundment location). The condition of stockpiled FA is highly variable, however weathering from decades of outdoor exposure often diminishes (possibly entirely) the reactive components, rendering them unsuitable as SCMs (BEIS, 2017). In any case, such stockpiled FAs are still carbonatable and can be used as both uncarbonated and carbonated fillers. During weathering stockpiled FA will passively take up CO_2, though at a slow rate (decades to centuries).

These factors discussed for FA are also broadly applicable to steelmaking slags (BEIS, 2017), and the majority of slags are already used in construction. Some exhibit binding properties and are used as SCMs (*e.g.* GGBFS) whereas many others are significantly less reactive and are thus used for lower value applications both in cement (e.g. fillers) and general construction (*e.g.* backfill, embankments, roadbases, *etc.*). Nevertheless, as with coal-fired power stations affecting availability of FAs, local availability of steelmaking slags necessarily relies on national steelmaking industries. This is not always guaranteed and several countries have begun importing slags, mostly from China who produce over 50% of global steel. For instance, steelmaking in the UK has seen steady decline, with imported slag from China accepted at the Redcar grinding facility since 2017 (with plans to accept up to 500 Mt of slag) (BEIS, 2017). Hence, the long term availability of these slags moving into the future is quite uncertain. Transitioning away from BF-BOFs and toward greater recycling of steel in EAFs will impact their availability, since the latter produces significantly less slag (*e.g.* BOFS is ~400 kg/tonne of crude steel, whereas EAFS is only ~170 kg/tonne) (World Steel Association, 2018). As with FAs, many countries have considerable waste stockpiles of steelmaking slags. Such stockpiles have potentially significant CO_2 uptakes for direct carbonation (296-337 kg/tonne of slag), passive carbonation (513-584 kg/tonne of slag) and enhanced weathering (422-481 kg/tonne of slag) (Pullin, et al., 2019). For instance, one review examining slag stockpiles in the UK suggests a cumulative potential of between 57-138 Mt of CO_2, including both accelerated carbonation and enhanced weathering (Riley, et al., 2020). Enhanced weathering is removal of material and enhancing the potential for CO_2 from the atmosphere to naturally carbonate the materials. Stockpiled heaps often have poor diffusion, meaning they are likely to only be partially carbonated (the same is true for stockpiled FA). Shallow weathering heaps with active management (*e.g.* size grading, controlled water, regular turning, *etc.*) can increase carbonation of these stockpiled materials (Pullin, et al., 2019), but will also incur financial and energetic costs. Thus stockpiled slags, which have undergone weathering and thus reduced reactivity, are generally suitable for use as fillers or aggregates (depending on particle size), not SCMs.

Overall, in terms of future prospects the reduction in coal-fired power generation and heavy industry in many countries seems likely to drive regional shortages of FA and slags, regardless of whether global coal combustion increases in the medium- to long-term. This will concentrate global production of these materials within fewer countries that retain coal-fired power generation and/or heavy industries (*e.g.* China, India, USA, Germany) (BEIS, 2017). Importing these materials is an option, however the transport incurs significant financial and emissions penalties (but the latter will not necessarily outweigh the CO_2 uptake from carbonation). Trucking costs have been estimated to be around £0.12 per km per tonne (Huseien, et al., 2019), though ocean shipping would be significantly cheaper (assuming a capacity of 180,000 tonnes, and cost of $20,000 per day (Dry Bulk Market International Shipping News, 2019) and a reasonable speed of 20 km per hour (McNicholas, 2016), costs for sea transport could be around £0.0005 per tonne per km (excluding loading and unloading time, and being careful to account for whether the ship can pass through the Suez canal).

8.0 Effects of carbonation on material utilisation in building products

In this section we discuss the effects of carbonation on the properties of the source materials (*e.g.* FA), and their subsequent potential to be used in building products. Our analysis is summarised in Table 8-1, and is elaborated on in the following sub-sections.

In general, carbonation of the materials mentioned above leads to stabilisation of calcite. Since calcite is almost always added in minor amounts to PC (∼5 wt%) as a beneficial reactive filler component these carbonated materials can generally always be added as a reactive filler or aggregate (depending upon particle size), as a substitute for natural limestone, unless they are substantially contaminated.

Higher mass fraction additions of calcite into PC will eventually lead to dilution of its cementitious properties. Therefore, the addition of carbonated materials to PC should not exceed the maximum level that calcite addition is beneficial or at least not detrimental. We expect that this is generally around ∼10 wt.% of the cement paste.

Table 8-1: Classification of materials, before and after carbonation in terms of their utilisation in building products (clinker/reactive filler/filler-aggregate), including a summary of the impacts of carbonation on their properties. The following symbols are used to designate positive and negative material properties: (++), very positive; (+), positive; (-), negative; (--), very negative. We exclude cement kiln feedstock as a potential use for carbonated materials since the aim of carbonating them is to store CO_2.

Material	Carbonated or uncarbonated	Currently utilised?	Potential utilisation	Material properties	Carbonation process considerations	Recommended utilisation
CKD	Uncarbonated	Yes, mainly as cement kiln feedstock	Cement kiln feedstock; SCM; reactive filler	(++) Expected SCM level reactivity; (++) similar composition to PC; (++) fine particle size		Cement kiln feedstock, substituting natural limestone
CKD	Carbonated	No	Reactive filler; filler	(+) Expected similar reactivity to fine limestone; (++) fine particle size	Expected fast carbonation rate; complete natural carbonation is possible	Reactive filler, substituting fine natural limestone
CBD	Uncarbonated	Yes, mainly as cement kiln feedstock	Cement kiln feedstock; SCM; reactive filler	(++) Expected SCM level reactivity; (++) similar composition to PC; (++) fine particle size; (--) high Cl content		Cement kiln feedstock, substituting natural limestone
CBD	Carbonated	No	Reactive filler; filler; non-cementitious applications	(+) Expected similar reactivity to fine limestone; (++) fine particle size; (--) high Cl content	Expected fast carbonation rate; complete natural carbonation is possible	Reactive filler, substituting fine natural limestone
CSW	Uncarbonated	No	Reactive filler; filler	(+) Expected similar reactivity to fine limestone; (++) fine particle size; (+/-) high water content		Reactive filler, substituting fine natural limestone

CSW	Carbonated	No	Reactive filler; filler	(+) Expected similar reactivity to fine limestone; (++) fine particle size; (+/-) high water content	Expected fast carbonation rate; complete natural carbonation is possible; a water removal process (filtration, drying) may be needed	Reactive filler, substituting fine natural limestone
RCA	Uncarbonated	Yes, mainly in non-structural applications	Filler; aggregate; non-cementitious applications	Compared to mined natural aggregates, RCA has (-) higher water demand, (-) is weaker, (-) requires more PC in the mix design		Filler or aggregate
RCA	Carbonated	Yes, mainly in non-structural applications	Filler; aggregate; non-cementitious applications	Compared to uncarbonated RCA, carbonated RCA is (+/-) smaller, has (+) better material properties for use as aggregate, (+) lower water demand. Emerging research suggests that controlled carbonation of RCA can produce a (reactive) supplementary cementitious material, although this technology is not yet utilised, so is excluded from our recommendations here.	Grinding is needed to separate aggregate from end-of-life cement paste, requiring energy	Filler or aggregate
FA, Class C	Uncarbonated	Yes, mainly as a SCM	Cement kiln feedstock; SCM; reactive filler	(++) SCM level reactivity; (+) fine particle size; (++) spherical particle shape improves fresh concrete workability		SCM
FA, Class C	Carbonated	No	Filler; non-cementitious applications	Expected to have significantly lower reactivity than uncarbonated Class C FA	Expected fast carbonation rate; complete natural carbonation is possible	Filler
FA, Class F	Uncarbonated	Yes, mainly as a SCM	Cement kiln feedstock; SCM; reactive filler	(++) SCM level reactivity; (+) fine particle size; (++) spherical particle		SCM

				shape improves fresh concrete workability		
FA, Class F	Carbonated	No	Filler; non-cementitious applications	Expected to have significantly lower reactivity than uncarbonated Class F FA	Expected fast carbonation rate; complete natural carbonation is possible	Filler
GBFS	Uncarbonated	Yes, mainly as a SCM	Cement kiln feedstock; SCM	(++) SCM level reactivity		SCM
GBFS	Carbonated	No	Filler; non-cementitious applications	Expected to have significantly lower reactivity than uncarbonated GBFS; (+) carbonation may add value to air cooled (unreactive) BFS although likely maintaining its utilisation potential as aggregate and non-cementitious application (e.g. roadbase, backfill)	Grinding is desirable to reduce particle size of air-cooled blast furnace slag for faster carbonation, requiring energy	Filler or aggregate
Other pozzolanic industrial by-products	Uncarbonated	Generally not	Utilisation potential needs to be assessed on a case-by-case basis, but these materials can sometimes be used as cement kiln feedstock, e.g. copper slag, and they have potential to be processed and used as SCMs	Often these materials (--) do not have SCM level reactivity or (--) have contamination issues; processing is usually required to upgrade their reactivity and remove impurities		Processing into SCMs where possible
Other pozzolanic industrial by-products	Carbonated	No	Utilisation potential needs to be assessed on a case-by-case basis, but these materials have potential to be used as reactive fillers, fillers, and aggregates	(+) Carbonation may add value but is unlikely to change its utilisation potential	Grinding and water removal may be needed or desired prior to carbonation	Reactive filler where possible

8.1 Potential use of carbonated PC-based materials

Material Properties Following Carbonation

CKD, CBD, and CSW have compositions varying approximately between CEM I and CEM II, with the exception that CBD contains large amount of Cl and SO_3 (see also section 6.1). These materials can be used as cement kiln feedstock or as reactive materials in cementitious systems. In the following section we discuss the transformations of these materials as they are progressively carbonated, and what these transformations mean for their use in a carbonated form. We recommend that they are used as cement kiln feedstock where possible, or if not, to use them as SCMs or reactive fillers. The remaining material, which will be small in comparison to the total, can be carbonated. To analyse their latter use as a carbonatable product, we compare the direct gaseous carbonation of a fully reacted PC (CEM I) to the carbonation of PC + FA (CEM II), as shown in Figure 8-1. This analysis provides an indication of how carbonation will affect the chemistry and thus properties of CKD, CBD, and CSW, since the chemistry of these materials approximately lies between CEM I and CEM II.

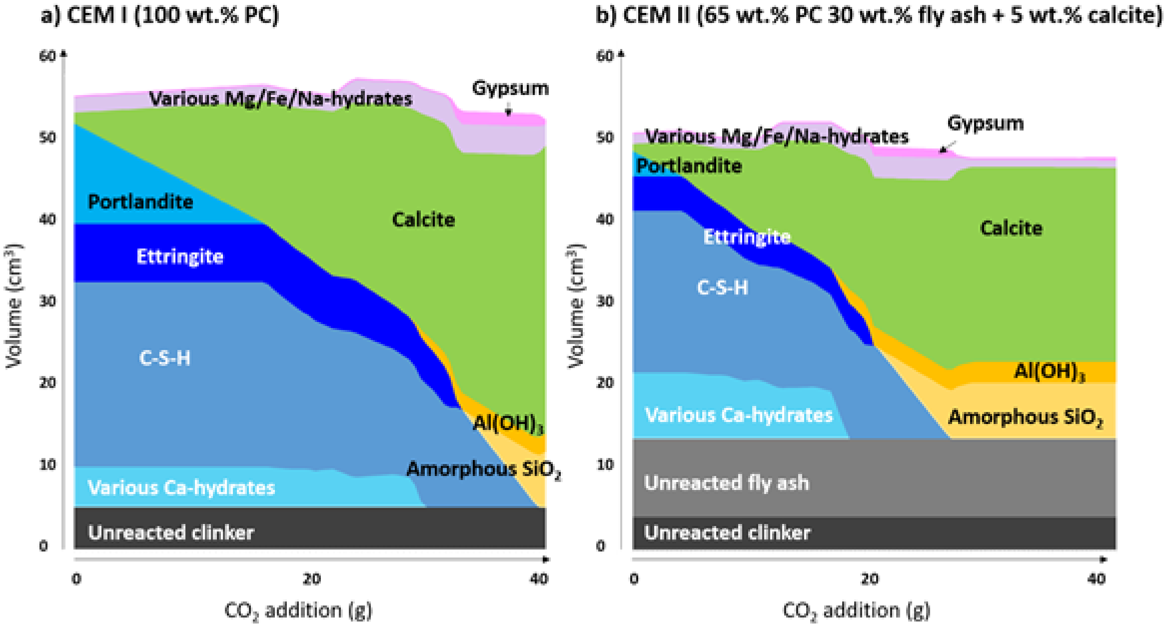

Figure 8-1: Schematic of the changes in the phase assemblage during carbonation of: a) PC, w/b = 0.5 and degree of reaction 90%; b) PC blended with calcite and fly ash, w/b = 0.5, degree of reaction of the clinker 80% and of fly ash 20%. The uncarbonated cement pastes are shown on the left-hand sides of the figures. Increasing CO_2 is added into the system towards the right-hand sides of the figures, which changes its chemistry. The figures have been produced by thermodynamic modelling using the CemGEMS App (https://cemgems.org/). 'Various Ca-hydrates' includes Si-hydrogarnet, stratlingite, and AFm phases, which are more susceptible to carbonation. 'Various Mg/Fe/Na hydrates' includes magnesium silicate hydrates, hydrotalcite-like phases, zeolite type phases containing sodium, and ferrihydrite, which are less susceptible to carbonation.

We observe that although the compositions of these initial mixes are different, carbonation has a similar effect on these materials. In Figure 8-1, portlandite is the first solid phase to destabilise upon addition of CO_2 (LHS of both panels A and B). Once portlandite has decomposed, increasing addition of CO_2 destabilises C-S-H and ettringite, which forms calcite. Further addition of CO_2 (Figure 5.1, towards the RHS of both panels A and B) destabilises the various other Ca-hydrates e.g. AFm, and both gypsum and disordered (alumino-)silicate gels (shown as $Al(OH)_3$, and amorphous SiO_2 here) are produced. Carbonation completes when the C-S-H has fully destabilised. Experimental studies show that in practice the $Al(OH)_3$ and amorphous SiO_2 phases illustrated in Figure 5.1 stabilise as a disordered (alumino-)silicate gel (Zajac, et al., 2020). We expect that this gel will mainly be silicate rich in carbonated CKD, CBD, and CSW, since these are low Al materials. Emerging research suggests that this (Al-)Si gel is pozzolanic, hence in addition to their dominant calcite content, we expect that carbonated CKD, CBD, and CSW possess some cementitious quality and can be at least utilised as reactive fillers (Table 5.1). Overall, the changes described here caused by carbonation lead to ±10% changes in porosity. Thus, we expect that the most CaO-rich phases in CKD, CBD, and CSW will decompose first during carbonation, and that the overall volume of particles will remain fairly constant.

Thus, if these materials (CKD, CBD, and CSW) undergo direct aqueous carbonation (as might be expected in land spreading), we expect that hydration will occur prior to carbonation, with CKD and CBD forming similar hydrate phases to those shown in Figure 8-1. This hydration should occur rapidly due to the fine particle sizes of CKD and CBD. We then expect that hydrated CKD, hydrated CBD, and CSW will decompose similarly to the trend described above for CEM I and CEM II and shown in Figure 8-1.Depending on the carbonation extent and alkali content of these materials (CKD, CBD, and CSW), phases such as zeolitic type materials, magnesium-silicate-hydrate (M-S-H), and stratlingite (‘various Ca-hydrates' and ‘various Mg/Fe/Na-hydrates’ in Figure 8-1) may stabilise. These phases can incorporate cations and/or anions into their structures, meaning that by managing exposure of CKD, CBD, and CSW to carbonation, we expect the carbonated output materials to have some potential to stabilise contaminants that may be present in industrial flue gases, and that carbonation can to some degree be considered as a waste treatment process. We mention this above in section 7.2 Portland Cement-based Wastes.

We expect carbonation products of CKD and CSW to be more similar to those formed in carbonation of CEM I and CEM II than CBD, since the latter contains larger amounts of SO_3 and Cl. Carbonation of CBD would thus produce some CaO-SO_3 based solids, decreasing the amount of calcite precipitated. Additionally, we do not expect Cl to incorporate into calcite or Al-Si gels, but rather in more highly soluble $CaCl_2$ or alkalis-Cl salts. These soluble solid phases will thus eventually dissolve and Cl will be released into the environment upon exposure to water.

Properties of RCA Post Carbonation

It is common to recycle end-of-life concrete into secondary aggregates (also known as ‘recycled cement aggregate’, RCA), using rough grinding as detailed in section 6.1. The replacement of primary aggregates by recycled aggregates in structural concrete leads to issues linked to increased water demand and reduced physical properties. Hence their use in concrete does not necessarily lead to a reduction in life cycle greenhouse gas emissions.

RCA can be carbonated prior to incorporation into mortar and concrete. This will likely require grinding to achieve a desirable high rate of carbonation. Wet carbonation leads to destabilisation of cementitious calcium hydrate phases, particularly portlandite ($Ca(OH)_2$) and C-S-H, as well as remnant unhydrated Portland cement clinker, resulting in the formation of mainly calcium carbonate phases and amorphous silica, see e.g. (Leemann & Loser, 2019). This is shown in Figure 8-1. The lower content of PC clinker and cementitious hydrates in the carbonated material means that there will be less demand for water in utilising carbonated RCA than uncarbonated RCA, which is one of its benefits. Additionally, it is expected that the precipitation of calcite will improve the physical properties of carbonated RCA relative to uncarbonated RCA, but confirmation of this requires further research.

We note here that while carbonated RCA are often considered to be inert and used as such (fillers and aggregates, Table 8-1), they are indeed reactive, at least similarly to natural limestone, and can thus at least substitute for natural limestone added into cement as a reactive filler/SCM. Additionally, if the cement in the RCA contains a sufficiently high amount of Al and Si containing SCMs, e.g. coal fly ash, carbonation of this RCA will stabilise calcite and an (Al-)Si gel within its solid phase assemblage (see Figure 8-1). Emerging research suggests that this (Al-)Si gel is pozzolanic, meaning that carbonated RCA may have potential to be used as a SCM in the future. Since cements and concretes are usually produced separately (by different companies and at different facilities), simultaneous use of fine natural limestone by the cement producer and use of carbonated aggregates by the concrete producer could overdose the system with CO_2 relative to the optimum calcium carbonate addition, which may thus ultimately decrease mechanical properties of the resulting concrete, and thus its environmental performance. Ideally concrete products should be specified to include the cement composition as a key factor.

8.2 Potential Use of carbonated Non-Portland Cementitious Materials

It is important to consider the effects of carbonation on the materials produced, in particular whether the process stabilises, or otherwise, trace elements within the matrix of the material.

Both FA and slag are less reactive than PC clinker, however they are still substantially reactive, standardised e.g. in EN 197-1, and widely used as SCMs. They are currently used to substitute ~20 wt% PC clinker in the UK, and including limestone the global clinker-to-cement ratio is 0.75 (Pamenter & Myers, 2021). Utilisation of these materials, calcined clays, and some other SCMs like silica fume, to substitute PC clinker in cement can be increased, at least up to a clinker-to-cement ratio of 0.5. Thus, it does not make sense to carbonate significantly reactive NPCMs. Poorly reactive NPCMs, and NPCMs with relatively high levels of contamination, should thus be targeted for carbonation.

Some types of FA and slag, including stockpiled materials, are known to have low reactivity and behave as fillers. These materials are suitable for carbonation. Carbonation of these materials results in the formation of calcite and Al-Si gels in addition to inert Al-Si phases. If the Al-Si gels gain reactivity, these materials may be suitable for use as reactive fillers, however, this requires further research.

Trace elements in FA and slags are usually stabilised within hydrated PC, either as hydroxide phases or in C-S-H and other cementitious phases, such as layered double hydroxides. These materials have high pH (>13). Stabilisation of trace elements is actually expected to increase at slightly lower pH environments (Sobiecka, 2013). But we expect complete carbonation of NPCMs to destabilise trace elements since this would reduce pH to relatively very low levels and calcite has limited sorption capacity. However, one way to stabilise trace elements in carbonated materials is to use them as additions (fillers, aggregates, etc.) in new concrete, since they would again be encapsulated in a cementitious matrix. This is demonstrated by the common worldwide use of NPCMs like FA and slag, which is perceived to carry very low risk to human health and the environment.

9.0 Design of a Carbonation Plant

9.1 Design Scenario

Given the preceding information in this report, the design of a carbonation plant suitable for processing industrial wastes was pursued. The design scenario involved the carbonation of cement bypass dust (CBD) as a candidate waste with flue gases from a cement plant, a schematic of which has been shown in Figure 9-1. The cement plant in this design was considered to have a typical clinker production capacity (1 Mt/y) with high annual plant operation (~90%, 7884 h/y). Two cases were considered based on the consumption of refuse-derived fuel (RDF) in the cement plant, namely (i) typical utilisation of RDF resulting in normal amounts of CBD ("Typical RDF") and (ii) doubled utilisation of RDF resulting in correspondingly more CBD ("Doubled RDF"). These analyses used process simulations in Aspen Plus to model the carbonation plant for each case, with further details given throughout subsequent sections. For both cases, the availability of CBD is consistent with such operation due to the elevated quantities of undesirable contaminants in RDF which necessitate purging through the bypass (and thus the formation of CBD). Importantly, although these circumstances are suitable for carbonation in this specific scenario, it must be reiterated that CBD should be preferentially considered as supplementary kiln feed when contamination is sufficiently low (as detailed in Table 8-1).

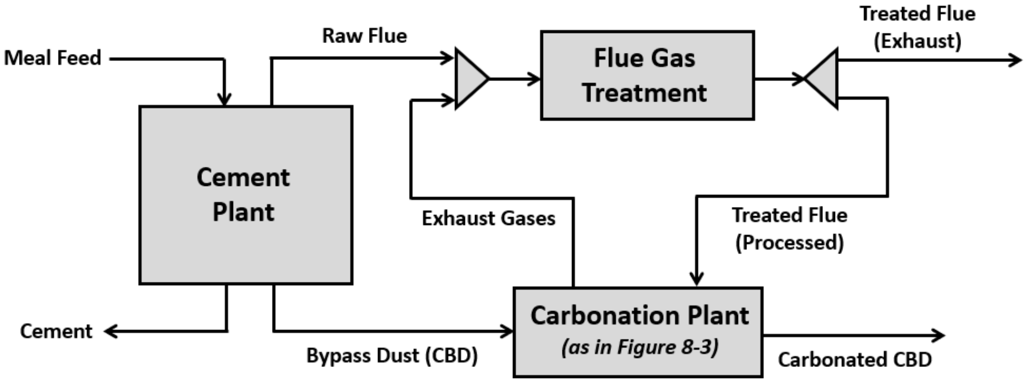

Figure 9-1: Schematic illustration of the design scenario considered in this research

The process considered in this design scenario is similar to the accelerated carbonation technology (ACT) developed by Carbon8 Aggregates, which has since separated to form the companies OCO Technologies and Carbon8 Systems. The latter has continued development of the technology into the CO_2ntainer system shown in Figure 9-2, which houses the required processing equipment within an ISO shipping container. The CO_2ntainer system has been successfully trialled at several industrial sites including the Montalieu cement plant (Lyon, France) operated by Vicat Group, as well as an waste-to-energy plant (Duiven, Netherlands) operated by AVR Energy, with both trials reporting positive results. The system carbonates solid waste using flue from the host plant, resulting in formation of carbonated lightweight aggregates. During testing at Montalieu, the unit was reportedly able to process ~7-12 kt/y of CBD and achieved ~20-30 wt% uptake of $CO_{2,}$ with other notable parameters including the feed temperature (~50°C), flue concentration (~20-30 vol% CO_2) and solid residence times (~15-20 min). Furthermore, the CO_2ntainer reportedly removes ~50% of the CO_2 from the processed flue, with further removal possible but likely undesirable (*i.e.* lower CO_2 concentrations in the reactor slowing kinetics and thereby limiting bulk solids throughput). Similar values were assumed/simulated in this research, with the aforementioned capacity of the CO_2ntainer corresponding to the "Typical RDF" case of this study (equating to ~0.8-1.5 t/h when assuming a plant operation of 90%).

Figure 9-2: Photograph of the CO_2ntainer unit developed by Carbon8 installed at the Montalieu cement plant (Lyon, France) operated by Vicat (AggNet, 2021)

9.2 Feedstock Conditions

Cement Bypass Dust

From the assumed cement plant, the generation of CBD for the two case studied was considered as ~3-13 kg/tonne (“Typical RDF”) and ~6-26 kg/tonne (“Doubled RDF”) of clinker, as detailed in section 7.2. This equates to a total CBD production of between ~0.4-1.7 and ~0.4-3.3 t/h for each case respectively. Based on this, the respective carbonation plants were designed for 1.7 and 3.3 t/h feed of CBD, meaning each plant would have the capacity to process the entirety of CBD generated on-site. The processed CBD can then be utilised on-site as carbonated material in the cement product, or supplied off-site to construction and/or agricultural applications (with the hazardous components remediated by carbonation). For simulations, the composition of CBD was based on those reviewed in Table 4-1, with special attention given to authors that identified/quantified the mineral phases (Kalina, et al., 2018) (Czapik, et al., 2020) (Hanein, et al., 2020). The composition of the CBD used in simulations (as in Table 9-1), was thus calculated by balancing the available mass of each component across the main phases identified in literature. Slight adjustments were made to the amounts of some components to ensure balancing across all species. This procedure gave a composition that was in agreement with literature and reflected the average quantity of free CaO available for carbonation (as this will have a considerable impact on simulations).

Table 9-1: Assumed composition of CBD for Aspen Simulations of Carbonation Process

Species	Phase	Phase composition[a] (wt%)
CaO	Free Lime	38.0
C_2S	Belite	17.1
C_3S	Alite	5.5
$CaSO_4$	Anhydrite	4.8
SiO_2	Quartz	3.5
Al_2O_3	Alumina	4.5
Fe_2O_3	Ferrite	3.0
MgO	Periclase	1.7
NaCl	Halite	3.0
KCl	Sylvite	10.9
K_2SO_4	Arcanite	8.0
TOTAL	-	100.0

[a]**Total Composition:** CaO (55.2 wt%), SiO_2 (10.9 wt%), Al_2O_3 (4.5 wt%), Fe_2O_3 (3.0 wt%), MgO (1.7 wt%), K_2O (11.2 wt%), Na_2O (1.6 wt%), SO_3 (6.5 wt%), Cl (7.0 wt%).

Regarding the physical properties of CBD, ranges for some properties include bulk density (~650 kg/m^3) (Lanzerstorfer, 2016), average particle size (~1-55 µm), and specific surface area (~0.35-1.1 m^2/g) (Kalina, et al., 2018) (Araizi, et al., 2016) (Khater, 2019) (Czapik, et al., 2020). Although these physical properties are not explicitly part of the subsequent Aspen simulations, they provide qualitative insight to the behaviour of CBD during processing. In particular, the small particle sizes evidence that size reduction processes (*e.g.* grinding) are unnecessary for this material feedstock. In subsequent calculations, the value assumed for bulk density was somewhat higher than above (1050 kg/m^3) to account for the wetted powders, with this value nonetheless in the range reported for the tapped bulk densities of CKD/CBD (~710-1280 kg/m^3) (Lanzerstorfer, 2016) and consistent with other cement powders.

Cement Flue Gases

Since the production of cement generates considerable amounts of CO_2, these exhausted flue gases can be used for carbonation. The quantity of flue gas produced is a function of many plant parameters (*e.g.* production rate, fuel characteristics, air leakages), however plants with clinker production between 0.7-1.1 Mt/y can be expected to produce between 220,000-350,000 Nm^3/h, corresponding to around 1.8-3.2 Nm^3/kg of clinker (Nazmul Hassan, 2005) (ECRA, 2016) (Tan, et al., 2014) (Gardarsdottir, et al., 2019) (Bosoada, et al., 2009) (Schorcht, et al., 2013). For the studied scenario, this corresponds to ~287,000 Nm^3/h of flue gas available for use in the carbonation plant (~2.6 Nm^3/kg of clinker).

Regarding composition, typical concentrations of CO_2 (22.4 mol%), N_2 (66.5 mol%), O_2 (2.1 mol%) and H_2O (9.0 mol%) were assumed during simulations, consistent with reviewed literature for cement plants in Table 7-2 (Schorcht, et al., 2013). In practise, exhaust gases often contain smaller quantities of other gases (*e.g.* NO_x, SO_x) (Schorcht, et al., 2013), however these were omitted from the simulation. Finally, although ‘raw’ flue gases leave the preheater at ~350°C, their temperature decreases significantly to ~110-160°C after utilisation and/or dust removal processes (ECRA, 2016) (Tan, et al., 2014) (Schorcht, et al., 2013). Since heat recovery from raw flue gases forms an important part of the BAT, simulations assumed only ‘treated’ flue gases were available for use in the carbonation plant with conservatively assumed temperatures of ~150°C.

9.3 Background on Rotary Reactors

As detailed in section 5.1, there are several routes that carbonation processes can take, with this study principally focussing on the direct carbonation by gas-solid contacting. Conceptually, there are a wide range of reactor designs that are suited to such gas-solid processes, ranging in complexity from relatively simple (*e.g.* travelling grates) to highly engineered (*e.g.* circulating fluidised beds). A commonly used reactor-type includes the rotary kiln, which is applied in a host of processes (*e.g.* drying, calcination, pyrolysis, *etc.*) that require sufficient mass and heat transfer between the gas and solid phases. Such equipment is technologically mature, and design procedures have been well documented (Moyers & Baldwin, 1997). A schematic illustration of a typical rotary kiln has been shown in Figure 9-3 to support discussion below.

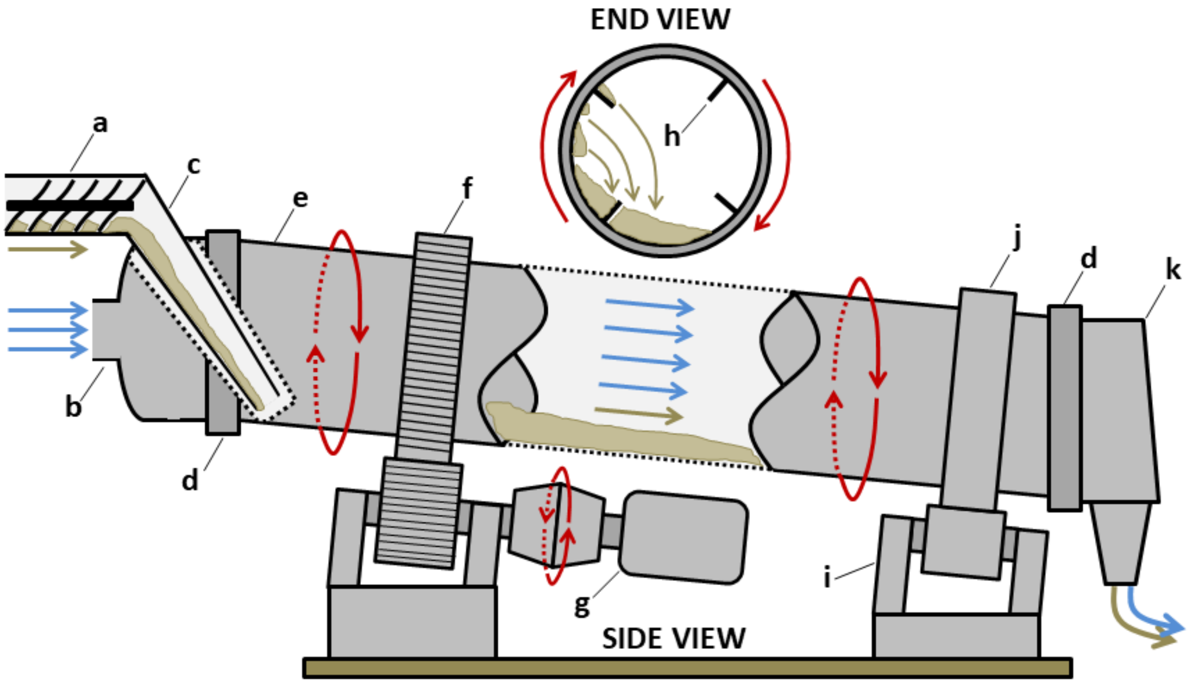

Figure 9-3: Schematic illustration of rotary carbonation reactor, namely (a) solids conveyer, (b) inlet head, (c) feed chute, (d) friction seal, (e) reactor shell, (f) thrust ring, (g) drive assembly, (h) lifting flights, (i) roll assembly, (j) rolling ring, (k) discharge head. Motion of solids (brown), gases (blue), and reactor (red). Adapted from (Moyers & Baldwin, 1997).

Fundamentally, rotary kilns consist of a cylindrical shell that is inclined at a slight downward angle (3-5^{o}) and slowly rotated (1-4 RPM) by an external drive assembly (Moyers & Baldwin, 1997). Figure 9-3 shows how solids are charged into the reactor through a feed chute and conveyer, with the rotation then causing gradual movement of the solids down the length of the reactor before eventual discharge. During operation, the feed rate is controlled to maintain a bed of solids (~10-20 vol%) within the reactor, known as the solid holdup (Moyers & Baldwin, 1997). Dams can be installed at various points along the reactor to ensure greater solid holdup (thereby forming a deeper bed of material within the shell).

Gas-solid contact is achieved by flowing gases the reactor, in either a cocurrent or countercurrent manner. Experience has established the former offers faster heating of solids and precise temperature control, whereas the latter achieves superior thermal efficiency. In either case, superficial gas velocities must be sufficiently low that blow-through of entrained particles is prevented (Moyers & Baldwin, 1997). This necessarily depends on the solid properties (*e.g.* density, particle size) however velocities in the range of ~0.5-5.0 m/s are generally reported (Moyers & Baldwin, 1997) (Davies, et al., 2010). Gas flow is accomplished with blower and/or exhaust fans, however blower-only configurations are discouraged since the above-ambient pressure within the reactor leads to gas (and often dust) leakage through friction seals (Moyers & Baldwin, 1997). Exhaust-only configurations maintain the internal pressure below ambient, and with properly maintained seals can limit air leakage into the reactor considerable (≤ 10%) (Moyers & Baldwin, 1997).

To improve gas-solid heat transfer, lifting flights are often installed throughout reactor on the shell walls. These agitate the bed of solids by dispersing them through the flowing gas as the reactor rotates (Moyers & Baldwin, 1997). Usually, straight flights are used in the early stages of the reactor to compensate for adhesive solids (*i.e.* wet powders), whereas in the middle-to-late stages these are angled/curved to better retain free-flowing solids (*i.e.* dried, fine powders) (Moyers & Baldwin, 1997). In the final stage, flights are not installed to prevent dust formation close to the reactor discharge. Chains can be also be installed to assist with heat transfer and to dislodge solids adhered on the surface of the shell (Moyers & Baldwin, 1997).

9.4 Aspen Simulation of Carbonation Plant

The process flowsheet principally used to simulate the process for both cases is shown in Figure 9-4. A brief description is given below, with details on each unit operation given in their respective sections. The treated flue gas from the cement plant (*FLUE-LP*) passes through the blower fan (*BLWR-FAN)* which slightly raises its pressure to achieve sufficient gas flow (*FLUE-HP*). This stream is mixed (*MIXER*) with incoming CBD and a small quantity of water (*WATER*) before reaction in the rotary reactor (*REACTOR*). The water is required due to insufficient moisture available in the flue gas. Following reaction, the products (*R-PROD*) are processed by a discharge cyclone (*CYCLONE*), which separates the freshly carbonated solids (*CARB-CBD*) from the exhausted gases (*EXHAUST*). The carbonated CBD is retained as the product, whereas the exhausted gases are returned to the flue stack for release to atmosphere.

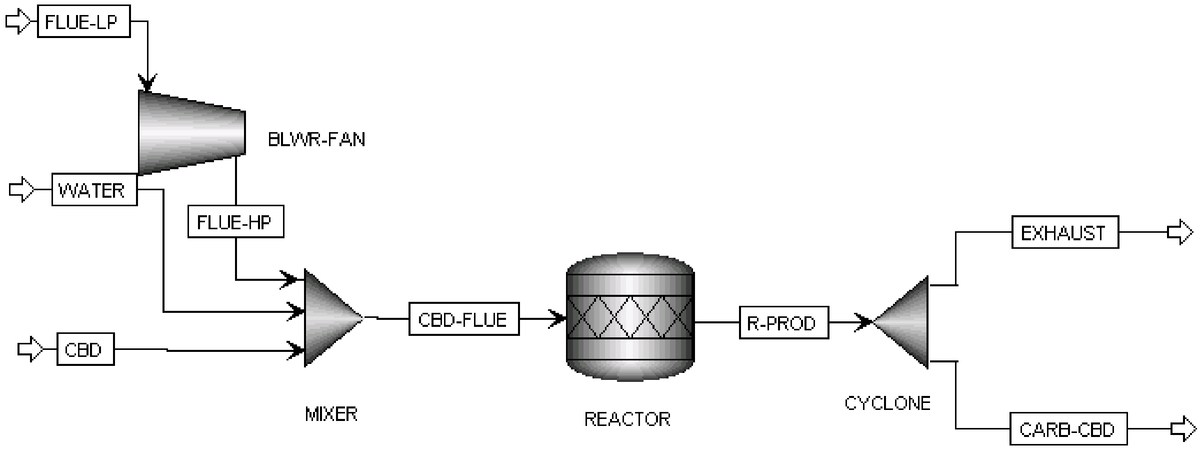

Figure 9-4: Process flowsheet of carbonation plant simulated in Aspen Plus

Screw Conveyer

On-site solid transport processes were not explicitly modelled in Aspen Plus, since such processes require more detailed design information (*e.g.* location of the bypass discharge relative to the carbonation plant). Conceptually, installation of the carbonation process adjacent to the bypass is ideal, since this minimises installation costs (*e.g.* piping, lagging) and allows convenient discharge of the CBD directly into the carbonation process. However, there are undoubtedly practical and/or operational reasons that could disallow this (*e.g.* insufficient space), meaning on-site transportation of CBD might be necessary. For both cases, a screw conveyer of nominal length (~3 m) was included in the costing, which was deemed suitable to introduce the CBD into the carbonation reactor (as seen on Figure 9-3).

Blower- & Exhaust-Fans

As mentioned previously, to limit gas and dust leakage from the friction seals of the rotary reactor the internal pressure must be kept sufficiently low. Hence, both cases considered the use of both blower- and exhaust-fans, which achieve gas flow without excessively raising the internal pressure. Only the blower-fan was modelled in Aspen Plus (*BLWR-FAN*, in Figure 9-4), however a second identical unit was considered during plant costing for the exhaust-fan. Simulations modelled the blower-fan as an isentropic compressor with high isentropic and mechanical efficiencies (90%). The process temperature was the same as the available flue gas (150 °C), whilst a reasonable discharge pressure was assumed (1.2 bar).

Sizing depends on the volumetric flowrate of flue gas (Q_a) being processed. However, this was limited by the allowable superficial gas velocity (u_G) through the reactor, which must be kept sufficiently low to prevent blow-through of entrained particles. As seen in Table 9-2, an assumed gas velocity (∼1 m/s) was used to calculate the maximum allowable flowrate of flue gases through the rotary reactor in each case. Reactor diameters (D_R) of 1.00 and 1.28 m were ultimately selected for the Typical RDF and Doubled RDF cases (as further justified below). This meant the allowable volumetric flowrates of flue gas through the respective processes was 2,400 and 3,718 m^3/h, which under normal conditions equates to ∼1950 and ∼3,050 Nm^3/h. Hence, the blower- and exhaust-fans for each case were simulated with design capacities of 2000 and 3100 Nm^3/h, which accounted for a nominal fraction of the total flue gas available in the design scenario (<2%). For adequate corrosion resistance under the conditions of the flue gas, both fans were specified as stainless steel and costed using the appropriate material factor (F_m = 250%) (Garrett, 1989).

Table 9-2 Sizing of rotary reactor according to superficial gas velocity ($u_G \leq 1$ m/s)

Case Study	Reactor Dimensions			Allowable Gas Flowrate[b]		
	Diameter, D_R (m)	Length, L_R (m)	Headspace[a] (m^2)	Actual, Q_a (m^3/h)	Normal, Q_n (Nm^3/h)	Percentage of Flue[c] (-/-)
Typical RDF	1.00	10	0.66	2,377	1,950	0.68
Doubled RDF	1.28	13	1.03	3,718	3,050	1.06

[a] **Headspace Area:** assuming uniform solids holdup (H_S = 20%) across length of reactor
[b] **Actual Gas Flowrate:** occurring at temperature (T = 150°C) and pressure (P = 1.2 bar)
[c] **Fraction of Flue:** fraction used of that available in the design scenario (∼287,000 Nm^3/h)

Rotary Reactor

The rotary reactor (*REACTOR*, in Figure 9-4) was modelled with an RStoic block in Aspen Plus, which operated at a fixed pressure (1.2 bar) and temperature (80 °C). This reduced temperature resulted from of the *FLUE-HP* (150 °C) and *CBD* (25 °C) streams, reflecting ideal heating of the solid material by the hot flue. The hydration and carbonation of reactive CaO and/or hydrated $Ca(OH)_2$ are known to proceed at such mild conditions (Lackner, et al., 1997) (Bobicki, et al., 2012) (Renforth, et al., 2011). The extent of reaction within the reactor was selected as an input parameter, and was based on relevant literature and previous sections of this report, with further details given in subsequent paragraphs and in Table 9-4.

For instance, the hydration of CaO to $Ca(OH)_2$ is known to proceed at moderate rates even at mild temperatures (90-200 °C), and under certain conditions can achieve near-complete conversion in several minutes (Maciel-Camacho, et al., 1997) (Galwey & Laverty, 1993) (Schaube, et al., 2012). Subsequent carbonation of $Ca(OH)_2$ is also known to proceed at similar temperatures. Reports in the literature show that $Ca(OH)_2$ readily carbonates under mild temperature (60-90 °C), relative humidity (50-80%) and simulated flue gas concentrations (12-40% CO_2). Under these conditions, the authors report conversions between ~23-34 wt% with slowing of the rate after ~30 min and minimal further conversion at ~60 min (Shih, et al., 1999) (Liu & Shih, 2008) (Liu, et al., 2010).

There was comparatively little effect on the reaction from changes in reaction temperature (between 60-90 °C) and CO_2 concentration (between 3-40%), but strong effects from relative humidity with the reaction not proceeding below a critical threshold value (~8%) (Shih, et al., 1999) (Liu, et al., 2010). This was the reason for the addition of water to CBD before entering the reactor (*i.e.* to boost the relative humidity inside the reactor and accelerate hydration of CBD). It is also worth noting these experiments used similarly sized particles (~6-90 µm) but with larger specific surface areas (~10-20 m^2/g) than those reviewed for CBD. Hence, carbonation of CBD would be expected to be somewhat slower due to increased mass transfer limitations compared to the aforementioned experiments.

Accordingly, the reactions in the reactor were modelled as complete hydration of the free CaO, C_2S and C_3S content of CBD to afford $Ca(OH)_2$ and SiO_2 (Eqns. 9.1-9.3), followed by limited carbonation of the $Ca(OH)_2$ to $CaCO_3$ (Eqn. 9.4). With the composition assumed in Table 9-1, complete carbonation of the CaO, C_2S and C_3S components would result in the maximum theoretical uptake previously calculated for CBD (~41 wt%, as presented in Table 6-5). This allowed the actual CO_2 uptake by the CBD to be varied by adjusting the conversion of the carbonation reaction. For this study, the set of values studied was 2, 5, 10, 25, 50, 75 and 100% of the theoretical uptake, which gave a suitably wide range for examination. In the absence of detailed heat transfer calculations (*e.g.* losses through reactor shell) the heat of reaction (ΔH_R) values (Eqn. 9.1-9.4) were neglected. Nevertheless, these reactions are exothermic and in practise self-heating to below ~100°C to be reasonably assumed depending on thermal ballast within the reactor.

$$\mathrm{CaO + H_2O \longrightarrow Ca(OH)_2} \quad \textbf{9.1}$$

$$\mathrm{C_2S + 2H_2O \longrightarrow 2Ca(OH)_2 + SiO_2} \quad \textbf{9.2}$$

$$\mathrm{C_3S + 3H_2O \longrightarrow 3Ca(OH)_2 + SiO_2} \quad \textbf{9.3}$$

$$\mathrm{Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O} \quad \textbf{9.4}$$

As previously, the reactor diameter was selected based on the superficial gas velocity and allowable flue flowrate within the reactor, leading to values for the Typical RDF and Doubled RDF cases (D_R = 1.00 and 1.28 m respectively). Based on these values, the other dimensions were iteratively adjusted to give an appropriate residence time (t_S) for the solids within the reactor. Empirical correlations in literature allow calculation of the residence time in terms of the length (L_R), diameter (D_R), rotation speed (n_R), and angle of inclination (β_R) of the reactor, as well as the volumetric feed rate (V_S) and angle of repose (θ_S) of the solids (Eqn. 9.5) (Chatterjee, et al., 1983) (Liu & Specht, 2006). The solid feedrates were the maxima specified for the "Typical RDF" (V_s = 1700 kg/h) and "Double RDF" (V_s = 3300 kg/h) cases respectively. Other properties including the bulk density (~1050 kg/m^3) and angle of repose (θ_S = 52^o) were taken from literature (Lanzerstorfer, 2016). Reasonable values were assumed for the rotation speed (n_R = 0.5 RPM) and angle of inclination (β_R = 3^o) of the kiln. This procedure calculated reactor lengths (L_R = 10 and 13 m) that gave sufficient residence time (t_S = 61 and 64 min) for the Typical RDF and Doubled RDF cases respectively, whilst also maintaining the superficial gas velocity (u_G = 1 m/s) and solids holdup (H_s = 20%).

$$t_s = \frac{0.1026\, {L_R}^3}{\dot{V_s}} \left(\frac{\theta_s}{\beta_R}\right)^{1.054} \left(\frac{\dot{V_s}}{{L_R}^3\, n_R}\right)^{0.981} \left(\frac{L_R}{D_R}\right)^{1.054} \qquad 9.5$$

Since calculations assumed uniform superficial gas velocity across the entire length of the reactor, the gas residence time (t_G) could be easily approximated from the respective reactor lengths in each case (t_G = 10 and 13 s). As both the solid and gas residence times were satisfactory, the reactors were costed at the above sizes. Again, due to the presence of alkaline solids the rotary reactor was specified for operation with corrosive materials and costed with the relevant material factor (F_m = 150%) (Garrett, 1989).

Discharge Cyclone

The conditions in the reactor are designed to minimise dust formation and entrainment, however smaller particles may be carried out of the reactor within the discharged gases. Hence, a final separation process is required to collect the carbonated CBD, whilst returning dust-free exhaust gas to the flue stack for release to atmosphere. During simulations, the discharge cyclone was considered to have an ideal removal efficiency (100%), meaning all carbonated CBD was recovered without any losses to the exhausted gas. In practise, entrained particles of CBD mean the exhausted gas may have to be redirected to the cement plant for additional dust removal (with associated cost). As was discussed for the fans, design specification of the discharge cyclone was based on the exhaust gas flowrate, which was conservatively assumed as identical to the inlet flowrate of flue (2000 and 3100 Nm^3/h for the Typical RDF and Doubled RDF respectively). As before, due to the possibility for corrosion by alkaline dusts the cyclone was specified as stainless steel and costed with the appropriate material factor (F_m = 180%) (Garrett, 1989).

Results of Simulation

The results of a representative simulation for the Typical RDF and Doubled RDF cases are summarised in Table 6.3 below. For each scenario the conversion of $Ca(OH)_2$ (Eqn. 9.4) was specified as 50%, corresponding to actual CO_2 uptakes of ~21 wt% in each case. This value was consistent with literature for carbonation of $Ca(OH)_2$ (23-34 wt%), as well as the experimental CO_2 uptakes reported for CBD (~26 wt% Table 6-5). Accordingly, this scenario was considered the most likely outcome and is the main focus of further analyses. However, in order to establish the effect of conversion over a wide range of uptake values, simulations were also performed for $Ca(OH)_2$ conversions of 2, 5, 10, 25, and 75%, as seen in Table 9-4. This allowed the impact of process performance on subsequent costing to be determined. The complete conversion of $Ca(OH)_2$ of 100% was also modelled to conveniently establish an absolute lower bound in subsequent costing, however this should not be interpreted as achievable performance since such conversions greatly exceed those observed experimentally. Overall, assuming plausible conversion values lie between 25-75%, the Typical RDF and Doubled RDF cases were modelled to produce ~2.1-2.3 and ~4.0-4.5 t/h of carbonated CBD respectively. This achieved the capture of ~0.18-0.53 and ~0.34-1.03 t/h of CO_2 for the Typical and Doubled RDF cases respectively, accounting for an annual removal of ~1.1-4.2 and ~2.7-8.1 kt/y of CO_2. Assuming the aforementioned conversion range for CBD, the carbonation plant was suggested to be able to remove 22-66 and 28-83% of the CO_2 from the processed flue.

Table 9-3: Stream inputs to Aspen simulations of carbonation plant for the (a) Typical RDF, and (b) Doubled RDF cases. Results are shown for an actual uptake (~21 wt%) that corresponds to 50% of the maximum theoretical uptake (~41 wt%) of CBD.

(a) Typical RDF	**CBD**	**WATER**	**FLUE-LP**	**FLUE-HP**	**CBD-FLUE**	**R-PROD**	**EXHAUST**	**CARB-CBD**
Process Conditions								
Temperature (^{o}C)	25	25	150	172	55	90	90	90
Pressure (bar)	1.0	1.0	1.0	1.2	1.2	1.2	1.2	1.2
Vapour Fraction (-/-)	0.00	0.00	1.00	1.00	0.60	0.528	1.00	0.00
Liquid Fraction (-/-)	0.00	1.00	0.00	0.00	0.03	0	0.00	0.00
Solid Fraction (-/-)	1.00	0.00	0.00	0.00	0.37	0.48	0.00	1.00
Mass Flowrates (t/h)								
TOTAL	1.700	0.230	2.694	2.694	4.624	4.624	2.424	2.200
CaO	0.646	-	-	-	0.646	-	-	-
C_3S	0.094	-	-	-	0.094	-	-	-
C_2S	0.291	-	-	-	0.291	-	-	-
$Ca(OH)_2$	-	-	-	-	-	0.597	-	0.597
$CaCO_3$	-	-	-	-	-	0.807	-	0.807
SiO_2	0.060	-	-	-	0.060	0.186	-	0.186
Al_2O_3	0.077	-	-	-	0.077	0.077	-	0.077
Fe_2O_3	0.051	-	-	-	0.051	0.051	-	0.051
MgO	0.029	-	-	-	0.029	0.029	-	0.029
$CaSO_4$	0.082	-	-	-	0.082	0.082	-	0.082
KCl	0.185	-	-	-	0.185	0.185	-	0.185
NaCl	0.051	-	-	-	0.051	0.051	-	0.051
K_2SO_4	0.136	-	-	-	0.136	0.136	-	0.136
O_2	-	-	0.064	0.064	0.064	0.064	0.064	-
N_2	-	-	1.660	1.660	1.660	1.660	1.660	-
CO_2	-	-	0.858	0.858	0.858	0.503	0.503	-
H_2O	-	0.230	0.113	0.113	0.343	0.198	0.198	-

(b) Doubled RDF	**CBD**	**WATER**	**FLUE-LP**	**FLUE-HP**	**CBD-FLUE**	**R-PROD**	**EXHAUST**	**CARB-CBD**
Process Conditions								
Temperature (^{o}C)	25	25	150	172	51	90	90	90
Pressure (bar)	1	1	1	1.2	1.2	1.2	1.2	1.2
Vapour Fraction (-/-)	0.00	0.00	1.00	1.00	0.44	0.34	1.00	0.00
Liquid Fraction (-/-)	0.00	1.00	0.00	0.00	0.06	0.00	0.00	0.00
Solid Fraction (-/-)	1.00	0.00	0.00	0.00	0.51	0.66	0.00	1.00
Mass Flowrate (t/h)								
TOTAL	3.300	0.450	4.214	4.214	7.964	7.964	3.693	4.271
CaO	1.254	-	-	-	1.254	-	-	-
C_3S	0.182	-	-	-	0.182	-	-	-
C_2S	0.564	-	-	-	0.564	-	-	-
$Ca(OH)_2$	-	-	-	-	-	1.160	-	1.160
$CaCO_3$	-	-	-	-	-	1.566	-	1.566
SiO_2	0.116	-	-	-	0.116	0.360	-	0.360
Al_2O_3	0.149	-	-	-	0.149	0.149	-	0.149
Fe_2O_3	0.099	-	-	-	0.099	0.099	-	0.099
MgO	0.056	-	-	-	0.056	0.056	-	0.056
$CaSO_4$	0.158	-	-	-	0.158	0.158	-	0.158
KCl	0.360	-	-	-	0.360	0.360	-	0.360
NaCl	0.099	-	-	-	0.099	0.099	-	0.099
K_2SO_4	0.264	-	-	-	0.264	0.264	-	0.264
O_2	-	-	0.100	0.100	0.100	0.100	0.100	-
N_2	-	-	2.596	2.596	2.596	2.596	2.596	-
CO_2	-	-	1.341	1.341	1.341	0.653	0.653	-
H_2O	-	0.450	0.177	0.177	0.627	0.345	0.345	-

Table 9-4: Composition of carbonated CBD product stream assuming different uptakes

Specified Conversion (%) **Actual Uptake (wt%)**	**2** **0.8**	**5** **2.1**	**10** **4.2**	**25** **10.4**	**50** **20.9**	**75** **31.3**	**100[a]** **41.7**
(a) Typical RDF	**CARB-CBD**						
Mass Flowrate (t/h)							
TOTAL	1.999	2.011	2.032	2.095	2.200	2.305	2.410
CaO	-	-	-	-	-	-	-
C_3S	-	-	-	-	-	-	-
C_2S	-	-	-	-	-	-	-
$Ca(OH)_2$	1.171	1.135	1.075	0.896	0.597	0.299	-
$CaCO_3$	0.032	0.081	0.161	0.403	0.807	1.210	1.614
SiO_2	0.186	0.186	0.186	0.186	0.186	0.186	0.186
Al_2O_3	0.077	0.077	0.077	0.077	0.077	0.077	0.077
Fe_2O_3	0.051	0.051	0.051	0.051	0.051	0.051	0.051
MgO	0.029	0.029	0.029	0.029	0.029	0.029	0.029
$CaSO_4$	0.082	0.082	0.082	0.082	0.082	0.082	0.082
KCl	0.185	0.185	0.185	0.185	0.185	0.185	0.185
NaCl	0.051	0.051	0.051	0.051	0.051	0.051	0.051
K_2SO_4	0.136	0.136	0.136	0.136	0.136	0.136	0.136
(b) Doubled RDF	**CARB-CBD**						
Mass Flowrate (t/h)							
TOTAL	3.880	3.905	3.945	4.067	4.271	4.474	4.656
CaO	-	-	-	-	-	-	-
C_3S	-	-	-	-	-	-	-
C_2S	-	-	-	-	-	-	-
$Ca(OH)_2$	2.273	2.203	2.087	1.739	1.160	0.580	0.061
$CaCO_3$	0.063	0.157	0.313	0.783	1.566	2.349	3.051
SiO_2	0.360	0.360	0.360	0.360	0.360	0.360	0.360
Al_2O_3	0.149	0.149	0.149	0.149	0.149	0.149	0.149
Fe_2O_3	0.099	0.099	0.099	0.099	0.099	0.099	0.099
MgO	0.056	0.056	0.056	0.056	0.056	0.056	0.056
$CaSO_4$	0.158	0.158	0.158	0.158	0.158	0.158	0.158
KCl	0.360	0.360	0.360	0.360	0.360	0.360	0.360
NaCl	0.099	0.099	0.099	0.099	0.099	0.099	0.099
K_2SO_4	0.264	0.264	0.264	0.264	0.264	0.264	0.264

[a] **Conversion:** Complete conversion is not reported experimentally, and so should not be interpreted as realistically achievable performance. This case has only been modelled to provide an absolute lower bound in subsequent costing.

These results evidence the technical viability for carbonation processes to be installed at cement plants according to this design scenario, mostly due to the free availability of both carbonatable solids and suitably concentrated CO_2. Furthermore, the relative simplicity of the carbonation process in this design means minimal additional inputs are required that do not impact operation of the host cement plant (*e.g.* heating, cooling, power, labour *etc.*). However, although technically feasible, the studied carbonation process cannot achieve meaningful reductions in net CO_2 emissions. Evidentially, the capacity of the carbonation process only represents a nominal fraction of the flue generated by the host cement plant (<2%, as seen in Table 8-2). Accordingly, even with reasonable CBD conversions (25-75%) with uptakes between 10-31 wt%, carbonation only results in the capture of ~0.3-0.9% of the direct CO_2 emissions from the cement plant. Even in the (unrealistic) scenario of complete carbonation with maximum uptake (41.7 wt%) only ~1.2% of the direct emissions are captured. With this perspective, it becomes evident that the value of carbonation lies primarily in its abilities for remediation of hazardous wastes that otherwise incur gate fees for disposal/landfilling (further shown in 8.0 Market Analysis).

9.5 Plant Costing

The carbonation process used in this design scenario was costed using a conventional procedure in literature (Sinnott, 2005), which was used to find the capital (CAPEX) and operating (OPEX) expenditures for both the Typical RDF and Doubled RDF cases. Initially, each piece of equipment was sized according to the respective sizing variables mentioned, with these values taken from the results of process simulations on Aspen (as detailed above). The purchase cost for each piece of equipment in 1987 was then taken from correlations by (Garrett, 1989), and converted from $\$_{1987}$ to $\$_{2020}$ using the corresponding CEPCI values for 1987 (324) and 2020 (596) (Vatavuk, 2002) (CEO, 2021). This was then converted to £$_{2020}$ using the current exchange rate (0.787 £$_{2020}$/$\$_{2020}$) to give the cost in the UK as of 2020. The purchase cost breakdown in Table 9-5 highlights the total purchase cost (TPC) in both cases is dominated by the rotary reactor (accounting for ~95% of TPC), with the Typical RDF and Doubled RDF cases costing around £0.85m and £1.1m respectively.

The CAPEX of the carbonation process was then calculated using a factorial method, as seen in Table 9-6. Subsequently, the working capital cost (WCC) was calculated which was assumed at a nominal value (~5%) of the FFC, since carbonation does not conceptually require significant working capital (*e.g.* no reagents that need stockpiling before operation). The cumulative sum of FCC and WCC values thus gave the total CAPEX for the carbonation process, which was evaluated at around £3.6m and £4.9m in 2020 for the Typical RDF and Doubled RDF cases respectively. The magnitude of this value was considered reasonable since the process is at limited scale (~2% of the host cement plant by processed solids) and requires relatively simple processing equipment.

Table 9-5: Total purchase cost (TPC) of process equipment required for the studied carbonation plant, for the (a) Typical RDF and (b) Doubled RDF cases respectively.

Equipment	**Sizing Variable**	**Size**		**Purchased Cost[a],[b]**	
				$\$_{1987}$	**£$_{2020}$**
(a) Typical RDF					
Screw Conveyer	Length	3	m	2,000	2,899
Blower Fan	Flowrate	2,400	m^3/h	5,300	7,683
Exhaust Fan	Flowrate	2,400	m^3/h	5,300	7,683
Rotary Reactor	Heat Input[c]	0.3	MW	570,000	826,208
Discharge Cyclone	Flowrate	2,400	m^3/h	1,413	2,048
Total Purchase Cost (TPC)				**$584,013**	**£846,520**
(b) Doubled RDF					
Screw Conveyer	Length	3	m	2,000	2,899
Blower Fan	Flowrate	3,718	m^3/h	6,522	9,454
Exhaust Fan	Flowrate	3,718	m^3/h	6,522	9,454
Rotary Reactor	Heat Input[c]	0.6	MW	769,713	1,115,690
Discharge Cyclone	Flowrate	3,718	m^3/h	2,668	3,867
Total Purchase Cost (TPC)				**$787,426**	**£1,141,364**

[a] **Plant Cost Index:** CEPCI(1987) = 324, CEPCI(2020) = 596

[b] **Exchange Rate:** Taken as 0.787 £$_{2020}$/$\$_{2020}$,

[c] **Rotary Reactor**: Sizing parameter is usually the heat input [MBtu/h], however due to zero heat input sizing was instead by minimum cooling duty [MBtu/h] predicted by Aspen simulations.

With regard to OPEX, similar calculations were performed as seen in Table 9-7. Both the CBD and flue gas were assumed delivered from the cement plant for negligible cost. For mains water the assumed price of £0.60/tonne meant costs were around £1,088 and £2,129 per year for the Typical RDF and Doubled RDF cases. There were also utility costs for electricity to power the blower- and exhaust-fans (~20 and 30 kW/ea for the cases respectively) and the single drive assembly (~40 kW) of the rotary reactor, meaning each case study required £56,700 and £73,000 per year with an assumed electricity price of £0.09/kWh in 2020 (BEIS, 2020). With an additional nominal factor for miscellaneous upkeep (5%), the total variable operating cost (VOC) was evaluated. Similar to with CAPEX, various factors were assumed to calculate the fixed operating cost (FOC), which is reported as the sum of maintenance costs (MC), operating labour costs (LC) and other costs (OC), as detailed in Table 9-7. MC was calculated by an assumed factor based on the PPC. Whereas, LC was calculated from suitable manning estimates (*i.e.* five shifts of one operator with salaries of £27,000, with the operation of the carbonation plant accounting for ~10% of one operators' time) and additional labour factors (*e.g.* supervision, laboratory, overheads, *etc.*). Altogether, these suggested the direct production costs (DPC) for the Typical RDF case as £0.85m per year, and £1.1m for the Doubled RDF. With an additional 20% for other post-production factors (*e.g.* sales, overheads, research, *etc.*) the annual production cost (APC) for each of these cases increased to £1.02m and £1.36m per year respectively.

Table 9-6: Breakdown of capital expenditure (CAPEX) for simulated carbonation plant

Parameter		Calculation	Typical RDF	Doubled RDF	Unit
Fixed Capital Costs					
Total Purchase Cost	(TPC)	-	846,520	1,141,364	$£_{2020}$
Direct Factors[a]	(f_1)	-	215	215	%
Total Physical Plant Cost	(PPC)	TPC x f_1	2,666,538	3,595,296	$£_{2020}$
Indirect Factors[b]	(f_2)	-	30	30	%
Fixed Capital Cost	(FCC)	PPC x f_2	3,466,500	4,673,885	$£_{2020}$
Working Capital Costs					
Working Factor[c]	(f_3)	-	5	5	%
Working Capital Cost	(WCC)	FCC x f_3	173,325	233,694	$£_{2020}$
Total Capital Cost					
Capital Expenditure	(CAPEX)	FCC+WCC	3,639,825	4,907,579	$£_{2020}$

[a]Direct Factors: Equipment erection (45%), piping (45%), instrumentation (15%), electrical (10%), process buildings (10%), utilities (45%), storages (20%), site development (5%) and ancillary buildings (20%).

[b] Indirect Factors: Design and engineering (20%), contractor fees (5%), contingency (5%)

[c] Working Factors: Initial maintenance, spares parts, *etc.* (5%)

As discussed previously, varying the assumed conversion of $Ca(OH)_2$ to $CaCO_3$ within the reactor allows a range of carbonation scenarios to be compared. The scenarios examined were 2, 5, 10, 25, 50, 75 and 100% of the theoretical maximum CO_2 uptake, which resulted in actual uptake values of 0.8, 2.1, 4.2, 10.4, 20.9, 31.3 and 41.7 wt% (as seen in Table 9-4). Given the simulated flowrates of carbonated CBD for the Typical RDF and Doubled RDF cases in

Table 9-4, this equated to a specific production cost (PC) with limits between £56-62/tonne and £38-42/tonne of carbonated CBD respectively (for 25-75% of theoretical carbonation). The absolute lower bound for production cost in each case (corresponding to 100% of theoretical) was £53/tonne and £37/tonne of carbonated CBD for the Typical RDF and Doubled RDF cases respectively.

Table 9-7 Breakdown of operating expenditure (OPEX) for simulated carbonation plant

Parameter		Calculation	Typical RDF	Doubled RDF	Unit
Variable Operating Costs					
Cement Bypass Dust	(CBD)	-	0	0	£$_{2020}$/y
Treated Flue Gas	(FG)	-	0	0	£$_{2020}$/y
Utilities	(Ut)	-	57,853	73,085	£$_{2020}$/y
Miscellaneous Factor	(f_4)	-	5	5	%
Miscellaneous Cost	(Misc)	MC x f_4	13,333	17,976	£$_{2020}$/y
Variable Operating Cost	(VOC)	CBD+FG+Ut+Misc	71,185	91,061	£$_{2020}$/y
Fixed Operating Costs					
Operating Factors[a]	(f_5)	-	114	114	%
Maintenance Costs	(MC)	PPC x f_5	266,654	359,530	£$_{2020}$/y
Operating Labour Costs	(LC)	LC x f_5	24,300	24,300	£$_{2020}$/y
Other Costs	(OC)	OC x f_5	485,310	654,344	£$_{2020}$/y
Fixed Operating Costs	(FOC)	MC+LC+OC	776,264	1,038,173	£$_{2020}$/y
Annual Production Cost					
Direct Production Cost	(DPC)	VOC + FOC	847,449	1,129,235	£$_{2020}$/y
Indirect Factors[b]	(f_6)	-	20	20	%
Indirect Production Cost	(IPC)	DPC x f_6	169,490	225,847	£$_{2020}$/y
Annual Production Cost	(APC)	DPC + IPC	1,016,939	1,355,081	£$_{2020}$/y
Specific Production Cost					
Solids Feed Rate	(m_{FEED})	-	13,403	26,017	t/y
Theoretical CO_2 Uptake	Th(CO_2)	-	41.1	41.1	wt%
Extent of Carbonation	(η)	-	25 to 75	25 to 75	%
Actual CO_2 Uptake	Ac(CO_2)	η x Th(CO_2)	10.4 to 31.3	10.4 to 31.3	wt%
Carbonated Product Rate	(m_{PROD})	m_{FEED} (1+ Ac(CO_2))	16,517 to 17,345	32,064 to 33,673	t/y
Production Cost (PC)		APC/m_{PROD}	56 to 62	38 to 42	£$_{2020}$/t

[a] Operating Factors: Maintenance (10%), operating labour (10%), laboratory cost (20%), supervision (10%), plant overheads (50%), capital charges (10%), local taxes (1%), insurance (2%), license fees (1%).

[b] Indirect Operating Factors: Sales, general overheads, research and development (20%)

From these analyses, several changes can be recommended to improve the viability of such a carbonation plant. In both Typical RDF and Doubled RDF cases, Table 9-5 showed the CAPEX was dominated by the installed cost of the rotary reactor, which accounted for the overwhelming majority (~95%) of the purchase cost of equipment (PCE). Hence, practically all efforts to reduce the CAPEX should focus on minimising the purchase cost of the reactor (as further discussed subsequently). This is especially important since Table 9-7 also showed the single biggest contribution toward OPEX was from Other Costs (OC) (~49% of APC, or ~58% of DPC), which highlighted that a significant fraction of the OPEX resulted from capital charges recovering the CAPEX. This was mainly due to the negligible costs for raw materials (*i.e.* assumption that CBD and flue sourced from the host cement plant without cost), as well as minimal costs for utilities including electricity (~5% of APC) and mains water (~0.2% of APC) for both the Typical RDF and Doubled RDF cases respectively.

Therefore, reduction in the cost of the rotary reactor will significantly improve the overall economic performance of the carbonation plant by simultaneously lowering the CAPEX and OPEX, resulting in a decreased production cost for carbonated CBD. There are several improvements that might be investigated to this end. Firstly, the maximising the solids holdup within the reactor would minimise its size (and therefore cost) by increasing material throughput. Although typical solids holdup (20%) is constrained by operational problems (*e.g.* short-circuiting of solids), higher holdups might be tolerated with altered reactor designs (*e.g.* more flights, discharge dams, *etc.*). Secondly, the reactor was specified for corrosive environments with an appropriate material factor (F_M = 150%), which increased costs above standard materials (*i.e.* mild steel, with F_M = 100%). Studies should ascertain if corrosion will pose significant problems under the conditions in the reactor. If the rate of corrosion is acceptable (relative to the lifetime of the plant), cost reductions might be achieved by simply using mild steel with a nominal corrosion allowance. Finally, if the quantity of processed material can be substantially increased (*e.g.* carbonating CBD from multiple cement plants in a single plant), better performance could be realised due to economy-of-scale effects. This can be seen in Table 9-5, where the Doubled RDF case already benefits from such effects, where although material throughput doubled (200%) the reactor cost increases non-linearly (135%) relative to the Typical RDF case.

10.0 Market analysis

10.1 Costs and value of carbonated products

The market analysis proposed in this section is based on the carbonation plant designed and costed in section 8, which adopts CDB as the candidate feedstock for the carbonation process. Hence, to facilitate the evaluation of different carbonated products on a consistent basis, we assumed that other materials can be carbonated in the same reactor. The levelized production cost of the carbonated products considers the OPEX associated with the carbonation process (Table 9-7) and the CAPEX of the carbonation reactor, *i.e.* ~ £3.6m and £4.9m for the Typical and Doubled RDF cases which has been annualized using a Weighted Average Cost of Capital (WACC) of 8%.

For the analysis, the sequestration potentials of the candidate feedstocks, *i.e.* PCMs and industrial waste, have been set to 50% of their theoretical CO_2 uptake capacity. Hence, beside the required capital and operating costs, it is assumed that by carbonating these materials, cement producers could avoid the payment of a 40 eur/t_{CO2} carbon tax. The analysis also accounts for the potential costs associated with acquiring some of these materials, together with the revenues generated from avoiding their landfill disposal.

Unlike CBD and CSW, which are generated throughout the life cycle of cement-based materials, ironmaking and steel slags need to be recovered from existing stockpiles or acquired from steel producers at a reference market price. For example, in the UK, deposits of iron and steel slags within the UK amount to over 190 Mt, over one third of these deposits are in close proximity to designated conservation areas and hence are difficult to recover (Riley et al. 2020). Land use analyses also showed that many disposal sites in the country have already been redeveloped for housing (nearly 30% urban cover). Given the potential physical and legislative constraints for resource recovery at many slag disposal sites, it is more likely that UK cement producers would purchase slags directly from active steelwork sites. Market prices of steelmaking slags are difficult to quantify since market data are generally not publicly available, and owning to low unit values, their prices are highly sensitive to transport distances. According to the U.S. Geological Survey, the average free on-board price for GGBF slag in 2019 was \$27.5/t (23.5 eur/t), while the prices of steelmaking slags, i.e. EAFs and BOFs, are generally lower than \$10/t (7 eur/t). Accordingly, here we assumed that cement producers would have access to GGBF and steelmaking slags for a fixed price of 23.5 eur/t and 7 eur/t respectively. The same assumptions have been adopted within the UK market, as described below.

Figure 10-1 presents the cost breakdown of the carbonated materials, *i.e.* CBD, CSW, iron and steelmaking slags and FAs for the Typical and Doubled RDF cases. Note that, based on the analysis presented in section 4.0 and 5.0 of this report, CKD has been excluded from the assessment. As Figure 10-1 shows, the net cost of carbonating these feedstocks range between £71.5 to £74.2/t (83-87 eur/t) for the Typical RDF case, with the operating costs making up the biggest share. Doubling the utilization of RDF results in 30% lower OPEX for all the feedstock considered, in line with the production cost values obtained in section 8 (Table 9-7). As a result, the net production cost range between £49.2 to £52/t (57-61 eur/t) for the Doubled RDF case, i.e. ~30% lower than for Typical RDF case. Moreover, in both RDF cases, the revenues generated from the avoidance of carbon tax is minimal, ranging between 1.3 - 8.6 £/t (1.6-10 eur/t), while significant economic benefits are associated with the remediation of CSW. This is because, given its high alkalinity, CSW is considered a hazardous waste, and its disposal is subject to a landfill tax of £98/t (113 eur/t) according to current UK legislation. By contrast in the EU, landfill taxes vary by country from 5 eur/t in Lithuania, which is also the country where the highest share of EU hazardous waste is disposed every year, to 100 eur/t in Belgium. Thus, as will be shown in section 9.2, we adopted an average European landfill tax of 30 eur/t to derive the marginal abatement cost curve (MAC) for Europe.

The following analysis compares the market value of carbonated materials with their traditional end use for clinker production, as SCMs, or as feedstock for alternative industrial activities. Main assumptions adopted in the scenario design are reported in Table 10-1.

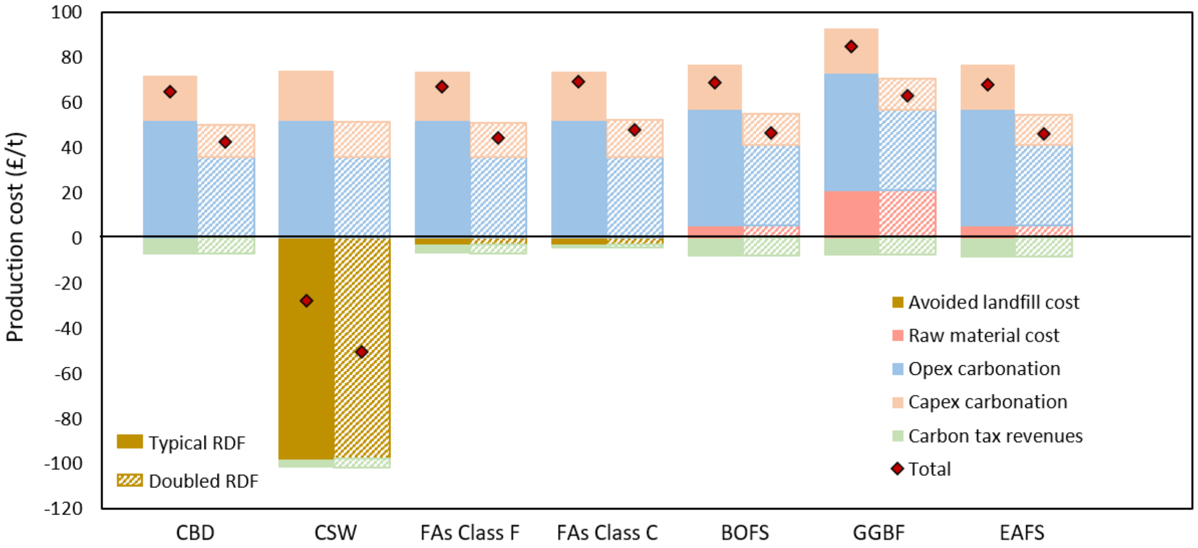

Figure 10-1 Cost breakdown of carbonated building materials in the UK for the Typical and Doubled RDF cases

As noted in Section 6.0, both GGBF slags and FAs are established SCMs for integration within cements, while owning to their high strength, density, and durability, BOFs and EAFS are generally used as aggregates for asphalt mixture or as reinforcement for shores and rivers. Typically, supply contracts secure cement companies a stable access to fly ash and slag at a fixed price. For instance, Drax power station currently supplies 50% of cement replacement ash in the UK for a fixed price of £24/t (28 eur/t), which allows the company to minimize the disposals of FA into landfill (landfill disposal would cost Drax £3/t).

Table 10-1 Scenario investigated and main assumptions (uptake is % of theoretical maximum uptake by the material).

Feedstock	Product	End-use	Revenues	Costs
CBD	Conventional	Clinker production	Clinker sales	None
	Carbonated	Carbonation	carbon tax assuming 50% CO_2 uptake	carbonation cost
CSW	Conventional	Landfill disposal	None	UK Landfill tax
	Carbonated	Carbonation	carbon tax assuming 50% CO_2 uptake + avoided landfill tax	carbonation cost
FAs	Conventional	Use as SCM	up to 50% of clinker substitution	raw material cost
	Carbonated	Carbonation	carbon tax assuming 50% CO_2 uptake + avoided stockpiling cost	carbonation cost
GGBF slag	Conventional	Use as SCM	up to 50% of clinker substitution	raw material price
	Carbonated	Carbonation	carbon tax assuming 50% CO_2 uptake	carbonation cost + raw material cost
EAF and BOF slags	Conventional	Use in road construction	steelmaking slag sales	None
	Carbonated	Carbonation	carbon tax assuming 50% CO_2 uptake	carbonation cost + raw material cost

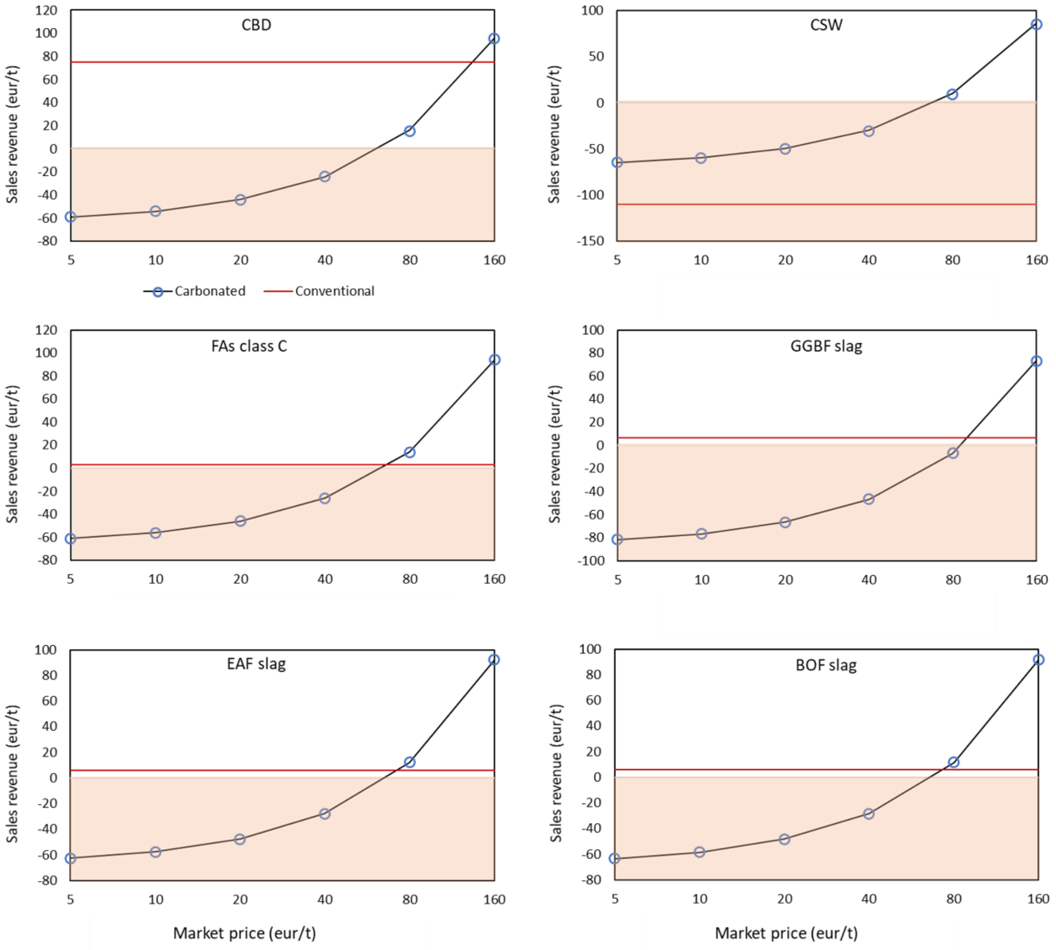

Figure 10-2 Revenues generated with carbonated products under different market prices in the UK ——. Also shown is value of material in alternate use ——. The orange box represents the region where cost of carbonation exceeds revenue, without consideration of alternative uses.

Figure 10-2 presents the market value of carbonating PCMs and NPMCs waste compared to their conventional uses. In the analysis, which considers the Typical RDF case, we assumed that carbonated product would be sold at market prices of 5, 10, 20, 40, 80 and 160 eur/t. The orange regions represent price ranges at which carbonation would generate negative profits, not considering alternative potential uses. In order to make a profit compared to the alternative use, the market price must be above the red line.

The relatively high CO_2 uptake potential of CBD, *i.e.* ~ 20.5 %wt, means that a market price of 64 eur/t is sufficient to offset its carbonation cost. However, since the average selling price of clinker is around 75 eur/t, carbonated CBD would need to be sold at a 140 eur/t to generate the same revenues, making CBD the least profitable material for carbonation. Assuming that FAs can be recovered from existing stockpiles, a benchmark selling price of 67 eur/t is associated with their use as carbonated materials. This is because, stockpiled FA are unlikely to be used as SCMs due to their lower reactivity, hence cement producers would necessarily procure FAs from MSW or coal combustion plants, at a price of 27 eur/t, as described previously. Steelmaking slags are relatively cheap feedstocks, and benefit from relatively high CO_2 uptakes. Hence, when sold at 80 eur/t, carbonated BOF slags are more profitable than as aggregates in road construction. Finally, looking at the trend of CSW in Figure 10-2, it is clear that its use as carbonated material represents the most profitable route, due to the combined avoidance of landfill and carbon taxes.

10.2 Market potential for carbonated products

Aggregates produced by carbonation (‘manufactured aggregates’), are derived from industrial manufacturing processes, and are distinct from ‘natural aggregates’ that are directly obtained from natural mineral sources and tend to be denser than manufactured aggregates. Manufactured aggregates are produced by processes including and similar to the Carbon8 Systems process (e.g. granulation followed by carbonation), and these are mainly used as ‘lightweight aggregates’ in concrete products (e.g. blocks). They can also be used in ready-mx, and in unbound applications like general fill (Carbon 8 Systems, 2021). The total production of aggregate in Europe in 2018 was 4353 Mt, of which 74 Mt were manufactured aggregates, 1,729 Mt sand and gravel and 2,157 Mt crushed rock (European Aggregates Association, 2020).

The use of aggregate in construction can be divided into seven classes, as shown in Table 10-2 Aggregates market size in 2019 (UEPG) and corresponding market value, based on European aggregate selling prices of 5-10 eur/tonbelow. According to UEPG, 20% of aggregate has been used in the construction of roads in, runways or other transport applications in 2019; 15% in infrastructure such as pipe bedding or embankments whilst 65% has been used in buildings. The market price of these aggregates varies by country with the lowest selling price registered in The Netherlands and Spain (5 eur/ton), while highest price levels are generally observed in the Balkans region (10 eur/ton). Note that these values are much lower than the benchmarking selling prices of carbonated products identified in previous section, i.e. 64-88 eur/ton (these values already consider the revenues generated from a 40 eur/ton carbon tax). Hence, whilst the market value of aggregates in Europe is around 10-20 billion eur/year, without appropriate incentive mechanisms, e.g. higher carbon taxes or removal credits, the market penetration of carbonated products is expected to remain low.

Another important thing to remember is that certain uses of materials (roads and railway ballast, for example) require very large availability in short timeframes, which would require some stockpiling of aggregates, adding to the price. Furthermore, certain applications within the broad classifications above, for example, applications within “roads” require a stronger aggregate than the lightweight carbonated aggregates. Construction materials are an excellent use of carbonated aggregates, since there is a steady demand through the year.

Table 10-2 Aggregates market size in 2019 (UEPG) and corresponding market value, based on European aggregate selling prices of 5-10 eur/ton

Use	Market size (Mt/yr)	Market share	Market value (Meur/yr)
Ready mix	506.75	25%	2,534-5,068
Precast	304.05	15%	1,520-3,041
Unbound	810.8	40%	4,054-8,108
Architectural	101.35	5%	507-1,014
Asphalt	202.7	10%	1,1014-2,027
Railway Ballast	40.54	2%	203-405
Armour Stone	60.81	3%	304-08
Total	2027	-	10,136-20,271

10.3 Marginal abatement cost curves (MACCs)

Since one economic driver of carbonation (in addition to waste treatment) is likely to be carbon storage, it is useful to convert the production costs into a marginal carbon abatement cost curve (MACC).Here, we considered both the production cost values obtained in section 8 (Table 9-7) and potential revenues arising from avoiding landfill costs, while excluding the carbon tax effect. The cost of producing each carbonated product in the UK or Europe, has been subsequently converted into abatement cost values by considering the following carbon uptake capacity: CBD: 20.5 %wt; CSW: 10.05 %wt ; FAs class C: 11.2 %wt; FAs class F: 3.8 %wt; GGBF slag: 21.8 %wt; BOF slag: 23.11 %wt; EAF slag: 24.26 %wt. These values correspond to 50% of the theoretical uptake capacity calculated in Section 6.0. The cost of abatement is then plotted against the quantity of carbon abatement, which is a direct function of the regional availability of each material. Figure 10-3 and Figure 10-4 are an example of such MACC for carbonated products in the UK and in Europe.

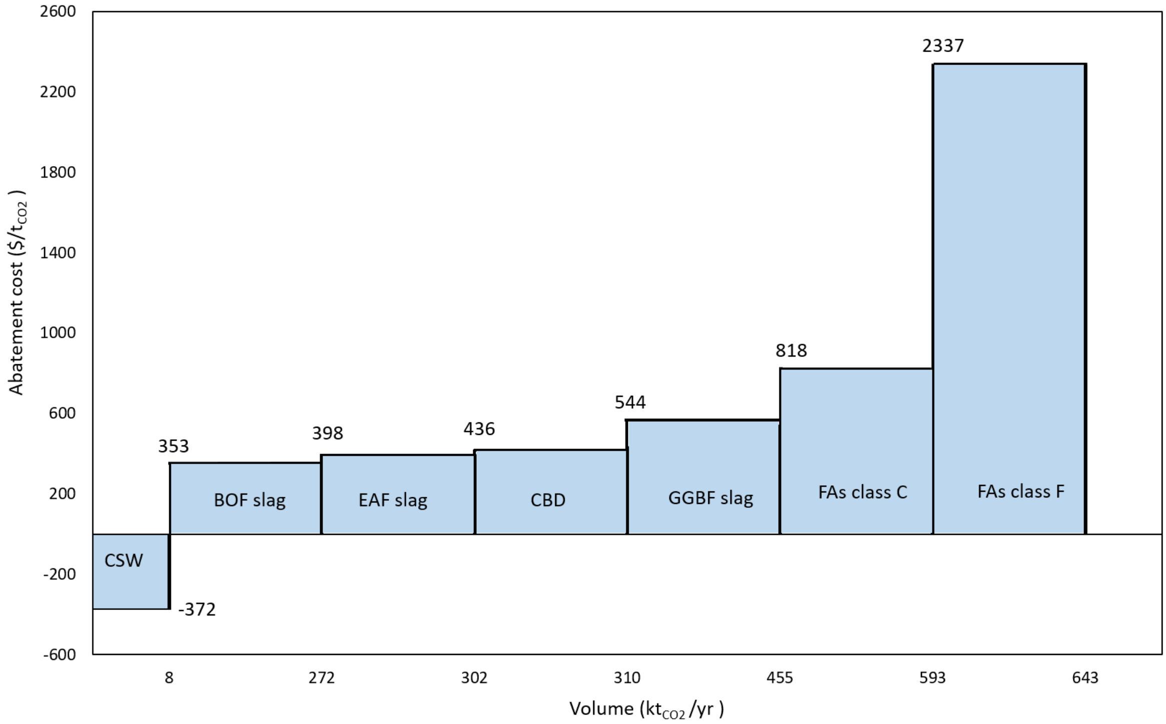

Figure 10-3 Marginal Abatement Cost (MACC) for carbonated products in the UK. As for the analysis presented in Section 9.1, production costs descending from Table 9-7 have been adopted for each carbonated product. Margins generated from landfill tax avoidance in the UK have been included in the assessment, while the effect of carbon tax has been excluded.

According to Shanks et al., around 6,153 kt of ready mix concrete are being produced annually in the UK (Shanks et al. 2019) , of which 2.5% return to batch plants as waste (Paolini & Khurana, 1998). As a result, ~ 77 kt/year of MSW can be processed into carbonated building materials, resulting in the sequestration of 8 kt$_{CO2}$/year otherwise going to disposal. Carbonating the entire amount of EAFs and BOFs slags produced in the UK, *i.e.* respectively 160 kt/year and 1.2 Mt/year, would allow to sequestrate ~ 300 kt$_{CO2}$/year at a cost of 436 eur/t$_{CO2}$,owning to the high CO_2 uptake capacity of these materials. However, reaching a higher level of mitigation is only possible with increasingly higher abatement costs: ~ 820 eur/t$_{CO2}$ are required to sequestrate ~600 kt$_{CO2}$/year in the UK, while carbonating hard coal derived FAs (class F), requires a marginal abatement cost of more than 2,000 eur/t$_{CO2}$ with marginal mitigation benefits, owning to the low CO_2 uptake capacity of class F FAs.

Whilst the production of CSW from ready mix concrete in Europe amounts to 51 Mt/year (Favier et al. 2018), its disposal costs in Europe are marginal compared to the UK. According to Cewep, the average landfill disposal cost for hazardous waste amounts to 30 eur/t in the EU, with some countries, e.g. Croatia, Germany, and Norway, not having yet implemented a landfill tax. As a result, the CO_2 sequestration potentials of carbonated MSW could sum up to 5160 kt$_{CO2}$/year, which could be sequestrated *via* carbonation at a cost of 305 eur/t$_{CO2}$.

Of the 16.3 Mt/year of steelworks slag in Europe, 52.3 % are BOF slag, 34.9 % are EAF slag and 12.6 % are other types of steelworks slag. Since slag generated through BOF processes have a CO_2 uptake potential of 23.11 %wt, when used for carbonation they could sequestrate up to 1.8 $MtCO_2$ per year at a marginal abatement cost of less than 400 eur/t$_{CO2}$. In general, looking at Figure 10-4, it is clear that for mitigation costs of ~540 eur/t$_{CO2}$ more than 8.6 $MtCO_2$

could be sequestrated in carbonated CSW, CBD and steelmaking slags. However, reaching higher carbon removals, would lead to increasingly higher costs, especially when feedstocks with marginal sequestration potentials, such as FAs, are adopted. Interestingly, high abatement costs are associated with material that are conventionally adopted as SCMs, such as FAs and GGBF, confirming their low value as a carbonated product.

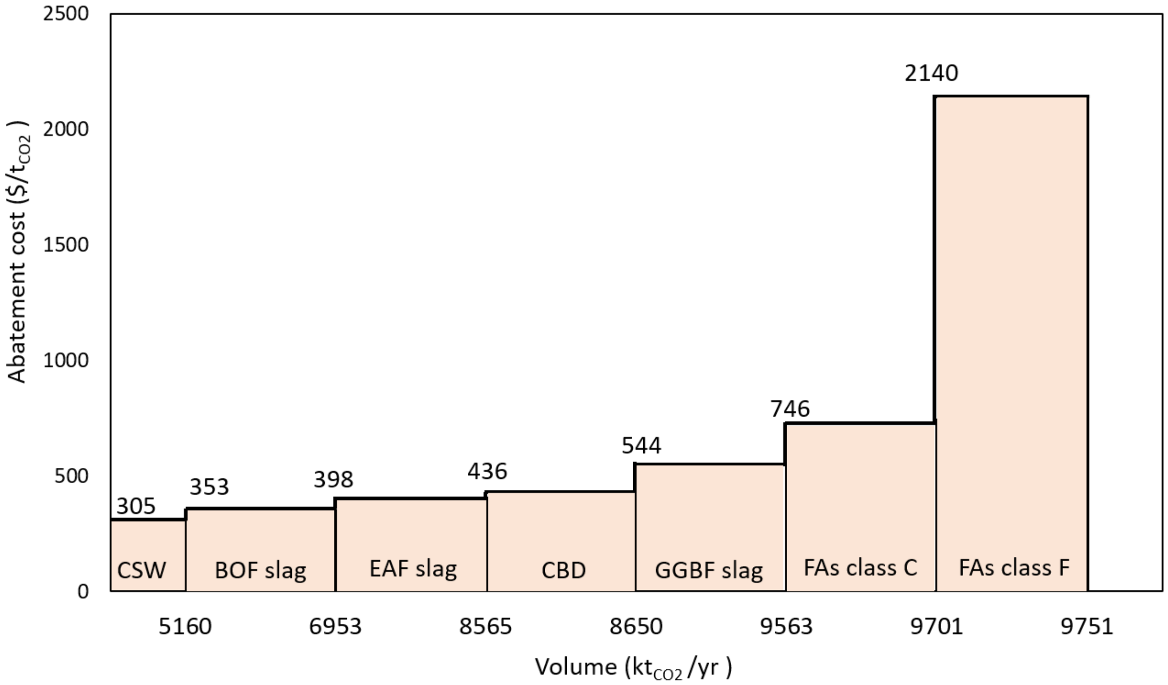

Figure 10-4 Marginal Abatement Cost (MACC) for carbonated products in Europe. As for the analysis presented in Section 9.1, production costs descending from Table 9-7 have been adopted for each carbonated product. Margins generated from landfill tax avoidance in Europe have been included in the assessment, while the effect of carbon tax has been excluded.

Combining the results obtained from the MACC curves with the market analysis presented above, two important conclusions can be derived. Firstly, FAs and GGBF slag are not only more economically valuable as SCMs but they also offer little CO_2 removal services, as they are either scarce (GGBF) or have low CO_2 uptake (FA class F). Secondly, whilst materials generated through the production of cement-based products such as CBD are abundant and could represent excellent materials for carbonation, the market price required for the use of CBD as carbonated building product is considerable, *i.e.* 140 eur/t, when compared to its conventional use for clinker production. Conversely, significant economic and mitigation opportunities could derive from the carbonation of CSW, especially in countries that have adopted stringent waste disposal policies, such as the UK. These facts suggest that the value of carbonation relies on its waste remediation potential rather than on its CO_2 mitigation benefits. In particular, costs for CO_2 mitigation of 300 – 600 euros per tonne should be considered relative to the cost of carbon capture and storage, where costs have been estimated to range between around $40 and $110 (33 – 90 Euros) for CO_2 capture from cement (Leeson, et al., 2017), per tonne of CO_2 avoided. It is also important to note that not all of the CO_2 in the flue gas will be captured, and that emitters will still need to pay the relevant carbon taxes for any CO_2 not captured, unless the plant is fitted with CCS and the exhaust from the carbonation process is rerouted to a CCS system.

11.0 Relevant Legislation, Standards and Market Pull

In terms of mechanical strength, etc, for aggregates, carbonated aggregates (and the materials that are produced from them) are sold into the same markets as other aggregate materials, and the products produced from them will be specified under the same building codes, where they will be certified for a given compressive strength, etc. The standards also include the composition and other features.

End of waste is an important certification for carbonated materials, which has been received by OCO technologies. In order to receive such certification, the waste has to be converted into a distinct and marketable product, which can be used in exactly the same way as a non-waste virgin material, and the processed substance must be able to be used with no worse environmental effects than a comparative virgin material.

OCO technologies, operate under licence to Carbon8 systems, and sell carbonated aggregate products, produced mainly from Air Pollution Control (APC) residues for applications including those under Specification for Highway Works (SHW): SHW 600 (fill and capping), SHW 800 (unbound / hydraulically bound mixtures) and SHW 1000 (concrete). Specifications that OCO have stated that it can comply with include BS EN 13055-1 (lightweight aggregates for concrete, mortar, and grout, though now superseded by BS EN 13055:2016), covering light weight aggregates of mineral origin having particle densities not exceeding 2000 kg / m^3 or loose densities not exceeding 1200 kg / m^3, and BS EN 13242 (aggregates for use in Unbound and Hydraulically bound mixtures). Carbon8 systems have applied for the inclusion of their aggregates under BS 13055. (Carbon8 Systems, 2015). The British Standard sets out the requirement to report a number of quantities for the aggregates produced, including density, size, particle shape, water content and absorption, bulk crushing strength, compressibility and the leachability of any water-soluble constituents, amongst a host of other quantities.

Considering the inclusion of new materials within the building codes, this requires end users to be keen to use them. Discussions with Carbon 8 systems (Carey (Carbon8), 2020) indicate that once there is pull from potential users, materials can be included within codes within a relatively short period (a few years, rather than a decade).

In terms of a price premium for the utilisation of carbonated materials within building products, it was clear from discussions with multiple industry figures that since there is no current price premium, these materials will be sold to compete with current products.

It is also clear that building products utilising carbonated aggregates can readily be included within current ASTM / BS / EN standards, and will be sold on a 'like for like' basis (i.e. based on discussions with stakeholders we can see no issue with lack of acceptance of such products provided that they do not attract a premium price over existing products and are tested according to current specifications). For example, OCO technologies has now processed a total of 500,000 tonnes of wastes in its facilities for further use in concrete blockwork (OCO Technologies, 2021) and these products are (clearly) already within the mainstream.

In terms of alternative cements such as those suggested by Solidia Technologies, progress will require inclusion of these cements within the appropriate codes, and this may be a slow process (up to a decade has been suggested in the past (IEA, 2019), though as discussed above, with sufficient push from users this can be reduced to a small number of years.

It was also clear from discussions with e.g. Carbon8 Systems, that there exists a significant role for government procurement, and architectural specifications to drive the initial market and proving processes for novel materials such as the aggregates produced here, or novel cement products such as those developed by Solidia. This is a concept which has firm academic underpinnings (Rissman, 2020) – government can play an important role in developing and commercialising new technologies – and in particular those that offer significant benefits to society, such as reduction of emissions. The use of government policy to preferentially purchase low-carbon products can lead to the development of a market for such products and ultimately assist in reducing incumbent advantage (Rissman, 2020). Of course, government can ultimately drive adoption of new materials through standards based on embodied CO_2.

Table 11-1 Applicable Standards for Supplementary Cementitious materials and carbonated materials

Standard Number	Description
Concrete	
BS EN 206:2013+A1:2016	Concrete – Specification, performance, production and conformity
ASTM C94	Specification for Ready-Mixed Concrete
Aggregates	
BS EN 13055:2016	Light weight Aggregates
BS EN 13242	Aggregates for Unbound / Hydraulically Bound Mixtures
ASTM C33 / C33M	Standard Specification for Concrete Aggregates
ASTM C330/331/332	Specifications for Lightweight Aggregates for a variety of uses
Use of SCMs	
BS EN 8500:2	Sustainable Concrete
BS EN 197-1:2011	Cement. Part 1: Composition, specifications and conformity criteria for common cements
ASTM C989 / C989 M	Slag cement
ASTM C618	Natural Pozzolans and Coal Fly Ash
ASTM C1240	Silica Fume
Cement	
BS EN 197-1:2011	Cement. Part 1: Composition, specifications and conformity criteria for common cements
BS EN 197-2:2014	Cement. Part 2: Conformity evaluation
ASTM C150 / C150M	Specification for Portland Cement

11.1 Green bonds

A significant development in 2020 was the development of a standard / taxonomy for "green" bonds within the European Union, and which are being rolled out globally. Draft legislation is currently passing through the EU parliament. An interview was conducted with Sean Kidney, founder and CEO of the Climate Bonds Initiative (CBI). These bonds are to fund projects which lead to a substantial reduction in CO_2 (this may be a challenge to justify in comparison to, for example, the total amount by which a cement plant can be decarbonised via the carbonation of a small proportion of the material flow through it). However, the CO_2 mitigation would certainly be permanent. Currently, carbonation of dusts and or other materials would not qualify (Commission of the European Union, n.d.) (the draft standard relates only to CO_2 captured and stored underground), but addition of such a process to the regulations would not be an insurmountable task. CBI have developed criteria focussed on Mitigation and Adaption, and are now exploring Pollution Prevention, Circular Economy and several other areas. The EU have committees currently looking at developing these criteria. Depending on the individual material/process, carbonation could qualify for some of these criteria (*e.g.* circular economy by reuse of dusts, recycled aggregates, *etc.*). Hence, such carbonated aggregates would generally come under the Climate Initiative, but might be more suited to other types of green bonds as they develop.

11.2 Carbon Pricing and Carbon Leakage

Particularly with the international trade in steel slags, and potential for trade of cementitious materials around the world, it is critical to ensure that materials which have been produced in a manner so as to have a significantly lower CO_2 footprint do not face external competition from those that are produced without such requirements.

With the change in government in the USA at the beginning of 2021, it is significantly more likely that climate change will be at the forefront of global thinking. Indeed, Joe Biden's current Secretary for the Treasury (Janet Yellen) was co-chair of a working group for the Group of 30 which discussed in their report "Mainstreaming the transition to a Net Zero economy" (Group of Thirty, 2020) the importance of a number of policy instruments to enable the transition to Net Zero. The European Union is also actively considering such policies (Marcu, et al., 2020)

The first recommendation was a carbon price, "which increases in a gradual and predictable way, [as] one key element of policy package". Another very important requirement, also discussed in (Group of Thirty, 2020), particularly for a traded commodity (for example, concrete blocks made using carbonated residues) will be the application of Carbon Border Adjustments (CBAs). Such instruments allow the maintenance of a level playing field between different regimes with different regulatory regimes (and hence different implied costs of CO_2 emission.

The development of a CBA regime is highly complicated, since they must both fulfil their primary aim of assisting in the reduction of CO_2 entering the atmosphere, whilst also maintaining competitiveness in the country applying them and finally also being compliant with the World Trade Organisation regulations (in this case, the General Agreement on Trades and Tariffs, GATT). Many of the issues were discussed in (Marcu, et al., 2020). Challenges include trading partners not engaging with the CBA, or challenging it in court, but the specific challenge which might be most difficult for a carbonated material made from wastes would be how the material which was made would be assessed.

Firstly, there would have to be an understanding that a material (e.g. cement) which was similar in physical properties to that in a protected area, but had a higher CO_2 emission was in fact a different type of product, or else the application of a CBA may fall foul of GATT Article III:4, III:2 or simply Article 1. In the case where it did, there is the recourse to GATT's Article XX: General Exceptions, which would allow measures to breach other sections of GATT provided that they are "relating to the conservation of exhaustible natural resources" and there is a general consensus that a liveable planet is an exhaustible natural resource. To pass such a regulation, it is frequently considered that a measure should be exclusively related to climate change, and not (for example) about preventing competitiveness impacts.

There are a number of different manners in which a CBA could be applied. Firstly, it is important to determine whether it is a tax or a regulation – this is very important for *exports* from a location with stringent CO_2 reduction policies to one with less stringent rules (an argument could be made that taxes could be refunded for export).

Overall, some general guidance was given (Marcu, et al., 2020):

"It may be illegal to:

● Require specific policies as a basis for exemption from CBA, as opposed to requiring that the exporter achieve some given level of climate performance.

● Implement exemptions or calculate adjustment levels based on the country of origin, as opposed to doing so at the level of the individual producers based on their environmental performance.

● Implement CBA before having tried to negotiate in good faith to reach some multilateral solution to the problem of carbon leakage.

● Implement a CBA that fails on the criterion of good governance (i.e., transparency, due process, etc.), if the result effectively makes the regime more arduous for foreign producers

● Include any exemptions from coverage of the CBA (e.g., for parties to the UNFCCC's Paris Agreement) not justified by the objective of mitigating climate change by preventing leakage."

In fact, a hypothetical producer in an area with lower CO_2 regulation that was looking to export to a higher carbon area, but who was planning to reduce emissions by applying e.g. the carbonation of residues to reduce the overall CO_2 impact of their goods should welcome regulations that are set at the producer (or good) level. This is because if they can demonstrate that they have indeed reduced the CO_2 emissions inherent in the manufacture of their good, their competitors in the same country would face higher BCAs (this is why BCAs must be set at the producer level, not the country level, if they are to be successful for climate mitigation and not just thinly disguised protectionism). The main challenge of such a regime is that it is complex to implement and requires traceability of the CO_2 emissions throughout the lifecycle of the good being produced.

It is potentially easier to apply CBAs to materials such as cement, iron and steel etc., which are part of a subset of materials which can collectively be called energy-intensive and trade-exposed (EITE), and where CO_2 emissions are very high compared to the value added, compared to goods such as iPads, etc. This is because tracking the raw materials, CO_2 emissions, etc., is less complex in such sectors.

In summary, Border Carbon Adjustments will be challenging, but not impossible, to apply. The analysis of (Marcu, et al., 2020) states that "[their] analysis confirms that CBAs can be a useful part of the solution, but they are not in and themselves a silver bullet."

12.0 Knowledge Gaps

The work conducted here has determined that there are several important knowledge gaps which require filling. The long-term performance of carbonated materials (novel aggregates, cements, binders, concretes, etc.) during service is a key area requiring improved understanding. This can be achieved through thermodynamic modelling and experimental testing, as well as lab to larger scale demonstrations and careful monitoring of demonstrations to be conducted. Such tests will require follow-ups on the scale of decades (for example, independent monitoring of the section of the floor of San Francisco Airport which uses Blue Planet aggregates).

It will also be necessary to continue careful monitoring and assessment of the long-term effects of CO_2 curing in accelerated carbonation processes e.g. Carbon Cure, moving all the way through to final demolition and disposal from a technical perspective. Complementary life cycle environmental assessments of these carbonation processes and products are also needed, to provide the quantitative evidence base to evaluate their environmental performance, which is currently poorly elaborated in the literature. For materials which desire certification in structural applications, modelling, testing, and demonstration is especially important to safely scale up these materials to larger scale deployment, and for them to be more widely recognised and accepted in the construction industry.

In the realm of accelerated carbonation, continued progress is necessary, examining the trade-offs between the carbonation extent of materials and their properties with respect to the products produced, and their environmental performance. E.g. reactivity would be a key criterion if the product is a supplementary cementitious material.

A final area of interest is to investigate carefully the integration of plants producing multiple outputs – for example a cement plant producing both ordinary Portland cement (or perhaps a variant such as composite or LC^3 cement) of course, fitted with CCS, but also potentially with a process to produce an alternative cement such as that proposed by Solidia Technologies. We expect that there will be systemic benefits of this integration which are currently poorly elaborated, due to the complexity and novelty of this multi-disciplinary perspective.

The continued production and verification of independent technology assessments examining likely prices for new cement technologies, CO_2 uptakes, and potential markets, will be an important ongoing area of research. This work should at the next level consider the impact of the trading of different commodities on an international basis, especially given the scarcity of some important cementitious materials like blast furnace slag, and limited generation of anthropogenic wastes like air pollution control residues.

13.0 Conclusions

This report has examined the carbonation of a variety of different materials, initially aiming at decarbonizing cement production, and their potential for use as media for accelerated carbonation. It starts by determining whether there are other, more profitable and environmentally beneficial uses for materials that could be carbonated; it is found that in many cases such as steel slags and some of the dusts produced during cement manufacture these materials should preferentially be used as a supplementary cementitious material or otherwise blended in to cement where this is possible.

Recycled concrete aggregate is effectively carbonated from air exposure. These materials can have improved properties than their uncarbonated counterparts, for example reduced water demand when used in concrete. Accelerated carbonation products are not currently widely used (at the scale of conventional cementitious materials like Portland Cement), but have the potential to be used as aggregates, fillers, reactive fillers, and supplementary cementitious materials, depending on the material carbonated. In some cases, we expect carbonation can significantly improve material properties (e.g. recycled concrete aggregate), but negligible changes or reductions for other cases (e.g. cement kiln dust and blast furnace slag, both of which we expect to have greater potential to be used as a supplementary cementitious materials in uncarbonated form). Thus, there is an active trade-off in accelerated carbonation of materials between use directly for CO_2 storage vs. other beneficial uses, which includes substitution of high-CO_2 Portland Cement clinker (which is the case for blast furnace slag). However, carbonation can act as a waste treatment process, stabilising heavy metals, which brings significant and genuine benefits to the valorisation of more unconventional and toxic or contaminated materials, like air pollution control residues (as pioneered by Carbon8 Systems). Future research is needed both to understand the potentials of more novel carbonated materials to store CO_2 and their production processes, as well as to understand their material properties. Both of these areas are currently poorly explored in the literature, which presents a risk that companies may claim false CO_2 emissions reduction potentials in the absence of this evidence.

Approximate costing of an accelerated carbonation process was done, this determined that the main driver for carbonation processes is the avoidance of landfill costs where they are applicable, and that unless there is a substantial avoided cost associated with raw material disposal (such as for concrete slurry waste in the UK) carbonation is a relatively expensive method of CO_2 utilization, costing around 300 – 600 euros per ton of CO_2 sequestered. In addition, whilst the market size of aggregates is considerable in Europe, with around 2,000 Mt being used every year, current market prices (aggregates are being sold at 5-10 eur/ton in Europe) suggest that the market for carbonated products is limited and will be closely linked to robust CO_2 pricing mechanisms that recognize and value the mitigation service of carbonation. It is also important to note that natural carbonation processes will also occur, over a time span of decades, reducing the additionality of accelerated carbonation.

It is clear that there is currently insufficient pull from the construction industry for products which are low in carbon, and that changing this may require product demonstrations, carbon standards, and increased carbon taxes. Development of the industry will require financing at a large scale, within which green bonds may help. Finally, it will be increasingly important to ensure that cross-border flows of materials such as both products of accelerated carbonation, supplementary cementitious materials such as blast furnace slag, and indeed cement, are treated appropriately in terms of carbon border adjustments.

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15.0 Appendix A - Industrial Interviews

Table A1: Interviews with industrial experts conducted as a part of this project

Interviewees	Company/Organisation	Expertise
Dr Paula Carey	Carbon8 Systems	Carbonation Process Design and commercialisation
Dr Tom Hills	Calix	Cement production
Dr Laury Barnes-Davin	Vicat	Cement production, Carbonation
Dr Richard Leese Rebecca Hooper Diana Casey Roger Griffiths Rachel Capon	Mineral Products Association	Cement production and volumes, cement by-product utilization and valorisation
Industry Source 1	Major Cement Producer	Cement production and market
Simon Frans De Vries	AVR Duiven	Carbonation process end user
Professor Sean Kidney	SOAS / Climate Bonds Initiative	Climate Bonds / Green Finance

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