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ACCELERATED CARBONATION OF WASTE CALCIUM SILICATE MATERIALS

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Abstract

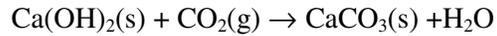
Accelerated carbonation has been successfully applied to non-hydraulic waste materials containing calcium silicates. In the first stage of this investigation several waste materials were subjected to a 100% CO₂ atmosphere at 3 bar for 24 hours. The level of CaO in the starting material was found to be the major control upon the degree of carbonation achieved. The water to solid ratio of the samples was also found to be important in controlling the effectiveness of carbonation. Having identified a slag from stainless steel manufacture as the most effectively carbonated of the waste materials investigated, the second phase of investigation focused upon using accelerated carbonation to cement this powder. Small cylindrical samples were produced, using the previously determined optimum w:s ratio. These were carbonated for two hours, stored in the laboratory and then tested for 28-day compressive strength. The slag has a wide grading curve with the different size fractions having different chemical and mineralogical compositions. Therefore the slag was investigated both as a bulk material and as two of its distinct size fractions. When ground, the γ -dicalcium silicate rich, finest size fraction and the bulk sample show compressive strengths of up to 10MPa.

Introduction

This paper presents the results from the initial phases of an ongoing investigation into the accelerated carbonation of calcium silicate waste materials. The need to identify ways in which emissions of carbon dioxide can be reduced is well established. There is also pressure to find ways in which to utilise waste materials as an alternative to disposal in landfill sites. The carbonation reaction provides a potential method to take CO₂ gas into a solid product. If waste materials can be modified into a useful product by this method then the benefit is increased.

The first phase of work identifies a range of waste materials and investigates the fundamental controls upon the maximum degree of carbonation achievable. One of the wastes is then further investigated for its potential to form a product which is self cemented as a result of accelerated carbonation.

Carbonation of mature cement paste involves the reaction of portlandite and C-S-H gel with carbonic acid to form calcium carbonate.¹ The reaction of Portlandite with carbon dioxide can be written as:



Concrete carbonation is in fact just one example of the reaction of materials with carbonic acid derived from atmospheric CO₂. Many materials are slowly weathered by carbonation,² however in most situations the products of the reaction are transported and there is little precipitation of carbonate minerals in situ.

Extensive work has been carried out to investigate the controls of the carbonation of concrete with the aim of reducing the rate at which it will occur.^{1,3} Key factors have been found to be the concentration of carbon dioxide in the atmosphere and the rate at which it can diffuse into the concrete surface. In concrete the rate of carbonation can be reduced by producing a high quality dense paste with low permeability.¹

Accelerated carbonation

Accelerated carbonation is the deliberate promotion of the rate and extent of carbonation. This has been used as a method of accelerated weathering to simulate extended periods of environmental exposure. Patents exist for the use of accelerated carbonation to rapidly harden OPC based concrete,^{e.g.4} the high early strength and dimensional stability achieved means that rapid production rates of precast products can be achieved. Accelerated carbonation has also been shown to be beneficial for the retention of heavy metals within OPC solidified/stabilised wastes.⁵ In this case accelerated carbonation has been found to be most effective when applied in the 'green' state, that is just after mixing with water and before significant hydration has occurred.⁵

When 'green' state accelerated carbonation is applied to the hydraulic phases present in OPC then the reaction path differs from that of normal atmospheric carbonation. This is because there is insufficient time for the normal hydration products to form.⁶ The reactions occurring here differ from the natural carbonation of cement hydrates in that calcium from the anhydrous phases is entering solution and initially precipitating with carbonate ions instead of hydroxide ions. The precise mechanisms of the reaction are not well understood although a proposed reaction-mechanism exists.⁷

Little work has been carried out applying accelerated carbonation to poorly hydraulic materials, although it is known that atmospheric carbonation contributes to the weathering of many natural non-hydraulic minerals. Work in the 1970's on the accelerated carbonation of the individual calcium-silicate phases of OPC was extended to include the poorly hydraulic γ -polymorph of C₂S, with some success.^{6,8}

Experiment 1: Accelerated carbonation of waste calcium silicates

Objectives

This study was carried out in two phases. In the initial phase, a number of waste materials were investigated to identify those that were amenable to accelerated carbonation. The degree of carbonation being compared with the chemistry and mineralogy. Having identified which waste was most effectively carbonated, the second phase of investigation concentrated upon using accelerated carbonation to cement small samples of this material and examining the compressive strength that could be obtained. The material chosen for the second phase of investigation was sorted and processed to investigate the effect of mineralogy upon the strength obtained.

Material sources

The materials chosen were selected on the basis of their range of bulk chemistries and their abundance. The materials and their origins are listed below.

- Pulverised Fuel Ash (PFA)- The ash produced by coal fired power stations which crush the fuel prior to combustion. Commonly used as an addition to OPC. Large volumes of unused low-grade ash exist in large stockpiles.
- Ground Granulated Blast Furnace Slag (GGBS)- Produced by rapid cooling of the molten slag produced as a by-product of steel manufacture. Also commonly used as an addition to OPC.
- Stainless Steel Slag – The slag from the manufacture of stainless steel. This material is not granulated and has a wide grading curve. Consequently it was ground to pass a 100 μ m sieve prior to carbonation. Currently this slag is disposed to landfill.
- Municipal Solid Waste Incineration Ash (MSWI)- Two Sources of this material were used. The combustion of solid waste is likely to increase as the space for disposal to landfill sites diminishes. Therefore it is expected that in the future large volumes of this material will be available which would be expected to have a wide compositional range.
- Deinking Ash – The ash resulting from the burning of the waste produced during the recycling of paper. The waste contains organic inks and some cellulose fibers giving it a high calorific value, the presence of calcium carbonate and other fillers give a calcium rich ash. Increased utilisation of waste paper for recycling means that the production of this material is likely to increase.
- OPC – For comparison purposes an OPC was included in the investigation.

The compositions of these materials are given in table 1.

Table 1 Bulk composition of calcium silicates (weight % oxide).

Sample	CaO	SiO ₂	MgO	Al ₂ O ₃	Fe ₂ O ₃
OPC	65.04	20.71	1.03	4.83	2.77
PFA	3.36	46.96	1.76	23.71	11.33
GGBS	41.38	34.59	6.84	14.02	1.51
MSWI-b	22.62	10.32	1.61	5.30	0.95
MSWI-f	35.89	15.29	1.29	6.25	1.11
Deink Ash	37.69	33.76	3.72	20.12	0.03
Stainless Steel Slag	46.66	27.92	9.75	2.91	1.22

Optimisation of the degree of carbonation

Method

The extent that each powder would react with carbon dioxide was assessed by the gain in dry weight achieved as a result of the carbonation procedure. The dry powder was thoroughly mixed with a known amount of water, loosely placed in a small container and carbonated in a low-pressure reaction vessel. Carbonation was carried out in a 100% CO₂ atmosphere at a pressure of 3 bar. After 24 hours the samples were dried at 60°C to constant weight. The gain in weight between the initial powder and the dried product being proportional to the amount of CO₂ that had combined with the sample. Each experiment was carried out in triplicate with control samples prepared in the same manner and stored under ambient laboratory conditions for 24 hours before drying at 60°C to constant weight. In order to establish the source of the gain in weight a subset of samples was thermally decomposed in a series of steps (105, 400, 600 and 800°C), and the change in weight recorded.

Results

The weight gained upon carbonation obtained using the stainless steel slag samples are plotted in figure 1, the optimum w:s ratio was determined at 0.125. As can also be seen from figure 1, the degree of carbonation is sensitive to the amount of water added to the sample. In the absence of water no reaction will occur and above w:s of 0.25 the reaction is effectively halted.

All samples showed some reaction as a result of carbonation as indicated by a weight gain that was significantly greater than that exhibited by laboratory cured controls. When this gain in weight is plotted against the calcium oxide composition of the starting material (figure 2) a clear trend in behavior is found. The results are plotted as the peak weight gains obtained upon carbonation. These maxima occur at a range of different water to solid ratios, which are unrelated to the chemistry of the samples. The apparently finer powders generally show peak carbonation at higher water contents.

Results from the thermal treatment of a subset of the carbonated samples showed that a small proportion of the additional mass was the result of combined water. However the weight gained upon carbonation was directly proportional to the weight loss between 600 and 800°C which can be ascribed to the loss of CO₂ from the sample.

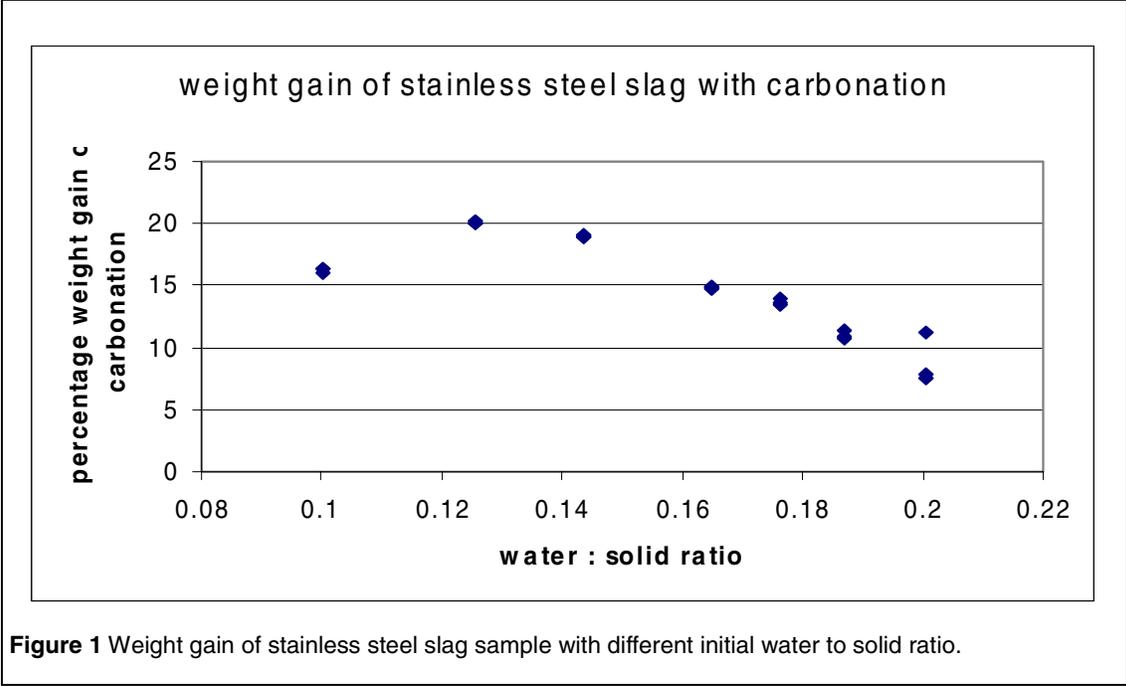


Figure 1 Weight gain of stainless steel slag sample with different initial water to solid ratio.

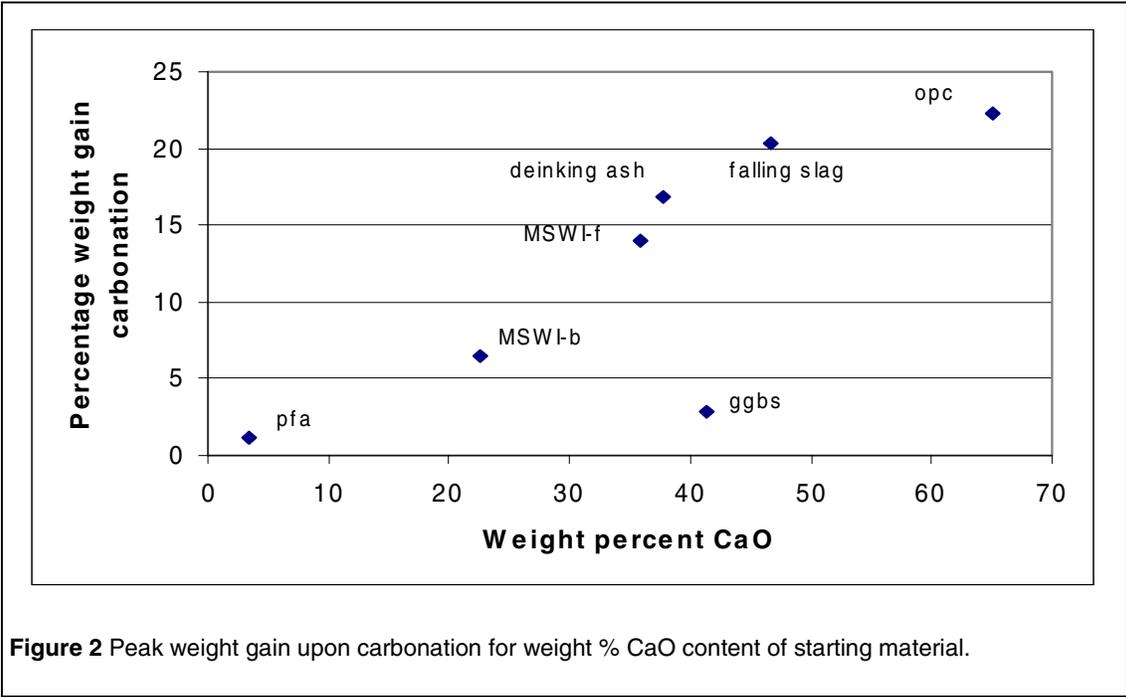
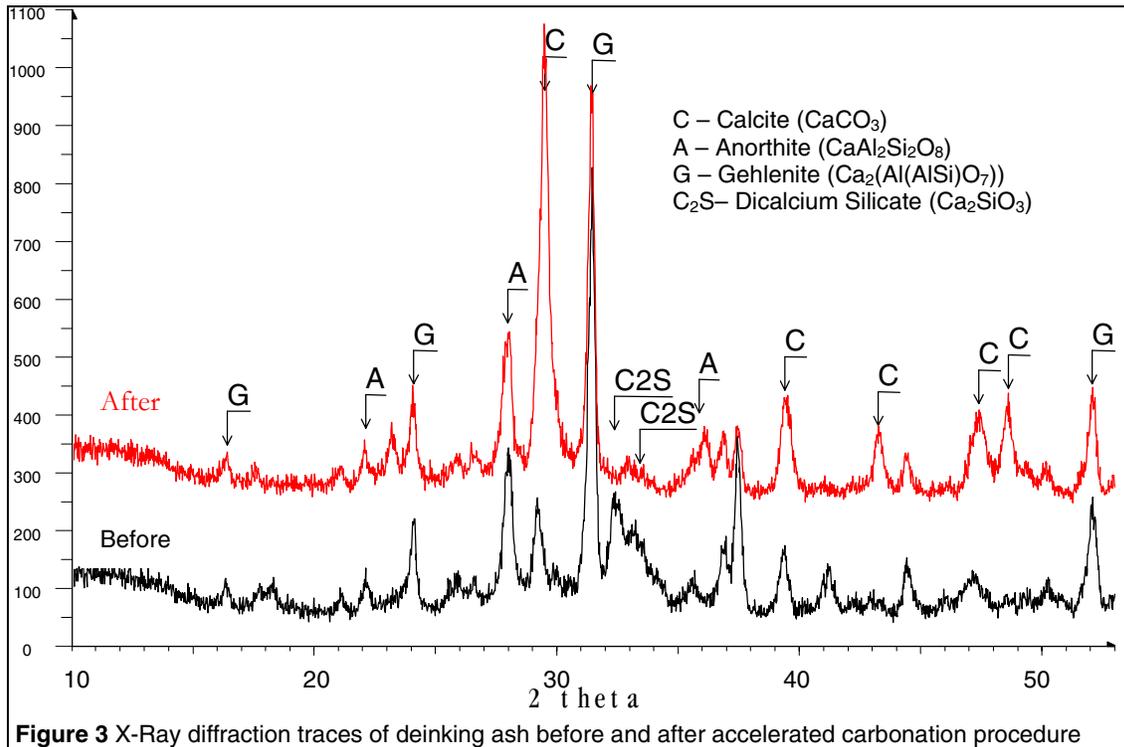


Figure 2 Peak weight gain upon carbonation for weight % CaO content of starting material.



X-ray diffraction of all treated samples, with the exception of GGBS and PFA, indicates the presence of calcite, formed as the product of the carbonation process. No change is observed in the trace from the GGBS and PFA samples. An example of the changes exhibited by the reactive material is shown in figure 3 which shows the before and after traces of the deinking ash

Experiment 2: Cementation of stainless steel slag

The stainless steel slag was chosen for the second phase of the investigation as it showed the greatest degree of reaction during the initial phase. Additionally the slag is known to contain a significant volume of the poorly hydraulic γ polymorph of C_2S , which is known to carbonate effectively⁷. In fact the presence of this phase leads to the alternative name of “falling slag” for this waste. The self pulverising phase transition, which occurs during cooling, between the beta and gamma polymorphs causes the slag to “fall” to dust.

As a result of the self pulverising effect in one of its mineralogical components, the slag has a wide grading curve and different mineral species are concentrated in different size fractions. This provided an easy method of extending the investigation to examine chemically similar materials with differing mineralogies. Therefore the slag was divided by sieving and three size fractions were chosen for the experiment. The bulk chemistries of these fractions are given in table 1. The naturally $<125\mu\text{m}$ fraction was used as received and ground to a much finer powder in order for a comparison to be made with the ground 4-8mm and bulk slag samples. X-ray diffraction of the starting materials confirmed the greater abundance of C_2S in the finer slag fraction and the

presence of a variety of calcium-magnesium silicates in all samples. These phases include Merwinite ($\text{Ca}_3\text{Mg}[\text{SiO}_4]_2$), Akermanite ($\text{Ca}_2[\text{MgSiO}_7]$) and, Cuspidene ($\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2$).

Table 2 Oxide composition of slag fractions used in preliminary investigation (weight %).

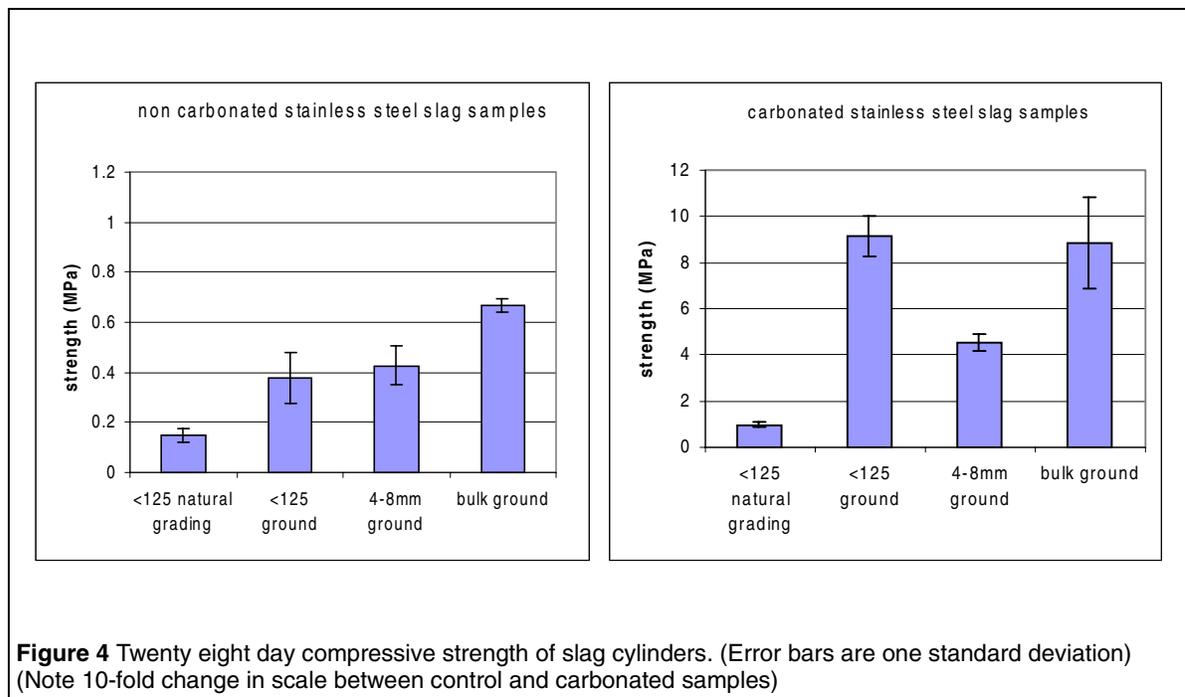
Fraction	CaO	SiO ₂	MgO	Al ₂ O ₃	Fe ₂ O ₃	Cr ₂ O ₃
<125 μm	51.05	25.80	9.32	2.31	0.72	0.50
4-8mm	43.18	30.83	9.83	3.38	1.97	4.74
Bulk	46.66	27.92	9.75	2.91	1.22	2.76

Method

The four powder samples were mixed with the optimum w:s of 0.125 determined in the first phase of the study and then formed into small cylinders with a diameter of 28mm, these were compacted in a modified syringe by applying a force of ~0.5MPa. Parallel faces were carefully cut to produce a sample height of 28mm. The samples were then carbonated at a pressure of 3 bar for 2 hours, after removal from the carbonation environment the samples were stored for 28 days and tested for uniaxial compressive strength (using a Monsanto Tensometer 20 with compression attachment and a crosshead speed of 1mm minute). Control samples were manufactured in the same manner and cured under ambient laboratory conditions for 28 days.

Results

The results of the 28-day compressive strength tests are shown in figure 4. The control samples were very weak, indicating no significant cementation, whilst carbonation clearly produced cementation and consequently an increase in compressive strength.



X-ray diffraction of the slag fractions before and after carbonation showed that the only phase that could be identified as having participated in the carbonation reaction was the C_2S which had diminished in the traces of the carbonated samples; the only new phase identifiable was again calcite. The control samples were unchanged with no hydrate phases being formed. Any change in the intensity of the peaks from the other calcium-magnesium silicates that make up the bulk of the slag was minor and could be ascribed to dilution of the sample by the addition of carbonate. The 4-8mm fraction being deficient in C_2S is found to react less effectively than the other samples and this is also reflected in its lower strength.

The nearly tenfold increase in strength obtained by grinding the finest fraction prior to carbonation is believed to be largely the result of reduced porosity, this is a consequence of closer packing of the finer powder. The increased surface area could however be expected to enhance the carbonation reaction and the production of fresh surfaces by the grinding process may also be of benefit. However, the ground C_2S rich fine fraction did not produce a material significantly stronger than the slag taken as a whole indicating that the efficacy of the reaction is not simply a function of the amount of reactive phase present.

It was noted that C_2S remained in the product after carbonation and that phenolphthalein staining of the broken samples after strength testing showed that carbonation was more effective in the surface of the sample. This indicated that diffusion of CO_2 into the sample is a factor in the reaction when carried out upon briquette type samples

Discussion

The results of the first phase of the investigation show that the degree of carbonation achievable for given starting conditions is strongly dependent upon the calcium content of the starting material. The results obtained with the ground granulated blast furnace slag are found to fall away from the trend exhibited by the other materials. This indicates that the GGBS has carbonated much less effectively than would be expected based upon its CaO content. Previous work¹ upon the carbonation of blast furnace cements and concretes has shown that carbonation of these materials is complicated. Competing effects resulting from the low rate of hydration, which gives an early opportunity for the ingress of CO_2 , and the low abundance of portlandite within these materials means that there is an absence of one of the reactants for natural carbonation. The slow hydration of GGBS is achieved by the breakdown of the glassy structure of the slag in alkaline conditions, therefore the absence of alkaline conditions and or the slow kinetics of reactions with the slag may hinder the accelerated carbonation of this material.

Work carried out as part of this investigation shows that the primary control upon accelerated carbonation after the chemistry of the sample is the use of a 100% CO_2 atmosphere. If the sample chamber is not completely purged of air prior to the experiment the rate and extent of the reaction are greatly reduced. The amount of water added to a sample alters the degree to which a sample will react, too much or too little and the reaction is almost completely inhibited.

Although the stainless steel slag was chosen for use in the second stage of the investigation based upon its more effective carbonation in the first stage, this material had an additional grinding stage prior to its use. This additional processing requires energy, which will have associated CO_2 emissions partially negating the removal afforded by the carbonation reaction. Thus, careful

consideration of the economic and environmental cost benefits is required with use of the material will need to be undertaken if the process is scaled up. Several of the other materials, such as the ashes, are naturally produced as fine powders and therefore may be amenable for use as produced.

Further work

Having identified the major controlling factors of the carbonation of waste calcium silicates, future work will investigate how changing the conditions of carbonation affect the resulting degree of reaction. This work will include looking at the effect of changing the particle size and hence surface area of the wastes under investigation. Crushing of the samples in order to do this has several implications. The production of increased surface area and fresh surfaces may enhance the degree to which the wastes will react. However the finer particles produced will naturally pack closer together reducing the ability of the CO₂ to ingress between the particles. The change in surface area would be expected to alter the optimum water content of the sample as a result of the wetting of particle surfaces.

The conditions of carbonation also have scope for further optimisation, the exothermic nature of the reaction drives water out of the sample, therefore control of the temperature and humidity at which the reaction occurs will be investigated. As part of this phase of investigation variable sample sizes will be used to investigate the effect of the thermal gradient induced within the sample by the exothermal reaction.

The range of starting chemistries and mineralogies will be increase by adding further materials to the study. These will include waste products and commercially available materials. Thermal methods such as TGA and DTA will be applied to both the starting materials and the products of carbonation in order to more accurately quantify the amount of carbonate produced and asnindication of which phases are effected by carbonation. This will involve x-ray diffractometry and the examination of the microstructural effects of carbonation using SEM techniques. This work will allow a more detailed appreciation of the carbonation process..

Conclusions

This work demonstrates the applicability of accelerated carbonation to a wide range of waste materials and identifies a number of factors that influence the extent of reaction. These include the intrinsic effect of the chemical and mineralogical content of the waste, particularly the calcium content and processing parameters, especially the water to solid ratio of the sample. Having identified these first order controls upon the efficacy of accelerated carbonation further work is being carried out to identify other less significant influences upon the reaction. and to investigate the microstructural alterations induced during carbonation.

The carbonation of these waste materials will eventually occur in the environment, given a supply of CO₂ and water. However, the rate at which this will occur will be very slow, especially if they are sealed into landfill sites, as is current practice. The pressure to reduce CO₂ emissions means that potential disposal options are required. If this can be achieved utilising other existing waste products, either to produce a useful product or just as an accelerated weathering method in order to produce a more stable product for disposal, then the potential benefit is obvious.

Acknowledgement

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