

## **Kinetic Study of the Accelerated Carbonation of MSW Incinerator Air Pollution Control Residues**

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Moist calcium silicate minerals are known to readily react with CO<sub>2</sub>. The reaction products can cause rapid hardening and result in the production of monolithic materials. In a patented application, carbonation has been accelerated and intentionally used to overcome the inhibiting effects of complex waste materials on the hydraulic and pozzolanic reactions responsible for effective stabilisation/solidification [1, 2], resulting in distinct materials with improved physical and chemical containment characteristics [3-8]. Therefore, Accelerated Carbonation, as it is known, has certain advantages in the treatment of waste residues and has great potential to engineer the properties of certain wastes, so that they can be reused as, for example, artificial construction aggregates. Thus, this process represents a viable and cost-effective solution to sustainable waste management, tackling the problems associated with the decrease in the number of available landfill sites, greenhouse gas emissions and the depletion of natural aggregate resources (gravel, sand, etc.).

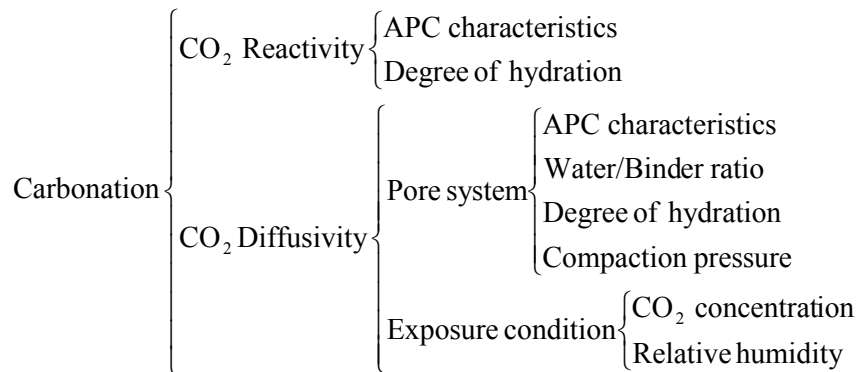
In the UK, incineration is becoming the preferred option for disposal of MSW as landfill space decreases. There are 12 incinerators in England, which are dealing with 9-10% of the municipal solid wastes, and they are producing nearly 3 million tonnes of ash per year, made up of bottom ash and Air Pollution Control (APC) residues. 88% of the APC residues are currently sent to landfill. APC residues are a mixture of fly ash, carbon and lime and are the result of the treatment process to clean the gases before they are released into the air. APC residues are classified as a hazardous waste due to the lime content, the high concentration of heavy metals and chlorinated compounds, in addition to soluble salts. Moreover, it consists of very fine particles, mostly <300µm.

The chemical and physical properties of this waste make it ideal for carbonation. The treatment imparts chemical and mineralogical changes on the ashes which reduce their environmental impact through encapsulation of hazardous components and cementation by carbonate precipitation. The application of accelerated carbonation for the treatment of MSW incinerator APC residues will be presented.

Data will be shown from laboratory experiments designed to elucidate the macrokinetics of the Accelerated Carbonation reaction of APC residues. When considering the carbonation reaction, three systems can be defined: the reactor in which the reaction takes place, the system formed by the ash particle and the CO<sub>2</sub> around it and the interior of the porous particle. This study will focus on the solid-gas interaction and the intraparticle phenomena.

The extent and quality of accelerated carbonation, as well as the fixation and immobilisation of specific contaminants, depends upon several parameters. The main ones

are the reactivity and the diffusivity of CO<sub>2</sub>. The following is a scheme of what these factors depend on (based on [9]):



The carbonation of APC residues is a very complex reaction. Not only are there physical and chemical processes occurring at the same time but there are also many different factors dependent on the nature of the solid (i.e. the nature of the surface, the particle size, the microstructure, the composition, the mineralogy). All of these influence the reactivity of the APC residues. Diffusivity of CO<sub>2</sub> is constrained by the pore system of the solid and the exposure conditions (i.e. concentration of CO<sub>2</sub>, degree of hydration, water-to-solid ratio, relative humidity).

The Accelerated Carbonation of APC residues is based on the following sequential mechanism [9]:

- 1st. Diffusion of CO<sub>2</sub> in the gaseous layer surrounding the solid
- 2nd. Diffusion of CO<sub>2</sub> through the solid
- 3rd. Solvation of CO<sub>2(g)</sub> to CO<sub>2(aq)</sub>
- 4th. Hydration of CO<sub>2(aq)</sub> to H<sub>2</sub>CO<sub>3</sub>
- 5th. Ionisation of H<sub>2</sub>CO<sub>3</sub> to H<sup>+</sup>, HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup>
- 6th. Dissolution of calcium containing phases
- 7th. Nucleation of CaCO<sub>3</sub>
- 8th. Precipitation of solid phases

The mechanism above can be summarised by the following overall reaction, which is the focus of this kinetic study:



The first step of kinetic modelling involves the determination of the mechanism controlling the rate of reaction. Then, the mathematical expression describing the experimental data is derived in terms of a kinetic triplet.

The experiments were carried out in a 5 litre reaction chamber, incorporating a cooling plate to control the temperature of the solid. The relative humidity was kept constant at 65%. The concentration of CO<sub>2</sub> was adjusted by mixing it with nitrogen. The reactor was filled up to a pressure of 3 bar with the gas. The drop in the pressure and temperature were recorded throughout the reaction. The pressure drop indicated the CO<sub>2</sub> that had been

consumed by the carbonation reaction. APC residues were dried at 105°C to constant weight prior to reaction. They were then mixed with the selected amount of water and placed in a holder in a uniform layer of 3 mm in depth. 15 grams of ash were reacted in each experiment.

To determine the controlling mechanism, the conditions of reaction were kept constant at their optimum value ( $t = 3$  hours,  $T = 20^\circ\text{C}$ ,  $\text{water/solid} = 0.3$  and 100%  $\text{CO}_2$  [10]). Parameters such as particle size, amount of ash and arrangement of the system were considered in order to study their influence on the mechanism of reaction. The results show that the carbonation of APC residues is diffusion controlled. The gas diffuses into the solid resulting in a growing ring of carbonated material surrounding an inner zone of non-carbonated material. Thus, for the kinetic experiments, the ashes were presented in a thin uniform layer, to ensure uniform availability of the gas at all surfaces of the solid.

The determination of the kinetic model that best describes the carbonation of APC residues required two different kinds of experiments. The first one involved varying the concentration of  $\text{CO}_2$  (from 10% to 100% by volume) at  $\text{water/solid} = 0.3$ . These tests revealed that the conversion achieved at 50%  $\text{CO}_2$  was just over 5% lower than that achieved at 80%  $\text{CO}_2$  (see Figure 1). These results are very encouraging if flue gases are to be used to carbonate APC residues. The temperature was maintained at  $\sim 23^\circ\text{C}$  for both series of experiments.

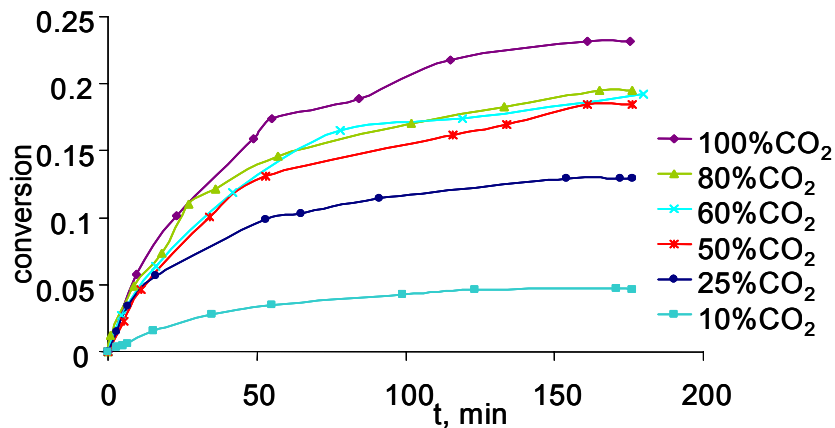


Figure 1 Conversion at different concentrations of  $\text{CO}_2$ ,  $w/s = 0.3$ ,  $T = 23^\circ\text{C}$

In the second set, the  $\text{CO}_2$  concentration was kept constant at 50% for different temperatures (from  $10^\circ\text{C}$  to approx.  $60^\circ\text{C}$ ). The selected  $w/s$  ratio was 0.3 (see Figure 2).

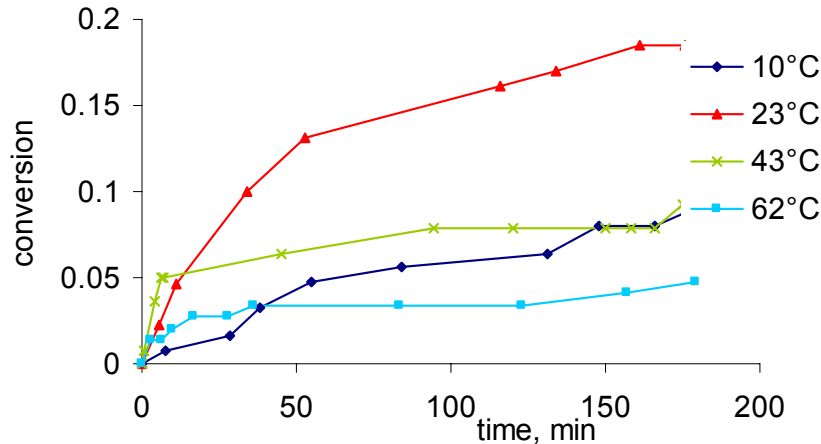


Figure 2 Conversion at different temperatures, 50%  $\text{CO}_2$ ,  $w/s = 0.3$

The selected variable to describe the degree of transformation or fractional reaction  $\alpha$ , is the partial pressure of  $\text{CO}_2$ . It has been selected on the basis that it is a directly measurable parameter and is proportional to the extent of reaction. Thus, experimental data were compared to each rate equation for diffusion controlled reactions, to see which gave the best fit. The kinetic laws considered for this study were those commonly used for solid state reactions: parabolic law, logarithmic law, linear law, Holt-Cutler-Wadsworth equation, Jander equation, Ginstling-Brounshtein equation, Carter equation, Zhuralev-Lesokhin-Tempelmann equation, Dunwal-Wagner equation and Komatsu-Uemura equation.

The model best fitting the data was the Holt-Cutler-Wadsworth model, for reactions of a cylindrical particle of radius  $r$ . Figure 3 shows the comparison of  $\alpha$ - $t$  experimental data for different concentrations of  $\text{CO}_2$  with the theoretical curve of the Holt-Cutler-Wadsworth model. The theoretical curve was obtained from numerical data in the literature [11]. The fit is better at initial stages of the reaction. The uncertainty towards the end of the reaction can be attributed to the physical changes of the particles e.g. increase in particle size and density, decrease of porosity, agglomeration, etc.

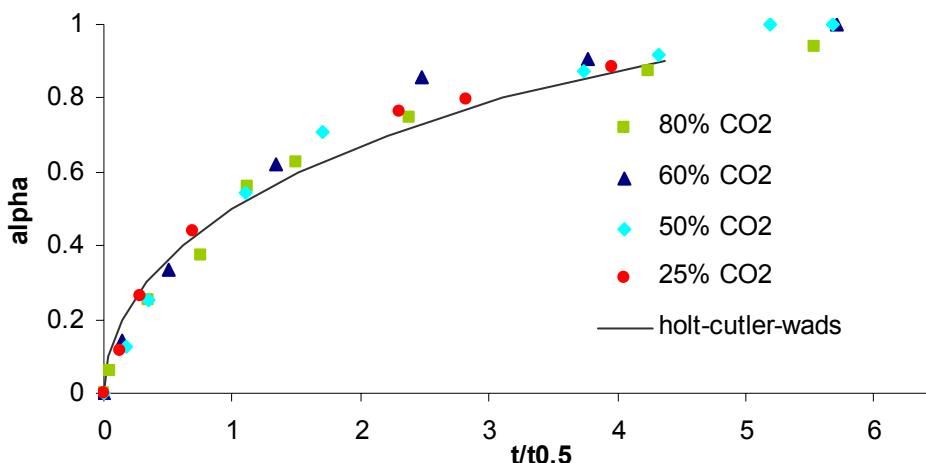


Figure 3 Fraction reacted  $\alpha$ , vs.  $t/t_{0.5}$  for concentrations of  $\text{CO}_2$  from 25 to 80%,  $w/s=0.3$ ,  $T=23^\circ\text{C}$

This information sets the basis for modelling the process. Once modelled, it will be possible to optimise the parameters required for the design of continuous large scale accelerated carbonation of MSW ashes using flue gas emissions of  $\text{CO}_2$ .

### Acknowledgements

The authors acknowledge La Caixa, The British Council and Millennium Chemicals for the financial support of M. Fernández Bertos. The work reported here was partly supported by the Biffaward Scheme (Grant no. B/1797a).

## References

- [1] US5,997,629 Hills C., Hazardous waste treatment. Imperial College of Science, Technology and Medicine. London, U.K. (7-12-1999)
- [2] WO 01/34294 A1 Hills C.D. and MacLeod, C. L., Silicate/Aluminate materials. GB (17-5-2001)
- [3] Walton, J., Bin-Shafique S., Gutierrez N., Smith R. and Tarquin A, Role of Carbonation in Transient Leaching of Cementitious Wasteforms. *Environmental Science and Technology* 31, 2345-2349 (1997)
- [4] Yousuf, M., Mollah, A., Hess, T. R., Tsai, Y.-N. and Cocke D.L., An FTIR and XPS investigations of the effects of carbonation on the solidification/stabilization of cement based systems-Portland type V with Zn. *Cement and Concrete Research* 23, 773-784 (1993)
- [5] Hills, C. D. and MacLeod, C. L., Recycling CO<sub>2</sub> in contaminated land. *Sustain' Built Environment Matters* 1(2), 34-35 (2000)
- [6] Lange, L. C., Hills, C. D. and Poole, A. B., The influence of mix parameters and binder choice on the carbonation of cement solidified wastes. *Waste Management* 16(8), 749-756 (1996)
- [7] Hills, C. D., Sweeney, R. E. H. and Buenfeld, N. R., Microstructural study of carbonated cement-solidified synthetic heavy metal waste. *Waste Management* 19, 325-331 (1999)
- [8] Polettini, A. and Pomi, R., 615, Fifth International Conference on the Environmental and Technical Implications of Construction with Alternative Materials (4-6-2003)
- [9] Fernández Bertos, M., Simons, S., Hills C.D. and Carey, P. J., A Review of Accelerated Carbonation Technology in the Treatment of Cement-based Materials and Sequestration of CO<sub>2</sub>. *Journal of Hazardous Materials* 112(3), 193-205 (2004)
- [10] Fernández Bertos, M, Simons, S., Hills C.D., and Carey, P. J., Investigation of Accelerated Carbonation Technology for Stabilisation of MSW incinerator ashes and sequestration of CO<sub>2</sub>, *Green Chemistry* 6, 428-436 (2004)
- [11] Sharp, J. H., Brindley, G.W and Nathaniel, C.P. Numerical data for some commonly used solid state reaction equations. *Journal of the American Ceramic Society* 49, 379-382 (1966).