

## **New Sustainable Process for Carbon Dioxide and Waste Management**

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### **Abstract**

Air Pollution Control (APC) residues are a mixture of fine products from combustion of municipal solid waste carried in the flue gases and the clean up materials of the gas itself, primarily composed of lime and activated carbon. This material is classified as hazardous waste in the European Waste Catalogue and currently has to be disposed of in special landfill sites.

A positive effect on the chemical and physical properties of these materials has been observed after carbonation [1], thus suggesting the possibility of carrying out a carbonation process to upgrade and recycle these waste materials as artificial aggregates [2]. The process would have the further beneficial effect of consuming carbon dioxide.

Interest in fluidizing the APC residues has arisen as part of an investigation into the suitability of using fluidized beds to conduct the carbonation process. APC residues show the characteristic cohesive behaviour of Group C powders in Geldart's classification [3]. In this work, the results from the fluidization of APC residues by means of a second fluidizable powder, namely Fluid Cracking Catalyst (FCC) powder (Group A), will be presented, thus providing experimental data specific for the fluidization of APC residues and useful for other powders with similar characteristics.

Since the carbonation process of APC residues is to be conducted in the presence of water, the behaviour of the system with moisture content has been investigated.

### **1. Introduction**

ACT is a controlled accelerated version of the naturally occurring carbonation process that affects a wide variety of calcium and magnesium based material on exposure to atmospheric carbon dioxide [1]. Carbonation has the effect of improving both the chemical and physical properties of selected materials, reducing the pH level and the concentration of heavy metal and dioxins in their leachate and increasing their mean strength [4]. ACT has the advantage of carbonating materials in minutes, rather than days or even weeks, rendering certain waste materials non-hazardous and giving them "engineering" properties. Hence, upgrading waste materials that are normally sent to landfill, ACT has the potential to reduce the volumes of waste to be disposed of, which is of added benefit to those countries in which space in landfill sites is becoming severely limited and providing an alternative source of aggregates, for which there is a worldwide diminution of natural resources. The process also consumes carbon dioxide (that is sequestered as a salt in the solid product), thus contributing to the reduction of greenhouse gas emissions.

An extensive review of waste materials, based on the European Waste Catalogue, has been carried out to identify the most suitable waste for AC treatment. The choice of APC residues was based on chemical properties, size distribution, hazardous nature, amount produced annually, etc.

Further restrictions on the disposal route of APC residues have been recently applied (16 July 2004), following the Landfill Directive (99/31/EEC). These restrictions have the immediate effect of increasing the operating costs faced by the incineration industries to handle this waste. These costs are related to the need for longer weathering treatments, larger spaces to be allocated for the storage of the treated waste, transport of the waste to special sites, higher taxes to dispose of the waste and higher costs for research programmes. Upgrading the APC residues, simply making them adequate to be disposed of in normal sites, would reduce these costs. It would even produce a net income, if upgraded APC residues were employed as artificial aggregate.

It is proposed here the possibility that ACT could be integrated with an incinerator plant, using the flue gas as the source of CO<sub>2</sub> and treating the APC residues on-site, resulting in a lower carbon dioxide emission energy production process coupled with sustainable waste and resource management.

## 2. Background

The carbonation reaction occurs in the presence of water. CO<sub>2</sub> from the gas phase adsorbs into water as carbonic acid and its ionic derivatives. Solvation of the solid phase produces calcium ions, which combined with the CO<sub>3</sub><sup>2-</sup> anions precipitate in the pore space of the solid as CaCO<sub>3</sub>, forming a solidified product. The process is exothermic. The complex equilibrium of species participating in the reaction is significantly influenced by the pH level and temperature.

Encouraging results for the uptake of CO<sub>2</sub> have been observed when operating in a batch system. In particular a 20% increase by wt uptake of CO<sub>2</sub> in APC residues has been observed during the carbonation process.

As a first approach to an industrial process, the carbonation method has been considered on a continuous basis, with the possibility of using fluidization to carry out the reaction being investigated. The fluidized bed reactor combines the advantages of both a continuous process and a single stage operation for the CO<sub>2</sub> absorption into water and the solid-liquid carbonation reaction. The high degree of inter-phase dispersion established inside the system enhances the mass transfer efficiency, whereas the high capability of heat exchange guaranteed by fluidized systems improves the thermodynamics of the reaction. The particulate nature of the raw material and the nature of the operations that have to be conducted, sensibly point to the fluidization as a suitable operation for ACT, provided the material properties are compatible.

The use of a fluidized bed for this process has been recognized to be essential to operate at a large scale. The optimal physical conditions to carry out the operation in a fluidized bed have been determined

## 3. Experimental

APC residues are in the form of a light, small and very wide size distributed powder and show the characteristic cohesive behaviour of Group C powders in Geldart's classification [3]. Because of the difficulties related to the fluidization of cohesive powders, industrial processes as well as research investigations have preferentially employed other powders, especially those belonging to the aeratable Group A. Nevertheless, the potential in industrial applications for fluidization of cohesive powders has been generally

recognized, as addressed by some authors [5], due to the large superficial surface area of such powders and the increasing interest in new nano-materials. Mixing the Group C powder with larger fluidizable particles reduces its cohesiveness and allows the powder to be fluidized, as investigated by Kono et al. [6-7] and experimented by others [8].

In this work, the fluidization of APC residues has been assisted using a second fluidizable powder, namely Fluid Cracking Catalyst (FCC) powder (Group A). This powder was selected due to its size and density characteristics and also its availability in UCL laboratories. It was chosen as a simulant to test process conditions and behaviour. In practice, a more suitable material (with similar physical properties) would be used in a real process, such as another waste stream that could also be carbonated. Such a waste could be for example a specific fraction of construction and demolition waste (rich in lime and abundant in industrialized countries). In our studies, sand was also tested as the carrier solid, but because of the high difference in density with APC particles the system resulted in segregation. The relevant characteristics of the particles are shown in Table 1. Tap water was used to wet the system.

Table 1. Powder properties.

	<b>APC residues</b>	<b>FC C</b>	<b>sand</b>
<b>Density [kg/m<sup>3</sup>]</b>	423	1420	2600
<b>Size [μm]</b>	66	49	210-250
<b>Geldart Group</b>	C	A	B

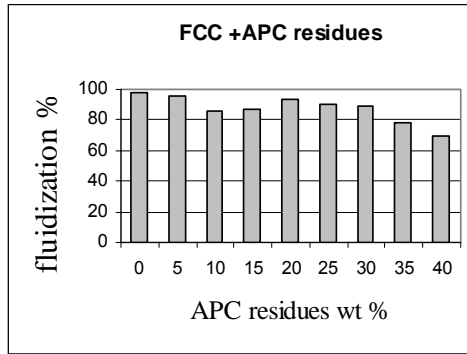
The experiments were conducted in a 0.138m inner diameter and 0.46m tall transparent Perspex column. A sintered porous bronze distributor, 0.005 m thick and with an average pore size of 15 μm, was adopted. Each experiment was run using 2 kg of powder with different relative amounts of APC residues. Powders were dried in an oven at 110 °C for 24 hours prior to the experiments. Dry air was used to fluidize the system. All the experiments were conducted at room temperature and atmospheric pressure. Measurements of bed expansion were made through visual inspection and a water manometer was used to evaluate the pressure drop across the bed.

Experimentation has been conducted in both dry and wet conditions, in order to determine the influence of water on the behaviour of the system. The degree of fluidization was evaluated by comparing the pressure drop with the weight of particles per cross-sectional area.

The homogeneous expansion of the system (if present) has been characterized by using the Richardson and Zaki equation [9-10], originally developed for liquid fluidized beds and subsequently applied to gas fluidized beds [11-12]. Experimental values of the expansion parameter  $n$  and the terminal settling velocity  $u_t$ , obtained from the expansion profiles, are discussed.

#### 4. Results and Discussion

Figure 1. Fluidization percentages in dry conditions.



The results obtained in dry conditions are shown in Figure 1, in which the fluidization percentage is reported for systems with different relative amounts of ash. When operating with the FCC alone the system is almost fully fluidized. A slight loss in the fluidization can be observed with a 5% in weight of APC residues and a further, more consistent drop in the fluidization percentage of the system is observed with 10% of APC residues. For percentage amounts of APC residues between 10 and 30% in weight, the system is fluidized for about 90% of the total amount. For higher amounts of APC residues (up to 40% in weight), the loss in fluidization is between 20 and 30%.

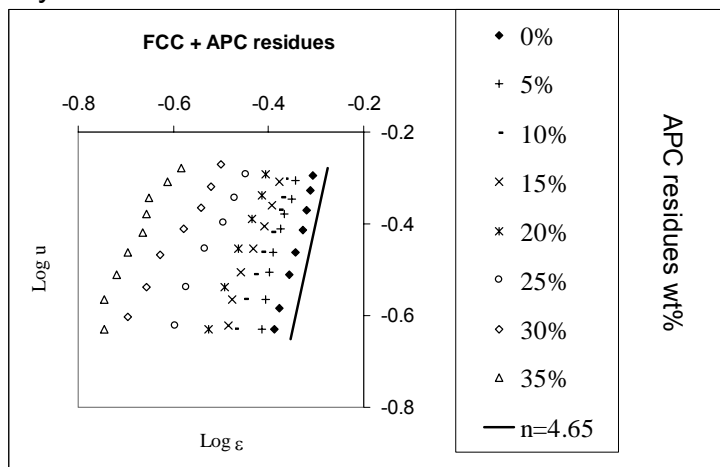
In Figure 2, data from the expansion profiles of systems with different amounts of APC residues are reported in the form of the Richardson and Zaki correlation:

$$\frac{u}{u_t} = \varepsilon^n \tag{4.1}$$

The solid line has the theoretical slope recommended by Richardson and Zaki for liquids in the viscous regime:

$$n = 4.65, \quad Re_t < 0.2. \tag{4.2}$$

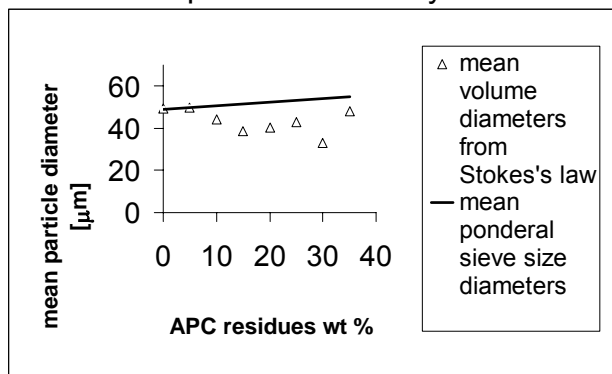
Figure 2. Expansion profiles of FCC + APC residues through Richardson and Zaki equation in dry conditions.



The experimental value of n for the FCC alone is close to that reported in (4.2) and according to other authors [13]. Homogeneous expansion has been observed for concentrations of APC residues up to 35% of the total amount. A gradual depression of the

system is however observed for increasing amount of the APC residues, suggesting an increasing cohesiveness of the system.

Figure 3. Mean powder diameters for different compositions of the system.



Estimated values of  $u_t$  (as the extrapolation of  $u$  at infinite dilution in the Richardson and Zaki correlation) and Stokes's equation for settling particles have been used together to evaluate the mean volume diameters of particles for different compositions of the system. The results of this back calculation, reported in Figure 3, can be used as a first approximation to show that the particles stay loose inside the system and no clusters are formed. Calculated volume diameters are in fact of the same order of magnitude of mean sieve size diameters.

Table 2. Fluidization percentages in wet conditions.

run	1	2	3	4	5	6	7	8
$X_A$	0.1	0.1	0.1	0.1	0.1 5	0.1 5	0.2	0.2
water wt %	0.2 9	6.2 2	8.9 2	20.3 1	4.8 7	3.0 7	1.7 4	5.8 2
fluid %	85	88	71	NA	69	76	60	38

In Table 2 the results of the experimentation conducted in presence of water are shown. The main effect of water is to depress the expansion of the system, already evident when using the fresh, moist APC residues without any further addition of water (run number 1). Using a 0.1 APC to FCC mass ratio, the powder was successfully fluidized with up to 9 wt % water, with the highest loss in fluidization being almost 30%. From the data shown in Table 2 it is clear that sufficient fluidization can be achieved operating at the conditions employed in run number 3, i.e. with 10 wt% APC residues and 10 wt% water.

## 5. Conclusions

The work reported here is investigating the suitability of a three-phase fluidized bed system to conduct the AC. Experiments on a laboratory scale fluidized bed indicate that defluidization of the APC residues is a crucial factor. Utilising an aeratable carrier solid has been seen as a possible method to achieve satisfactory fluidization behaviour. The optimal phase to phase ratios to operate the fluidization have been elucidated and reported. Satisfactory fluidization has been generally achieved in dry conditions. Absence of clusters suggested by the back calculation analysis is confirmed for the three phase system would guarantee a better configuration of the system for the carbonation reaction, due to a better inter-phase contact.

The results show that ACT can be used to upgrade APC residues and sequester CO<sub>2</sub> in a fluidized bed unit. Current work is looking at the suitability of other waste streams as the carrier solid. This material may also benefit from carbonation, thereby extending the sequestration potential of the process. Examples include incinerator bottom ash, cement kiln dust and stainless steel slag other than the construction and demolition waste. The effects of the carbonation reaction on the fluidization behaviour are also being studied, together with the CO<sub>2</sub> consumption, extent of carbonation and the physico-chemical properties of the solid product.

## Acknowledgements

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## Notation

$n$	exponential coefficient of Richardson and Zaki equation
$Re_t$	Terminal Reynolds number
$u$	gas velocity
$u_t$	terminal velocity of settling particles
$X_A$	APC residues / (APC residues + FCC) wt/wt

## Greek letters

$\varepsilon$	bed voidage
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