

# The removal of carbon from fly ash using supercritical water oxidation

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## ABSTRACT

The presence of excessive carbon in pulverised fly ash (PFA) is regarded as a serious issue in the developed world due to its effect on plant efficiency and the possibility of landfill taxes related to the nature of the ash. Variable or unacceptable carbon contents adversely affect ash utilisation. Consequently there is a need to be able to remove carbon from PFA streams, ideally completely or, at least, to significantly lower levels.

Carbon removal has been shown to be possible by the treatment of high-carbon fly ash with supercritical water (SCW). Above the supercritical point the properties of water change from a polar liquid to a fluid with a low dielectric constant and low pH. Organic substances including particulate carbon are capable of being oxidised under these conditions.

Since power stations already produce superheated water, it would be feasible for a power generator to modify its operations in order to treat the PFA it produces to remove residual carbon. This would avoid landfill duties and increase market opportunities for the ash, due to its 'improved' composition.

## INTRODUCTION

The removal of carbon from fly ash remains a serious issue in the UK and other countries with the possibility of landfill taxes proportional to carbon content. The UK government currently levies a charge of £2 (~\$3) per tonne for fly ash disposal as landfill, [1], although the charge in Germany, for example, is much higher at a cost equivalent to £40, (\$55-60) per tonne. With this as the background, it is evident that there is a need to be able to remove a significant proportion of the carbon from a fly ash stream, to enable the highest value by-product to be put on the market.

The need for power generators to comply with NO<sub>x</sub> emission regulations has lead most to install, as a first step, low NO<sub>x</sub> burners (LNBS). Although effective at reducing NO<sub>x</sub>,

the process by which this is achieved also results in an increase in unburnt carbon in fly ash. The presence of increased levels of carbon in boiler fly ash is undesirable for a number of reasons. The main concern is that it represents an efficiency loss to the boiler as incompletely combusted coal is discarded with the ash. Higher than normal carbon in ash also results in a collection efficiency loss in the electrostatic precipitator (ESP). The consequences are an increase in stack opacity and possible contravention of the regulatory dust emission limits. Finally, an area of concern, which is likely to increase in the future, is the disposal of fly ash. Although markets exist for a number of qualities of combustion by-products, the presence of excess carbon in fly ash can change a valuable revenue earner into a waste product whose disposal costs are presently high and increasing.

This paper will describe a novel application of a process which can remove a significant amount of carbon from fly ash and in doing so release its heat content. If commercialised, the process will ensure that the income stream from fly ash can be maintained and that boiler plant efficiency will be increased.

## **FLY ASH BENEFICATION METHODS**

Existing fly ash beneficiation methods rely mainly on physical methods to separate the carbon from PFA. Developed and on-going technologies include methods involving combustion, separation, (either wet, dry or electrostatic), air classification, vibratory methods, froth flotation and sieving. The progress of these activities has been presented annually since 1995 at the Unburnt Carbonaceous Materials on Utility Fly Ash conferences held in Pittsburgh by US DoE, [2].

Although there now exist a variety of methods for the removal of carbon, all suffer from some disadvantages. Most of the physical separation methods can only lower the unburnt carbon levels by relatively small amounts and do not treat all of the ash, whilst the more efficient methods of carbon separation and utilisation may result in significant capital costs. In addition, the separated carbon is likely to be very unreactive for combustion purposes and returning it to the power station coal bunkers will not guarantee that it will burn out satisfactorily, since it failed to burn out during its first pass through the boiler.

There is believed to be a need for a simple process in which carbon is substantially and reliably removed from PFA. It is important that the heat content of the carbon is utilised and that the process will have low capital and operating costs. We believe that the supercritical water oxidation (SCWO) of carbon in fly ash might be such a process.

## **NATURE & PROPERTIES OF SUPERCRITICAL FLUIDS**

A supercritical (SC) fluid is defined as a substance that is at conditions of temperature and pressure that are above its vapour-liquid critical point. At supercritical conditions, a fluid does not behave entirely as a liquid or as a gas, but somewhere in between. The

properties of supercritical fluids combine the solvating powers of liquids with the diffusivities of gases.

The critical point for water is at 374°C, (706°F) and 218 atmospheres, (22MPa, 3,191psi). The changes in the properties of water once supercriticality has been reached are remarkable. The familiar, polar liquid with its high dielectric constant of 78.5 changes to an almost non-polar fluid with a value of less than 5, approaching that of ambient hexane at 1.8. The density of SCW is found to decrease to around 0.15g/ml, depending upon conditions. SCW possesses properties which enable it to become miscible with organic molecules and with gases.

## **APPLICATIONS OF SUPERCRITICAL WATER OXIDATION (SCWO)**

SCWO is a high temperature and pressure technology that uses the properties of supercritical water in the destruction of organic compounds and toxic wastes. Under SC conditions, the oxidation reactions occur in a homogeneous phase where carbon is converted to carbon dioxide, hydrogen to water, nitrogen-containing substances to nitrogen and sulphur-containing substances to sulphuric acid. An important factor in the context of this application of SCWO is that the reactions are exothermic and the process can become thermally self-sustaining if the appropriate concentration of oxidisable substances is present.

SCW is known to be highly effective at rapidly oxidising organic matter in for example, aqueous waste streams. Its application to the complete destruction of hazardous and toxic wastes has been extensively studied, [3]. Much effort is currently being expended in applying SC techniques in a variety of applications. Some of the most recent results are available in the proceedings of the 5th Symposium on Supercritical Fluids, [4]. It is our intention to show the feasibility of a SCWO system for removing unburnt carbon from fly ash.

## **WORK PROGRAMME**

Fly ash samples from different coals have been subjected to a batch process of SCWO. The use of fly ashes from a number of well-characterised coals is intended to provide an opportunity in the future to examine the effect of SCWO on the morphology and intrinsic reactivity of the residual carbon. The experiments are designed to discover whether certain char types are more susceptible to oxidation than others.

## **EXPERIMENTAL**

### **Samples**

Fly ashes from a 1MW combustion test facility (CTF) owned and operated by a power generator in the UK were obtained and analysed for loss-on-ignition, (LOI). LOI and carbon are used interchangeably in this paper although this is not strictly correct.

Selected coal data is shown in Table 1.

| Identity and country of origin of coal used | Fuel ratio | % Unreactives | Ash content, (% dry) |
|---|------------|---------------|----------------------|
| Ensham--Australia                           | 2.11       | 11.5          | 12.3                 |
| Prodeco--Colombia                           | 1.47       | 3.7           | 8.9                  |
| Kuzbass--Russia                             | 1.60       | 7.2           | 12.5                 |
| Goedehoop--South Africa                     | 2.31       | 21.3          | 13.5                 |
| Tyne Blend--UK                              | 1.71       | 7.0           | 12.5                 |
| Bailey--USA                                 | 1.57       | 4.2           | 9.8                  |
| Guasare--Venezuela                          | 1.63       | 5.3           | 7.6                  |

Table 1. Selected properties for the coals in the study

In addition to the fuel ratio and ash content, a value known as % Unreactives has been included. This is a parameter developed at the University of Nottingham [5] in which the overall light reflectance of a whole coal sample is measured. From this data an estimate of the burnout potential of the coal can be reliably predicted. The higher the % Unreactives, the poorer is likely to be the carbon burnout.

### Equipment

The fly ash samples were treated with SCW in a supercritical water oxidation rig which is shown in Figure 1. The equipment consists of a Gilson model 305 HPLC pump fitted with a 25SC head which is connected in series to a pressure transducer (RDP model A105), Bourdon gauge and pressure relief and non-return valves. The pump has been modified so that it can be cooled to below 5°C to allow pumping of hydrogen peroxide. A 7m coil of 1/8" tubing, wall thickness 0.035" serves as a heating coil with a Pye 104 GC oven, allowing temperatures of up to 460°C to be reached. This ensures that all of the hydrogen peroxide has decomposed to molecular oxygen before entering the reaction vessel. The coil leads to a reactor consisting of 1/2" o.d. tubing, wall thickness 0.083". Following the oven, a water-cooled heat exchanger leads to a filter (Nupro 8TF) with a 0.5 micron sintered metal element and a back pressure regulator (Tescom).

### Method

The sample of PFA, (3.0g), was charged into the vessel between glass wool plugs. The vessel was sealed and the system pressure tested to 300atm using cold water. The oven and cooling system were turned on. After the oven had reached ca. 460°C, a 2% solution of hydrogen peroxide, (Aldrich, 30% w/w diluted with demineralised water), was injected at a rate of 15ml/min. A volume of between 250 and 300ml of hydrogen peroxide was injected. This represents a 3 fold excess of oxidant for 3g of PFA with 10% LOI. At all times the reaction vessel was maintained at supercritical conditions, i.e. temperature >400°C and pressure >240atm. The vessel was maintained at these conditions for 30 minutes then cooled and the treated ash removed.

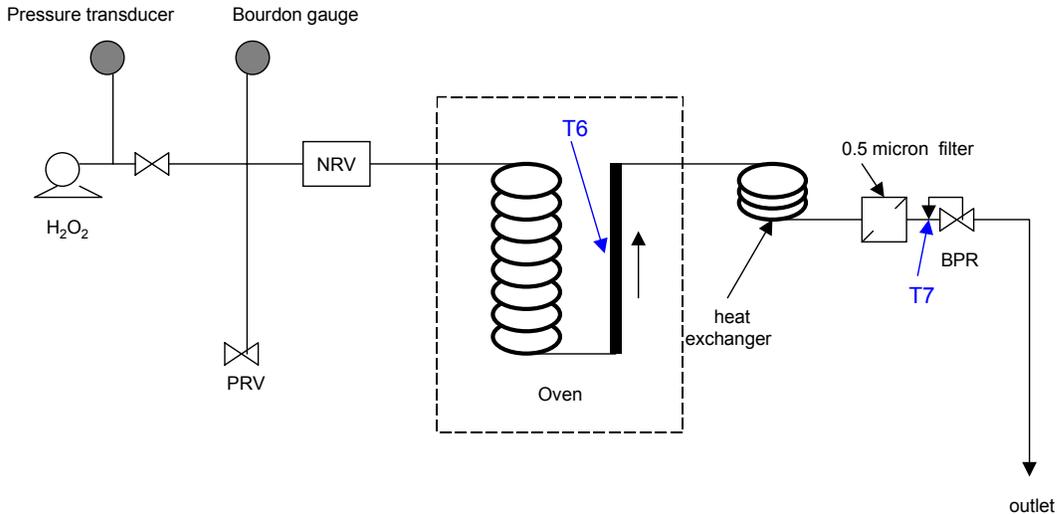


Figure 1. Supercritical Water Oxidation Rig

## RESULTS AND DISCUSSION

Data on the carbon content of the PFA samples before and after treatment with SCW is shown in Table 2, together with the reduction in carbon content expressed as LOI.

All of the PFA samples have shown a reduction in their LOI values but there are significant differences in the removal efficiency. At this time process optimisation for maximum carbon removal has not been investigated although it is planned.

Nevertheless, it seems that certain factors appear to have affected the degree of carbon oxidation. Under the selected conditions it seemed that the best removal efficiency was associated with those ashes with the highest LOI, (>20%). It should also be realised, however, that these samples were from South America coals which are generally regarded as being reactive, (see % Unreactives in Table 1).

There is also a suggestion that a correlation may exist between remaining carbon and the % Unreactives. The highest remaining carbon was found in the Goedehoop sample which also has the highest % Unreactives. This seems to suggest that the nature of the residual carbon, which is related to the petrography of the coal, may be a factor. Further work, however, needs to be carried out to establish the effect of char morphology on ease of oxidation.

All of the samples were treated in a similar manner and although the LOI values for some of the PFA samples were high, sufficient oxidant was introduced to potentially reduce all of the unburnt carbon that was present.

It should be recognised that the results presented at this time are preliminary and are intended to demonstrate the concept.

| Identity and country of origin of coal used | LOI <i>before</i> SCWO (% dry) | LOI <i>after</i> SCWO (% dry) | Reduction in LOI, (%) |
|---|--------------------------------|-------------------------------|-----------------------|
| Ensham--Australia                           | 7.64                           | 4.56                          | 40.3                  |
| Prodeco--Colombia                           | 20.68                          | 3.62                          | 82.5                  |
| Kuzbass--Russia                             | 4.37                           | 3.54                          | 19.0                  |
| Goedehoop--South Africa                     | 12.37                          | 6.14                          | 50.4                  |
| Tyne Blend--UK                              | 7.89                           | 4.98                          | 40.1                  |
| Bailey--USA                                 | 10.90                          | 3.35                          | 69.3                  |
| Guasare--Venezuela                          | 22.56                          | 4.73                          | 77.9                  |

Table 2. Loss-on-ignition data for fly ashes

The concept of SCWO is not new but has been plagued by various technical difficulties in the recent past. In order to allay possible fears regarding the use of SCWO of fly ash for carbon removal, a brief discussion of the important factors is deemed appropriate at this time. These problem areas have been recently summarised by Kritzer and Dinjus, [6]. They relate to corrosion of the reactor vessel, plugging of the system by inorganic salts and the difficulty of assessing the cost of a scaled up commercial system.

The corrosion is attributable to chlorine, sulphur and phosphorus in the wastes which is converted into hydrochloric, sulphuric and phosphoric acids, respectively. At the necessarily high operating temperatures, corrosion resulting from the presence of these elements is a serious problem. However, in the case of carbon removal from fly ash, the oxidisable fraction is almost exclusively carbon with very little sulphur and nitrogen and no chlorine or phosphorus. Thus corrosion should not be a major issue.

Changes in the properties of water when it reaches supercritical conditions mean that soluble inorganic salts no longer remain in solution and will precipitate out. Since coal fly ash generally contains little water-soluble material and since the operating system involves treatment of a slurry, the question of plugging is not likely to be an issue. Indeed, the extremely fine nature of fly ash ensures that SCW is able to make good contact with the carbonaceous particles and thereby effect its oxidation.

The costing issue cannot be addressed at this time due to the present early stages of process development.

## CONCLUSIONS

The supercritical water oxidation of carbon in fly ash has been demonstrated. The efficiency of carbon removal was found to be variable for similar test parameters. The highest removal efficiencies were found with high LOI fly ash samples from the more

reactive South American coals. There is a possibility that removal efficiency may be linked to the reactivity of the coals. Further work is in progress to optimise the oxidation process and to understand what links exist between the nature of the residual carbon and its ability to be oxidised.

## **ACKNOWLEDGEMENTS**

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