BENEFICIATION OF COAL FLY ASHES
BY OXYGEN CHEMISORPTION

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Abstract
This paper addresses the problem of unburnt carbon in fly ashes from coal-fired power stations. It has been shown that carbon-in-ash has much lower combustion reactivity than the original coal, because of the extensive thermal annealing experienced in the boiler. Thermal annealing reduces the rate of the first reaction step of which carbon combustion is composed, namely oxygen chemisorption. In the present work experiments have been carried out in order to verify if a preconditioning stage consisting of mild pre-oxidation with air is able to promote oxygen chemisorption thus increasing the combustion reactivity of ashes. Fly ashes with high LOI have been exposed to air at temperature <400°C for times up to 300min. Results show that a satisfactory extent of oxygen chemisorption can be attained at 300-400°C with 1-2 hours holding time. After this conditioning, samples have been tested to check their combustion reactivity by means of non isothermal thermogravimetric analysis. Additionally, combustion experiments have been carried in a purposely designed suspension reactor at temperatures up to 1000°C. Results confirm that ash pre-conditioning reduces the burn-out time of carbon in ash. The concept has been finalized into an international patent application.

The conceptual frame for ashes beneficiation
The level of unburnt carbon (also referred to as LOI) in fly ashes from coal combustion makes the difference between the possibility to sell ashes to the cement industry, with an economic revenue, or pay for their disposal, posing an additional burden. The maximum LOI tolerable for cement industry varies between 3-7% by weight according to individual National Standards. Combustion of the residual carbon-in-ash can be pursued by means of recycle of fly ashes to the boiler. Alternatively it can be pursued in ancillary equipments dedicated to ash post-combustion. In any case post-combustion is problematic because of the distinctively low combustion reactivity of carbon in ash compared to the parent coal. Senneca [1] in a previous paper estimated the loss of reactivity to be in the order of 100 for a bituminous coal burnt in a front-fired boiler. Several studies in the last decades have clarified that the reactivity of carbon in the last stages of its lifetime in an industrial boiler is depressed by thermal annealing phenomena [2-9]. This is also the reason for the low reactivity of residual carbon in ash [1].
However recent kinetic models of coal combustion have underlined the possibility that thermal annealing does not reduce all the reaction steps that lead to carbon combustion to the same extent [10-12]. It must be recalled indeed that carbon combustion involves a multitude of series-parallel reactions, that can be roughly lumped in three steps. The first step, namely chemisorption, implies that molecular oxygen is uptaken by the carbon matrix and forms complexes on the carbon active sites. This reaction step reads:
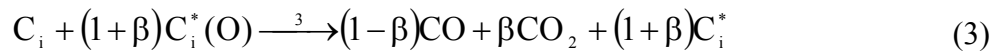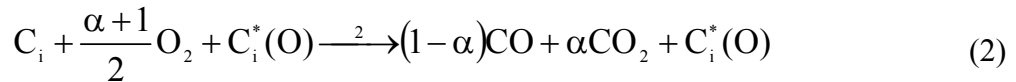
$$C_i^* + 0.5 \cdot O_2 \xrightarrow{\quad 1 \quad} C_i^*(O) \qquad (1)$$
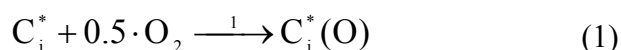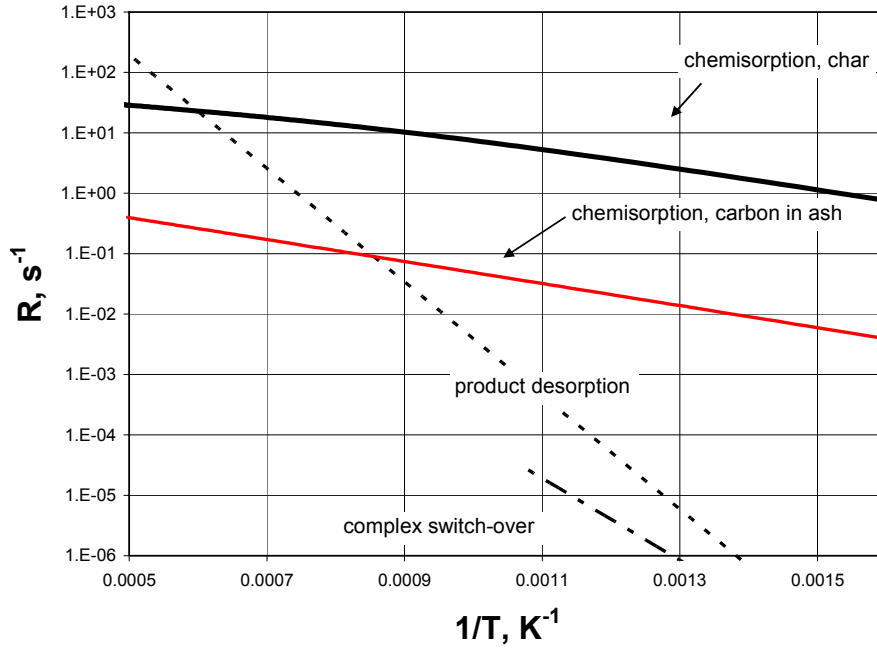
Figure 1. Rate of individual reaction steps for bituminous char and for carbon-in-ash

Surface oxides may then undergo either switch-over or desorption reactions, both of which produce gaseous products CO and CO_2.

These reaction steps read:

$$C_i + \frac{\alpha+1}{2}O_2 + C_i^*(O) \xrightarrow{\ 2\ } (1-\alpha)CO + \alpha CO_2 + C_i^*(O) \tag{2}$$

$$C_i + (1+\beta)C_i^*(O) \xrightarrow{\ 3\ } (1-\beta)CO + \beta CO_2 + (1+\beta)C_i^* \tag{3}$$

It has been inferred that the microstructural transformations associated with thermal annealing affect the propensity of carbon to uptake oxygen and form oxygen complexes, thus reducing primarily the rate of oxygen chemisorption [10-11]. The effect of annealing on the rate of desorption may be less remarkable.

Figure 1 reports the relative rates of reaction steps 1-3 as a function of temperature for a bituminous char and for carbon-in-ash, given a particle size of 50μm and oxygen partial pressure of 0.1 bar. For char particles the rates of individual reaction steps are calculated assuming the kinetic parameters provided by Hurt and Calo [13]. Notably the effects of annealing are neglected in this case and chemisorption turns out to be the rate-limiting step at temperatures >1400°C. In the case of carbon-in-ash, we know from previous work that the overall rate of combustion is lower than that of the original bituminous coal by a factor of about 100. If we make the additional assumption that this loss of reactivity is mainly due to the reduced propensity to chemisorb oxygen, we then estimate the rate of the reaction step 1

Table 1. Elemental and ICP analysis of ashes

Elemental analysis w%	
C	23
H	1.6
N	0.7
ICP ppb	
Al	1.8E+08
Fe	6.0E+07
Ca	2.8E+07
Mg	4.6E+06
Ti	2.1E+06
Na	1.6E+06
P	1.5E+06
K	1.2E+06
Sr	8.6E+05
Ba	6.2E+05
Mn	3.3E+05
V	1.6E+05
Zr	1.4E+05
Ni	6.0E+04
Cr	5.9E+04
Ce	5.4E+04
Zn	1.3E+05
As	4.6E+04
Cu	5.0E+04
Pb	1.2E+05

for ashes to be lower than that of the young char by a factor of 100 too, the rate of the desorption step remaing instead comparable. Under these hypotheses it can be observed that chemisorption starts to limit the overall rate of combustion of carbon in ash already around 1000°C.

Analysis of Fig. 1 in the case of ashes suggests also that at moderate temperature the situation is reversed, in fact chemisorption is faster than the desorption and switch-over steps. Accordingly exposure of ashes at temperatures in the order of 200-400°C for a long enough time should lead to build up of oxygen. Oxygen complexes so formed would be desorbed at high temperature, upon recycling of ashes to the boiler, thus leading to complete carbon burnout.

Experimental

A first set of experiments was directed to assess the propensity and the time-scale of oxygen uptake on fly ashes at different temperatures. Ashes used for the experiments were collected at the last rows of the electrostatic precipitators of a front-fired boiler fed with bituminous coal. In a previous paper the same samples had been characterized by means of granulometric and chemical analysis and their combustion reactivity had been assessed by means of thermogravimetric analysis and in an heated grid reactor. A summary of the properties of ash samples is reported in table 1. The SEM micrograph shown in Fig. 2 shows that ashes include spherical inorganic-rich particles together with irregularly shaped carbonaceous-like particles.

Chemisorption experiments were carried out in the TG-DSC apparatus Netzsch 409. In each test a sample of 20-40mg of ashes was heated in a flow of 200ml/min of air at the heating rate of 50°Cmin. Heating was followed by an isothermal stage of variable duration at the desired temperatures of 200-300 and 400°C. After chemisorption, the sample was cooled down to 100°C and heated again in air up to 900°C at the lower rate of 5°C/min till complete carbon burnout. This procedure allowed to estimate both the amount of oxygen uptaken during the first chemisorption step and the rate of combustion of the sample after the conditioning.
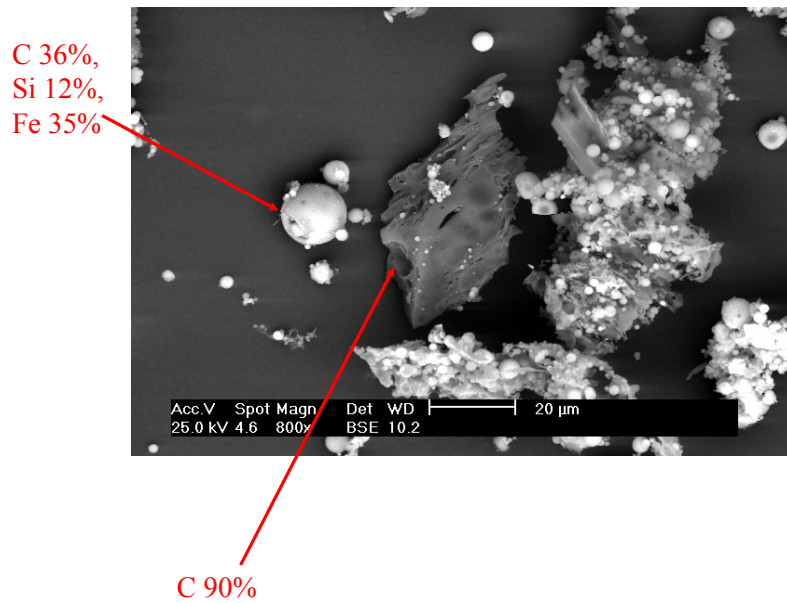
Alternatively chemisorption was carried out in a lab scale fluidized bed reactor of 40mmID. This allowed to prepare larger quantities of conditioned sample for further analysis. These samples were used also to perform high temperature combustion experiments and temperature desorption experiments (TPD) in an novel reactor, the Aerodynamically-Levitated Particle Reactor (ALPR), shown in Fig. 3.

C 36%,
Si 12%,
Fe 35%

C 90%

**Figure 2**. SEM picture of typical ash particles

The core of the ALPR reactor consists of a divergent section where the gas, preheated by electrical furnaces, flows upwards and attains different velocities along the vertical axis. Particles are fed from the top of the reactor and are aerodynamically suspended by the gas flow at vertical positions (corresponding to different gas velocities) which depend on their weight and size. The absence of contact with any solid surface allows particles to be heated uniformly and heterogeneous reactions to proceed under conditions similar to suspension firing. The gas   temperature inside the core region of the reactor is measured by
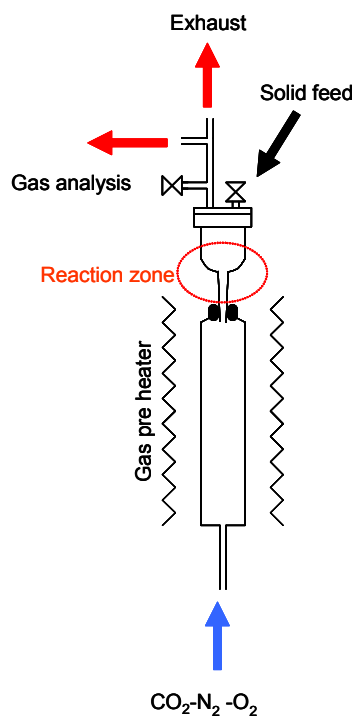
Figure 3. The ALPR reactor.
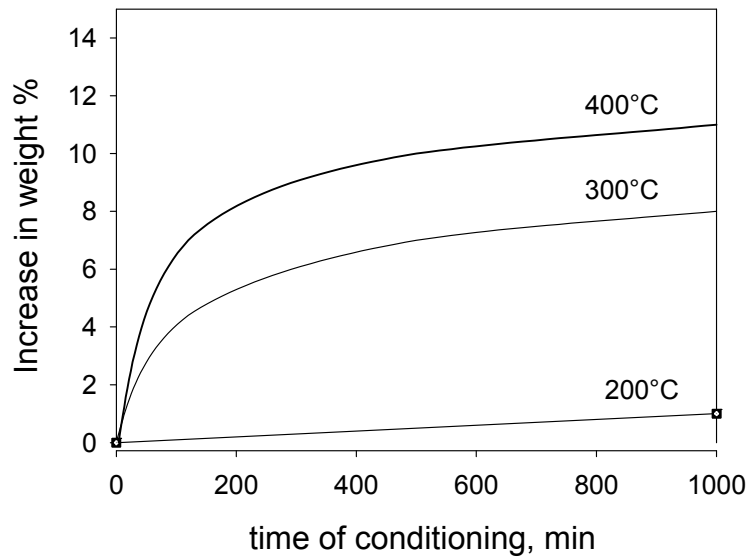
**Figure 4**. Oxygen uptake upon conditioning.
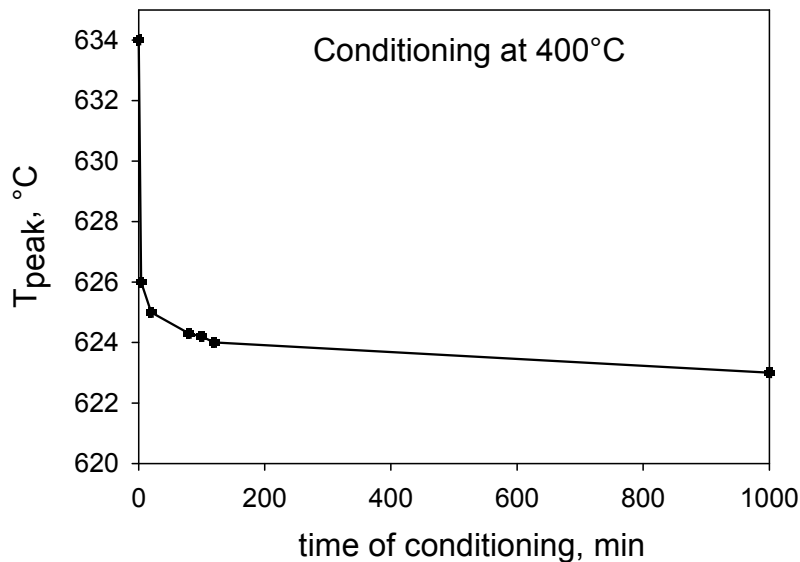
Figure 5. Temperature of DTG peak of combustion of ashes conditioned at 400°C for different times.

thermocouples and can be as high as 1100°C.

In combustion experiments a bunch of ashes in the order of 10mg was fed to the preheated reactor at temperatures T_R in the range 800-1000°C. The gas composition was 4% oxygen in pure nitrogen. The progress of combustion was monitored by means of on-line CO/CO_2 Hartman and Braun IR analyzers.

In TPD experiments the ashes were fed to the reactor at ambient temperature and heated in a flow of pure nitrogen up to 1050°C at a constant heating rate of 10°C/min, followed by an isothermal stage. CO and CO_2 evolved were analysed on line throughout the experiment by IR analyzers
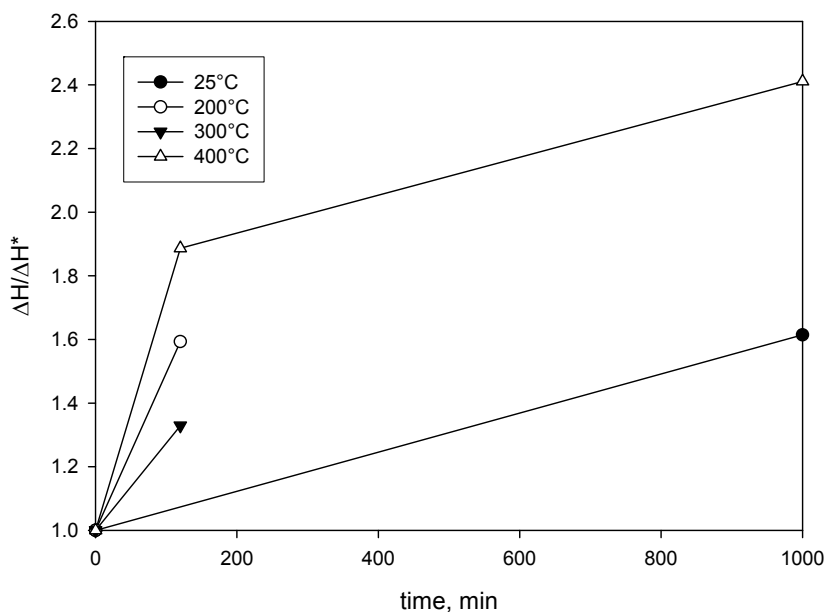
Figure 6. Heat of combustion of the conditioned ashes over heat of combustion of raw ashes as a function of the temperature and duration of the conditioning

Results

Results of chemisorption experiments are shown in Fig. 4. The figure reports the total increase in sample weight measured after conditioning with air as a function of the temperature and duration of the pre-oxidation. Notably a maximum uptake of 12% by weight is attained after a treatment of 1000 min at 400°C, which is equivalent to 0.2 moles of O_2 per mole of C in ash. After 2h an encouraging result of 7% weight increase is accomplished, which means 0.11 moles of O_2 per mole of C . Experiments carried out on other ash samples, not reported in the present work for sake of brevity, showed that the carbon content in the ashes affects the amount of oxygen uptake but not the time-scale of the process.

The weight loss measured by TG during the non isothermal combustion step has been worked out to calculate the derivative of the weight loss represented by the DTG plots. These curves showed one marked peak. Notably peak temperature T_{peak} varies according to the severity of the preceeding treatment of oxygen chemisorption. Figure 5 shows the progressive decrease of T_{peak} as the duration of the conditioning treatment is increased, indicating that the overall rate of combustion increases with the extent of oxygen uptake. Figures 6 reports the ratio of the heat of reaction (ΔH) measured by the DSC during combustion of conditioned ashes over the heat of combustion (ΔH^*) of the raw ashes as a function of the temperature and duration of the conditioning. It shows that pre-conditioning yields also an increase in heat of reaction. These results further support the idea that exposure of ashes to air at moderate temperature can effectively increase the reactivity of carbon in ashes. On the basis of the analysis of Fig.1 it is expected that this effect should be even more significant at temperatures above 1000°C, when chemisorption limits severely the overall rate of combustion. The combustion tests in the ALPR reactor at high temperature were purposely done to check this hypothesis.

Figures 7 and 8 report the profiles of CO and CO_2 at the exhaust measured during isothermal combustion of ashes in a FB reactor and then fed to the ALPR reactor at 800 and 1000°C, respectively. In particular the results obtained for raw ashes are compared with those of ashes that have been preconditioned at 400°C for 2h. Concentration data have been normalized with respect to the weight of the samples used in each experiment and reported in arbitrary units.
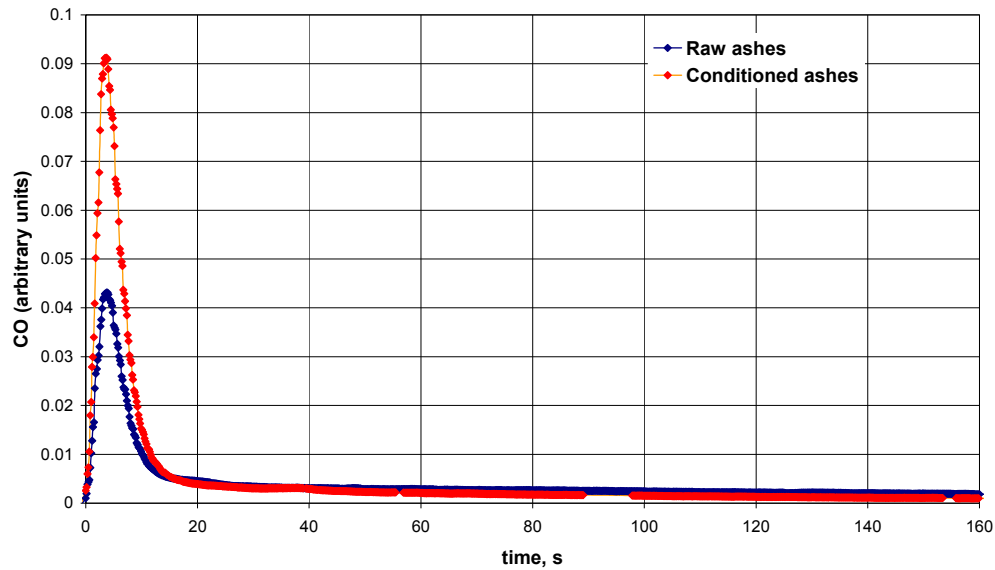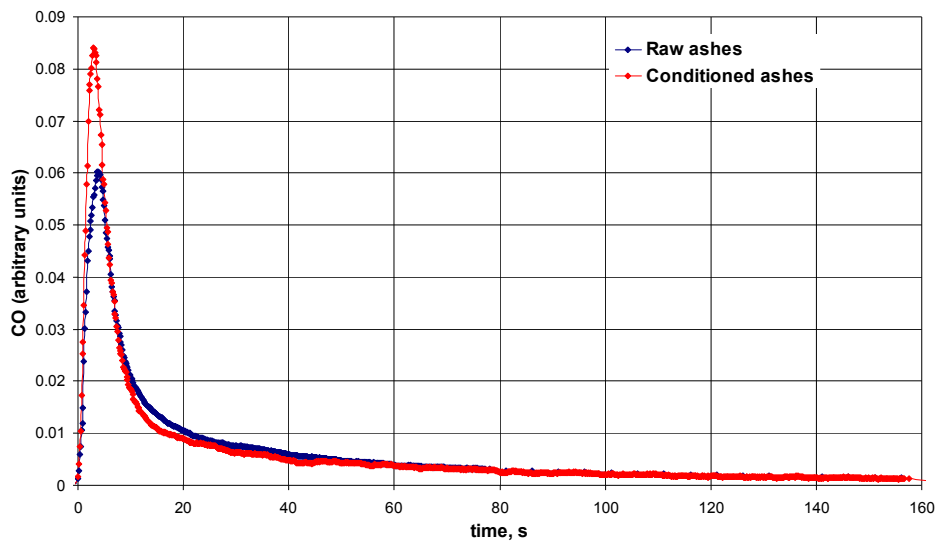
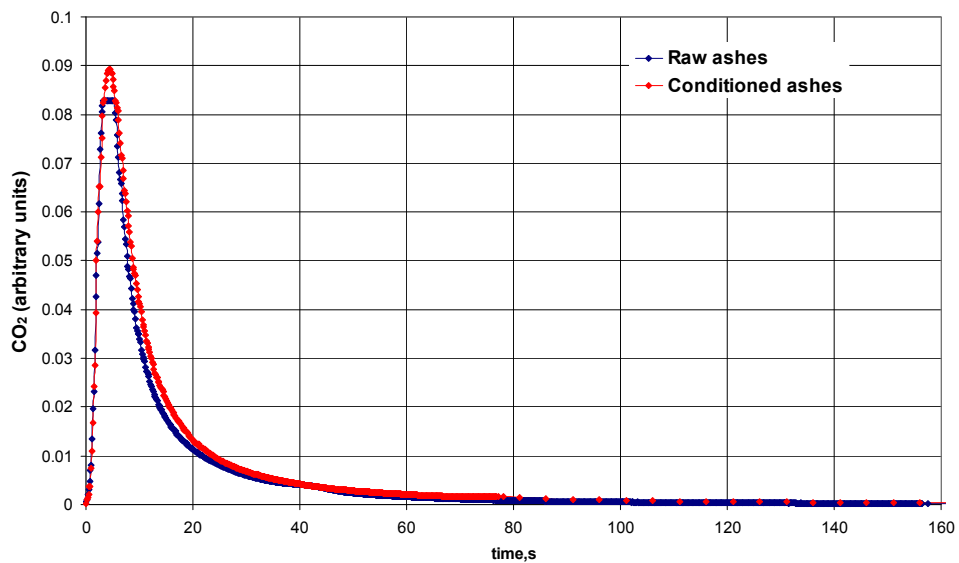**Figure 7A**. Profiles of CO released during combustion of raw and conditioned ashes at 800°C with 4% oxygen
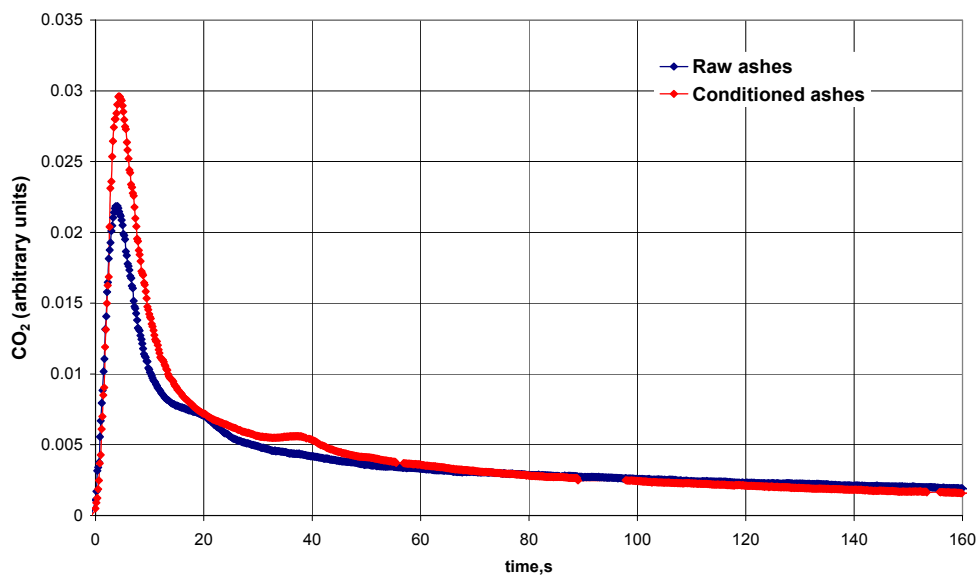
Figure 7B. Profiles of CO_2 released during combustion of raw and conditioned ashes at 800°C with 4% oxygen

Notably the peak of CO and CO_2 are sensibly higher for the pre-conditioned sample, confirming the positive effect of the pre-conditioning.

Figure 9, finally, reports the cumulative amount of CO and CO_2 released during TPD experiments on raw ashes and ashes conditioned in air at 400°C for 2hr. The much higher release of CO and CO_2 by the pre-conditioned ashes confirms that oxygen complexes formed during the pre-treatment can be desorbed as CO and CO_2 at high temperature.

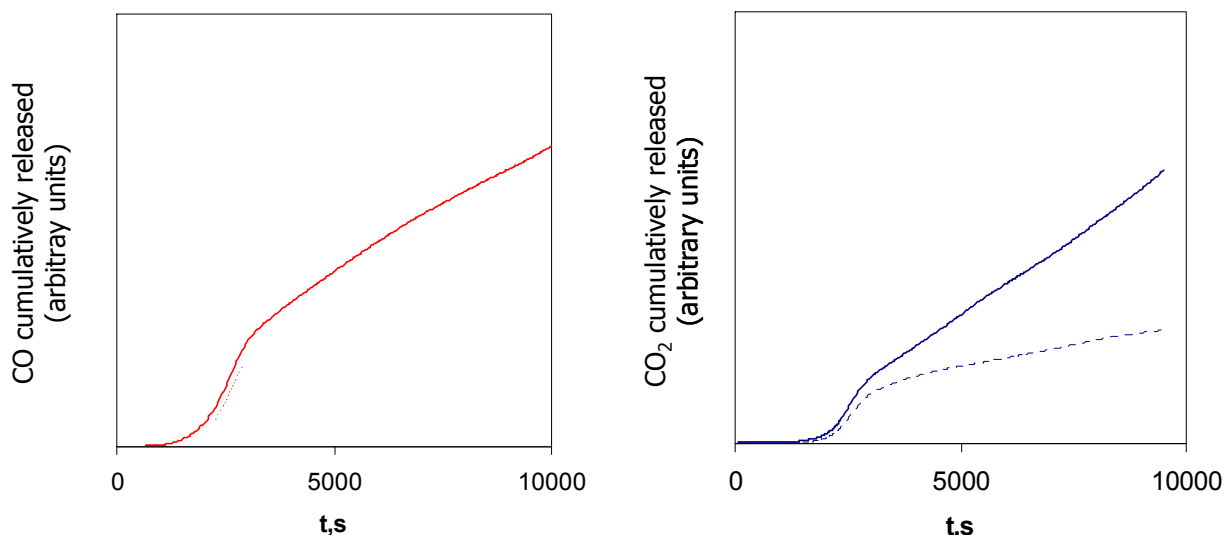**Figure 8A**. Profiles of CO released during combustion of raw and conditioned ashes at 1000°C with 4% oxygen.

Figure 8B. Profiles of CO_2 released during combustion of raw and conditioned ashes at 1000°C with 4% oxygen.

Discussion and conclusions

Experimental results show that pre-oxidation of ashes in air at temperatures between 200-400°C allows the build up of carbon surface oxides. The rate of build up progressively decreases with the amount of oxygen uptaken/time of treatment. At 400°C the build up reaches 0.07 moles of O_2 per moles of C in ash after 1hr, 0.1 after 2h and 0.2 after 15hr.

The results of TPD experiments on raw and conditioned samples suggest that conditioning promotes the formation of carbon-oxygen complexes, which are indeed released during the TPD stage. The results of combustion by means of TG and ALPR confirm that conditioning

Figure 9. Profiles of CO and CO_2 released during TPD of raw (dashed line) and conditioned ashes (solid line) in nitrogen at 10°C/min

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reduces the burn-out time. Results are encouraging as regards the possibility that mild pre-oxidation of ashes in air at moderate temperature can significantly improve their combustibility when they are recycled to a boiler, thus helping to control the level of unburnt carbon in ashes within acceptable levels. This concept led to the preliminary formulation of an integrated process which is the subject of a pending international patent application [14].

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