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Fly ashes reactivity in relation to coal combustion under flue gas recycling conditions

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Abstract

Samples of fly ashes generated from two different coals fired in a CO_2-rich atmosphere by recycling part of flue gas have been characterized for chemical composition and particle size distribution. They have also been tested for reactivity against lime and gypsum in hydratory mixtures of interest in the field of pre-formed building materials. It has been found that firing coal in unusual conditions (mainly as far as flame temperature and flue gas composition are concerned) does not alter the reactivity of fly ashes in the systems referred to above. The main factor that affects fly ash reactivity is particle size distribution, as for the ashes produced in ordinary air firing operations. © 1997 Elsevier Science B.V.

Keywords: Fly ash; Coal firing; Pre-formed building materials; Ettringite

1. Introduction

Many countries rely on coal supply for feeding power plants. However, among fossil fuels, coal is the one whose combustion generates the highest amount of carbon dioxide, and this is of the great environmental concern in relation to greenhouse effect. Recently, many attempts have been made to design reduced carbon dioxide emission or zero emission power plants [1,2]. Among the various proposed technologies alternative to air firing, coal combustion in a mixture of pure oxygen and recycled flue gases appears to be particularly promising for retrofitting existing utility boilers [3]. In this way, the heat transfer characteristics can be kept as close as possible to those for which the unit was originally designed. Furthermore, the absence of nitrogen raises the concentration of carbon dioxide in the flue gases and this makes its recovery easier. Therefore, carbon dioxide can be used for enhanced oil recovery, which seems to be the most practical and effective application of recovered carbon dioxide among the many proposed [4].

In these processes coal combustion conditions are markedly different from those that are encountered in a traditional air-fired boiler, especially as far as flame temperature and flue gas composition are concerned. These two factors are obviously correlated to each other and it is of a special concern the fact that the flame temperature can be even 400–500°C lower than in a traditional boiler. It is well known that the reactivity of fly ashes depends very strongly on their

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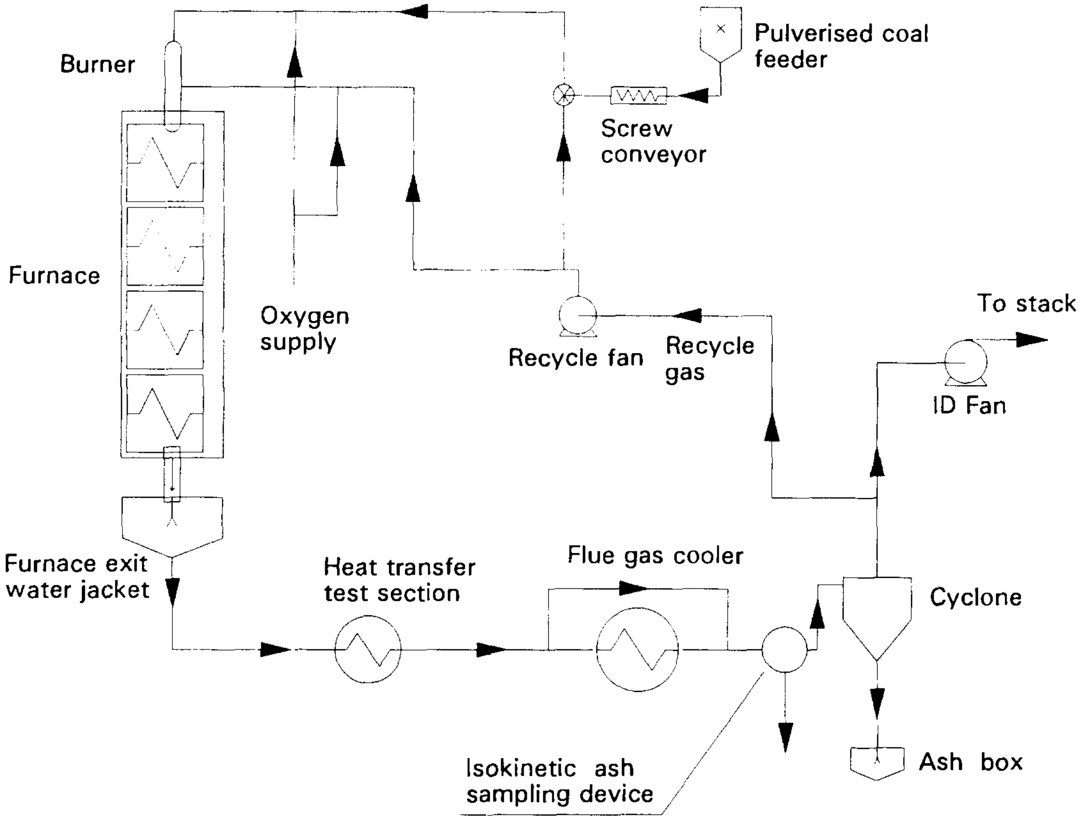

Fig. 1. Schematic of combustion test facility.

temperature–time history within the combustion chamber and along the flue gas path. Fly ashes owe their pozzolanic activity to the fact that they are partially melt in the burning process and then the melted fraction retains vitreous structure upon rapid cooling. Evidently, a 400–500°C flame temperature difference can have strong effect on fly ashes properties.

Within a joint research project on O_2-enriched coal combustion with partial flue gas recycling, the 160 kW experimental rig schematically shown in Fig. 1, was set up and operated at Mitsui Babcock Energy Limited, Renfrew. Two different types of coal were burned in the rig and fly ashes were sampled for characterization and testing. Specifically, this paper reports a study on the effect of coal burning conditions on the reactivity of fly ashes against $Ca(OH)_2$ and $CaSO_4{\cdot}2H_2O$. Differential thermal analysis was the main investigation tool.

2. Experimental

The combustions runs were carried out at Mitsui Babcock Energy Limited using an experimental combustion rig. Two different coals were used, Dawmill coal (from UK) and a polish export coal shipped from the port of Gdansk, whose proximate and ultimate analysis are reported in Table 1. Baseline air firing and recycling tests at various flue gas recycle ratios were carried out. For each operating condition, fly ash samples were taken both at the cyclone exit and at the isokinetic sampling device (Fig. 1). Some of them were characterised and tested for reactivity against lime and gypsum. They are labelled D1–D5 (from Dawmill coal) and G1–G6 (from Gdansk coal) and are listed in Table 2 together with the conditions under which were generated and collected.

The various samples of fly ashes were analysed for chemical composition according to ASTM C 311

Table 1
Proximate and ultimate analysis of Dawmill and Gdansk coals

		Dawmill	Gdansk
Proximate, wt%	Moisture	5.8	1.9
	Volatile matter	31.3	33.3
	Fixed carbon	48.4	58.6
	Ash	14.5	6.2
	Total	100.0	100.0
Ultimate, wt%	Moisture	5.80	1.9
	Carbon	64.92	75.14
	Hydrogen	4.28	4.49
	Sulphur	1.41	0.62
	Chlorine	0.25	0.27
	Nitrogen	1.16	1.40
	Oxygen	7.68	9.98
	Ash	14.50	6.20
	Total	100.00	100.00
Calorific value, kJ kg^{-1}		26,440	30,640

Standard Test Method. They were also analysed for particle size distribution and specific surface area by means of a Malvern Instruments Master Particle Sizer M6.01.

Hydratory mixtures made of each sample of fly ash, lime and gypsum in the weight ratio 60 : 40 : 20 were cured at 25°C and 100% R.H. with water to solid ratio equal to 0.6 (0.66 for sample D4). Hydration was stopped after 1, 3, 7, 14, 28 and 56 days by grinding each hydrated sample under acetone followed by washing with diethyl ether. Such samples were submitted to thermal analysis with a Netzsch STA 409 apparatus fitted with a DSC head. Non-evaporable, chemically combined water has determined by ignition at 1000°C for 1 h. Mixtures fly ash–lime–gypsum in weight ratio 60 : 20 : 20 were also tested in the case of ashes from Gdansk coal.

3. Results and discussion

3.1. Fly ashes characterization

Table 3 shows the chemical composition of the ash samples. It can be seen that the ashes from Gdansk coal are much poorer in silica than those from Dawmill coal, with the only exception of sample G2. Also, in the case of ashes from Dawmill coal, the most widely varying parameter is loss on ignition (LOI). On a LOI-free basis, the differences in composition among samples from D1 to D5 only appear to be statistic. Apart from sample G2, the ashes from Gdansk coal show a more uniform composition.

The results of the analysis for particle size distribution are reported in Table 4 and show the higher efficiency of the isokinetic sampling device in respect to the cyclone upstream the fly ash box. Furthermore, the efficiency of the latter device strongly increases with the flow rate and then the particle size distribution of the fly ash box samples is much coarser in the case of air firing (sample G2). As fly ash is a heterogeneous material, the loss of a considerable amount of finer

Table 2
Summary of ash samples and operating conditions

Sample	Sampling device	Recycle rate, %	Flue gas O_2 concentration, %	Flue gas CO_2 concentration, %	Adiabatic flame temperature, °C
D1	Cyclone	61.5–65.3	3.57–4.11	68.10–83.08	1588–1741
D2	Cyclone	69.6–71.5	6.50–6.71	68.15–68.45	1454–1730
D3	Cyclone	72.2–76.0	1.70–1.83	70.25–73.19	1469–1785
D4	Cyclone	75.3–80.8	3.58–3.87	77.14–80.35	1520–1627
D5	Cyclone	Air firing	2.76–2.84	14.58–14.79	1726–1764
G1	Isokinetic	Air firing	2.36–3.31	14.25–15.40	1838–1888
G2	Cyclone	Air firing	2.36–3.31	14.25–15.40	1838–1888
G3	Isokinetic	68.3–76.4	4.01–5.10	72.37–73.23	1621–1808
G4	Cyclone	68.3–76.4	4.01–5.10	72.37–73.23	1621–1808
G5	Isokinetic	79.2–82.4	3.68–4.98	70.43–73.94	1755–2021
G6	Cyclone	79.2–82.4	3.68–4.98	70.43–73.94	1755–2021

Table 3
Principal chemical components of fly ashes, wt%

	Sample										
	D1	D2	D3	D4	D5	G1	G2	G3	G4	G5	G6
LOI	2.48	2.74	3.20	18.12	9.74	7.24	2.20	4.79	4.92	6.29	5.05
SiO_2	46.58	45.63	44.76	38.54	45.45	26.57	45.08	27.16	27.07	25.96	25.21
Al_2O_3	22.93	21.76	21.24	18.77	19.67	21.66	22.64	19.67	21.92	21.06	20.84
Fe_2O	10.16	9.55	10.76	7.73	8.57	10.85	7.63	11.27	8.71	10.13	10.15
CaO	11.99	12.67	11.91	9.78	10.57	18.11	14.02	20.17	21.19	17.53	17.73
MgO	1.59	2.21	1.95	1.47	1.32	8.00	2.43	7.81	7.95	7.60	8.03
SO_3	1.61	2.14	1.50	1.50	0.88	1.24	3.10	1.90	2.85	3.43	3.32
MnO	0.20	0.18	0.21	0.17	0.11	0.22	0.18	0.22	0.22	0.21	0.21
K_2O	1.45	1.56	1.68	1.31	1.39	0.83	1.11	0.77	0.78	0.78	0.75
Na_2O	0.34	0.56	0.37	0.44	0.27	0.68	0.21	0.50	0.42	0.62	0.88
Total	99.33	99.00	97.40	97.83	97.97	95.40	98.59	94.27	96.03	93.61	92.17

Table 4
Particle size distribution of fly ashes, Vol %

Size range, μmm	Sample										
	D1	D2	D3	D4	D5	G1	G2	G3	G4	G5	G6
188.0–87.2	4.2	2.9	1.3	1.5	4.7	1.4	5.1	2.4	0.8	3.2	1.1
87.2–53.5	13.0	6.3	12.3	5.5	10.3	5.3	14.0	6.7	3.3	10.1	8.5
53.5–37.6	15.4	6.8	12.7	7.3	9.9	6.9	14.8	8.2	4.7	10.4	8.4
37.6–28.1	14.7	7.7	12.6	8.7	10.4	8.0	13.5	8.7	5.6	9.4	5.8
28.1–21.5	15.2	10.7	13.5	10.9	11.9	9.0	13.4	9.2	6.9	9.1	6.4
21.5–16.7	13.0	12.3	12.9	12.7	12.7	9.1	12.0	9.0	7.9	8.6	10.4
16.7–13.0	8.2	11.3	10.3	12.3	12.2	8.0	8.8	8.0	8.4	7.3	11.7
13.0–10.1	5.5	10.9	8.2	10.6	10.3	7.2	6.4	7.3	9.1	6.4	10.1
10.1–7.9	4.1	11.0	7.2	9.2	8.0	7.3	4.7	7.7	11.0	6.4	10.1
7.9–6.2	2.5	9.2	5.6	7.7	5.3	8.5	2.9	8.8	13.7	7.0	11.3
6.2–4.8	0.9	2.7	1.6	4.3	1.8	6.5	1.1	6.8	10.7	5.3	5.6
4.8–3.8	0.6	1.4	0.4	2.3	0.6	4.7	0.6	4.5	6.2	3.5	2.8
3.8–3.0	0.6	2.2	0.2	1.8	0.4	4.2	0.6	3.4	3.9	2.9	2.8
3.0–2.4	0.5	1.6	0.2	1.5	0.4	3.8	0.5	2.8	2.7	2.7	2.0
2.4–1.9	0.7	1.3	0.4	1.7	0.5	4.3	0.7	2.9	2.5	3.2	1.6
<1.9	0.9	1.7	0.6	2.0	0.6	5.8	0.9	3.6	2.6	4.5	1.5
Spec. surf. area, $m^2 g^{-1}$	0.37	0.61	0.39	0.64	0.41	1.04	0.37	0.84	0.89	0.84	0.67

particles made the composition of this sample much richer in silica than the others from the same coal.

3.2. Hydration in mixtures containing $Ca(OH)_2$ and $CaSO_4{\cdot}2H_2O$

Fly ashes from D1 to D5 and from G1 to G6 were tested for reactivity against lime and gypsum. The scope of these experiments was to investigate the effect of the operating conditions on the reactivity of fly ashes.

Reactive fly ashes may be effectively employed in mixtures containing lime and gypsum for the production of pre-formed building materials [5–9]. It was proved that the kinetics of hydration of these systems is such that hydrated calcium silicate (CSH) and trisulphoaluminate hydrate (ettringite) form starting from the oxides present in the mixture (CaO, SiO_2, Al_2O_3 and SO_3) [10,11].

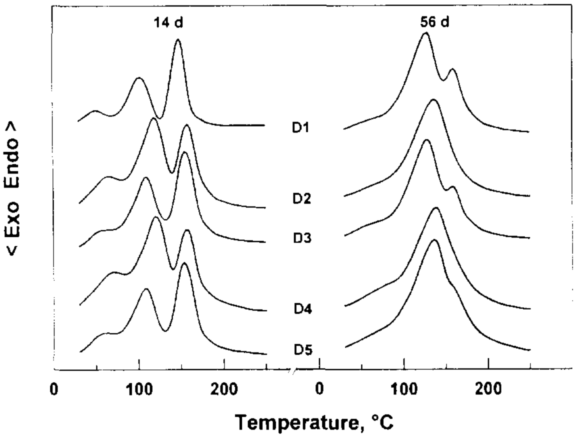

Fig. 2. Results of thermal analysis for samples of systems D1–D5 aged 14 and 56 days.

The results of thermal analysis carried out on some of the cured samples of the systems of composition fly ash : lime : gypsum=60 : 40 : 20 are reported in Figs. 2 and 3 as DSC traces in the 30–250°C range. They confirm what stated above that the reactants produce CSH and ettringite. The endotherms relative to these products and unreacted gypsum are detected at 60±10°C, 115±25°C and 146±14°C, respectively.

Fig. 2 shows the thermograms of samples of mixes containing ashes D1–D5 aged 14 and 56 days. The comparison of the intensities of the endotherms relative to the products on one side and the intensity of the endotherm relative to unreacted gypsum on the other allows to assess the following reactivity scale: D4 > D2 > D5 > D3 > D1. As expected, this result is strongly influenced by the particle size distribution, which is the main factor that affects fly ash reactivity. The endotherm relative to CSH is of lower intensity after 56 days ageing than after 14 days ageing. This apparently anomalous result is due to both partial overlapping with the ettringite endotherm and a reduction of the content of hydration water in CSH with increasing ageing [11]. It is very important to point out that the operation in unusual recycling conditions (mainly as far as gas composition and temperature are concerned) does not negatively affect the reactivity of fly ash in systems containing lime and gypsum.

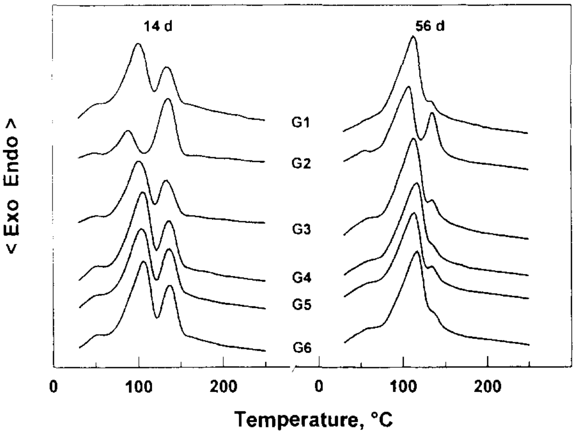

Fig. 3. Results of thermal analysis for samples of systems G1–G6 aged 14 and 56 days.

Similar mixes were hydrated containing ashes G1–G6. The thermograms of these mixes relative to 14 and 56 days ageing are shown in Fig. 3. A comparison of the results of Fig. 3 with those of Fig. 2 at 14 days ageing clearly indicates that the ashes from Gdansk coal are more reactive than those from Dawmill coal. The lower reactivity of sample G2 in respect to samples G1 and G3–G6, can be ascribed to the particle size distribution. However, the reactivity of ashes G1 and G3–G6 is not strongly influenced by the particle size distribution, proving that increasing the fineness beyond a certain limit does not make the reactivity increase any longer. At 56 days ageing the conversion of gypsum into ettringite is almost complete for any of the samples G1 and G3–G6. Due to the lower reactivity, sample G2 shows the presence of significant quantity of unreacted gypsum.

Due to the lower silica content of fly ashes from Gdansk coal, it was judged that the composition fly ash : lime : gypsum=60 : 40 : 20 could not be optimum with regard to lime consumption. Other mixes, labelled from G1′ to G6′, were prepared and cured as before. Their composition is fly ash : lime : gypsum=60 : 20 : 20 and the results relative to the samples aged 14 and 56 days are reported in Fig. 4. It can be seen that the systems take advantage from this composition lower in lime, as in some cases the formation of ettringite at 14 days is enhanced. As for the previous composition, the conversion of gypsum into ettringite is almost complete after 56 days ageing, with the only exception of mix containing ash G2. The formation of CSH seems to be unaffected by the lime content in the composition range investigated. Even in the case of Gdansk coal, the operation under

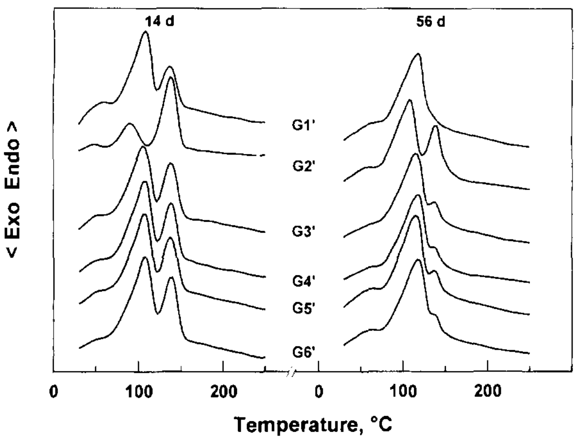

Fig. 4. Results of thermal analysis for samples of systems G1′-G6′ aged 14 and 56 days.

recycling conditions does not negatively influence the reactivity of fly ashes.

Quantitative data are reported in Figs. 5–8. Fig. 5 shows the amount of chemically combined, non-evaporable water as a function of ageing time for systems D1–D5. It can be seen that these quantitative data confirm the reactivity scale stated above from the examination of the results of thermal analysis.

Fig. 6 is analogous to Fig. 5 except for systems G1–G6. The observation that can be made in this case are as follows. First of all, it is confirmed that sample G2 is much less reactive than the others. Furthermore, the overall reactivity is almost the same for samples G1 and G3–G6 up to 14 days; then some differences arise that cannot be fully understood from the amounts of unreacted gypsum observed in Fig. 3. To this regard, it is to be pointed out that, at later ages, the formation of CSH influences the hydration kinetics in a way which is hardly characterized by thermal analysis data. In other words, it is not possible, neither from the quantitative data of Fig. 3, nor from thermal analysis, to distinguish to what extent chemically combined water is bound in CSH and in ettringite. Finally, it is

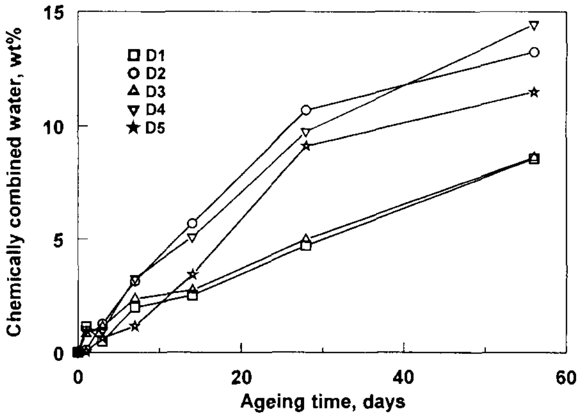

Fig. 5. Chemically combined water for systems of composition fly ash : lime : gypsum=60 : 40 : 20 containing ashes from Dawmill coal fired in different conditions.

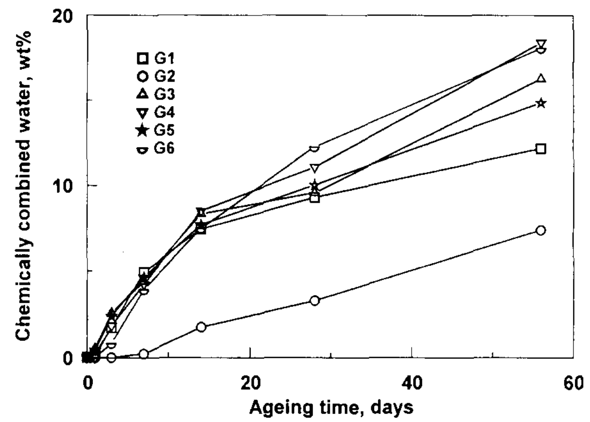

Fig. 6. Chemically combined water for systems of composition fly ash : lime : gypsum=60 : 40 : 20 containing ashes from Gdansk coal fired in different conditions.

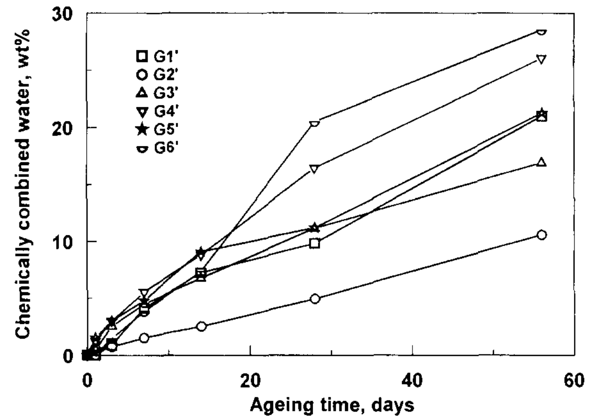

Fig. 7. Chemically combined water for systems of composition fly ash : lime : gypsum=60 : 20 : 20 containing ashes from Gdansk coal fired in different conditions.

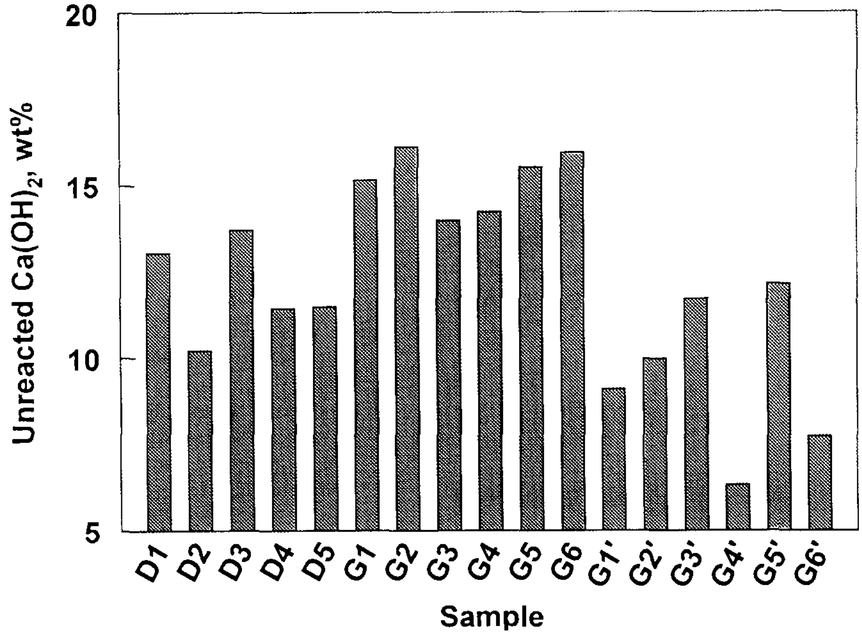

Fig. 8. Unreacted lime at 56 days ageing for all the systems tested.

also confirmed that the ashes from Gdansk coal are more reactive than those from Dawmill coal (except sample G2) as the values of chemically combined water found in the former case are, on average, well above those found in the latter.

The quantitative data of chemically combined water for the systems G1′–G6′ containing the ashes from Gdansk coal and poorer in lime are reported in Fig. 7. In this case it is seen that the amount of chemically combined water is higher than in the case of systems G1–G6 and also that the differences in reactivity among the systems G1′–G6′ are enhanced by the lower availability of lime.

Finally, Fig. 8 shows the amount of unreacted lime found in all the samples aged 56 days by quantitative thermogravimetry. Despite the higher reactivity, these values are, on average, the highest for the systems G1–G6 due to the lower silica content. Also, it can be seen that the ashes from Gdansk coal take advantage from the composition tested lower in lime, as the conversion of such a reactant is significantly higher in the systems G1′–G6′ than in the systems G1–G6.

The quantitative data of Figs. 7 and 8 confirm that the composition lower in lime of systems G1′–G6′ is better formulated in terms of overall water uptake and lime consumption.

4. Conclusions

The ashes generated from two different coals in unusual firing conditions have proved to retain good reactivity against lime and gypsum. Under recycling conditions the flue gas composition and flame temperature can be very different from those that can be encountered in a traditional air fired boiled. In spite of this, no influence on fly ash reactivity has been found. The results have shown that the most significant factors that affect fly ash reactivity are fly ash origin and particle size distribution.

This study is of importance to assess the feasibility of firing coal in a CO_2-rich atmosphere, in as much as reuse of fly ashes in the fields of blended cements and pre-formed building elements relies on their reactivity in processes based on systems similar to those studied herein. High-reactivity fly ashes can be sold as secondary raw materials, while low-reactivity ones must be disposed of.

Acknowledgements

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