DESULPHURISED RESIDUES EFFECT ON THE POROSITY AND PORE SIZE DISTRIBUTION OF CEMENT BASED PASTES DURING THE EARLY AGES OF CURING

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Abstract

This research is a part of a research concerned with the use of flue gas desulphurisation waste residues in construction applications. In this paper, some results on pore size distribution of cement paste containing desulphurised waste during the early stages of hydration are reported. The desulphurised waste used was a combination of 85% fly ash and 15% gypsum (by weight) and was referred to as simulated desulphurised waste (SDW). The SDW was chosen due to the variability in composition of actual desulphurised waste. The cement was replaced with 0%, 20% and 40% SDW (by weight). The water to powder ratio was 0.5. The binder consists of cement or cement and SDW. Paste specimens were cured only for 24 hours (i.e. 1 day). The porosity and pore size distribution of cement pastes with and without SDW are reported. Increasing the amount of SDW leads to an increase in the pore volume of the paste and an increase in the size of pore.

Keywords: Desulphurised waste, FGD waste, porosity, pore size distribution

1 INTRODUCTION

Burning fossil fuel such as coal causes major environmental problems and the coal power industry contributing a big part. Upon burning, harmful gases such as SOx, NOx and CO_2 are emitted into the atmosphere. It is anticipated that many countries in the world including many Eastern and Western European countries, Turkey, China and India as well as many other countries will continue to use coal in the production of power for the foreseeable future. However, there has been increasing pressure on world's governments to consider reducing the emission of harmful gases. These include SOx and NOx. Many power generation industries have installed desulphurisation systems which introduce alkali powder such as limestone and this reacts with the SO_2 to produce waste residues [Mangat et al. 2006; Khatib et al. 2007; Khatib el al. 2008; Khatib et al 2013a; Khatib et al 2013b; Khatib 2014; Khatib et al 2014].

There are different types of desulphurisation process and these include; the wet process, the dry and semi dry processes. The main difference is the type of wastes produced. Using the wet process, pure gypsum is produced and this waste is normally utilised in many applications such as the plaster board industry. For the other processes, a mixture of fly ash and calcium sulphate or sulphite is produced. Assessing the reactive properties of these wastes is important so proper utilisation can be identified. Using these wastes in construction applications may be a possibility and there investigating the behaviour of construction materials containing these wastes is important. Of such properties is the porosity and pore size distribution of the materials as this will affect the performance when in service.

The porosity and pore size distribution affect the strength properties and durability properties of construction materials such as concrete [Older et al. 1985; Fukya et al. 1991; Mangat et al. 1992; Calleja 1986; Khatib and Mangat 2002]. Many attempts have been made to show that there exists a correlation between porosity and pore structure and other properties including paste, mortar and concrete [Kolias 1994; Jiang et al. 1999]. The main relationships tend to indicate that strength is related to total porosity, whereas, permeability tends to be influenced more by pore size distribution. A low permeability material would restrict the flow of fluid and the ingress of harmful ions. The use of traditional mineral admixtures in concrete applications such as fly ash, slag and silica fume is well documented and the effect of such admixtures on porosity and pore structure of blended cement paste [Singh et al. 1996; Wee et al. 1995; Cook et al. 1999; Wild et al. 1995]. There is not much information on the use of desulphurised wastes in construction or concrete applications and if these materials are to be used their influence on basic engineering properties need to be investigated. This paper report limited data on porosity and pore size distribution of cement paste containing simulated desulphurised waste (SDW) during the early ages of curing. SDW was used because the chemical composition variability of actual desulphurised waste. The SDW was prepared by mixing 85% fly ash with 15% gypsum.

2 EXPERIMENTAL

Portland cement (C), fly ash (FA), gypsum (G) and water were used to prepare the pastes. The simulated desulphurised waste (SDW) was a mixture of 85% fly ash and 15% gypsum. Table 1 gives the oxide compositions of cement, fly ash and gypsum. Three pastes were used to conduct this investigation.

Tab. 1: Chemical composition of binder

	Major oxide (weight)							
Material	CaO	Fe_2O_3	Al_2O_3	SiO_2	MgO	K_20	Na_2O	SO_2
Cement (C)	64.80	2.80	4.49	21.10	1.03	0.65	0.15	3.12
Fly ash (FA)	6.74	4.62	31.74	48.91	1.51	1.20	0.60	1.75
Gypsum (G)	35.55	0.07	0.21	0.38	0.02	0.02	0.01	49.20

The control paste P1 contains 100% C and no simulated desuplhurised waste. In pastes P2 and P3, the cement was replaced with 20% and 40% SDW (by weight) respectively. Table 2 shows the powder proportion of the pastes. The water/powder ratio was kept constant at 0.5. The powder materials consist of cement and SDW.

Tab. 2: Mix composition of pastes

		% by weight of binder	
Mix	**MIX ID**	**Cement**	**SWD**
P1	REF (100C)	100	0
P2	80C20SDW	80	20
P3	60C40SDW	60	40

Paste specimens were cast in steel mould of dimensions 50mmx50mmx50mm. After casting, specimens were left in a mist curing room at a temperature of 20ºC±1ºC and 95%±5% relative humidity for 24 hours. After that demoulding took place and specimens were tested for compressive strength. Samples were then taken from the middle of crushed cube. The samples were dried in an oven at 70ºC to remove moisture until a constant weight was achieved. Mercury intrusion porosimetry technique used to determine total porosity and pore size distribution of the paste [Khatib et al. 1996; Khatib et al. 2003; Khatib et al 2013a; Khatib 2014].

3 RESULTS AND DISCUSSION

The effect of desulphurised waste (SDW) on the total pore volume of pastes cured for 1 day is presented in Figure 1. The results indicate that the incorporation of SDW increases the total pore volume (i.e. porosity) of pastes. The intruded pore volumes ranged from 278 mm^3/g to 343 mm^3/g for pastes containing 0% to 40% SDW. The increase in pore volume for pastes containing 20% and 40% SDW is 8% and 23% respectively. The increase in pore volume at this early age of curing is much lower than those reported at longer curing times as reported in another investigation. At the early stages the fly ash particles did have enough period to hydrate. Normally the pozzolanic reaction of the fly ash particles start to be noticeable after 28 days of curing.

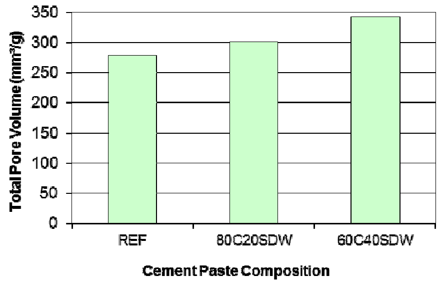

Fig. 1 - Influence of SDW content on the total pore volume (TPV) of pastes at 1 day of curing.

The threshold diameter for pastess containing 0%, 20% and 40% SDW content (Pastes P1-P3) cured for 1 day is shown in Figure 2. The threshold diameter is the diameter on the pore size distribution curve before the pore volume rises sharply. Further information on the determination of the threshold diameter is reported in a previous investigation12. A larger threshold diameter tends to indicate coarser pore sizes. The reference paste exhibited the smallest threshold diameter of about 1.7 μm whereas the threshold for pastes containing 20 and 40% SDW were about 2 μm. This may indicate that there is a coarser pore size when SDW is included in the pastes during this early stages of curing.

Figure 3 shows the influence of SDW content in cement paste on the percentage of small pores (SP); pores whose diameter is below 0.1 μm cured for 1 day. The percentage of small pores are about 29%, 24% and 19% for pastes containing 0%, 20% and 60% SDW respectively. This suggests that as the percentage of SDW in the paste increases, the percentage of small pores decreases indicating that there is tendency to have pores with larger pore sizes in the presence of SDW at 1 day of curing. The fly ash particles in cement paste requires longer period of curing for the pozzolanic reaction to take place. Normally, after 28 days, the influence of fly ash can be observed. In this present work, the pastes were test at 1 day of curing and longer period of curing is required to realise the potential of pozzolanic activity of the fly ash if calcium hydroxide is present.

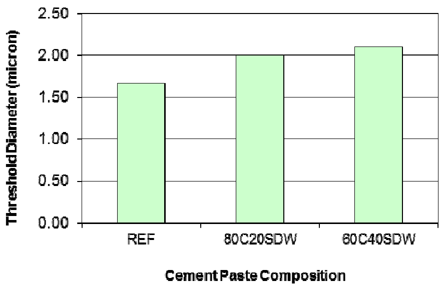

Fig. 2 - Influence of SDW content on the threshold diameter (TD) of pastes at one day of curing.

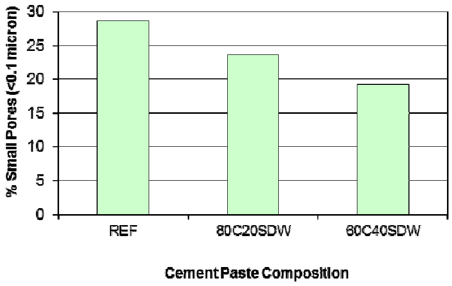

Fig. 3 - Influence of SDW content on the percentage of small pores (<0.1μm) of pastes at 1 day of curing.

4 CONCLUSIONS

Replacing cement with 20 and 40% simulated desulphurised waste (SDW) tends to cause increase the total intruded pore volume of the cement paste at 1 day of curing. The threshold diameter and the percentage of large pores increase as the SDW in the paste increases, thus indicating coarser pore structure during this early period of curing. This does not mean that desulphurised waste should not be used in construction application. Long-term curing results that are reported in previous work suggest that pore size becomes much smaller compared with the data presented in this paper.

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