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Effect of desulphurised waste on long-term porosity and pore structure of blended cement pastes

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ABSTRACT

This paper presents some results on the porosity and pore size distribution of cement paste containing simulated desulphurised waste (SDW) cured for 90 d. The SDW was chosen for the investigation due to the variability in chemical composition of real desulphurised waste as explained in previous papers. The SDW is a combination of 85% fly ash and 15% gypsum. The cement in the pastes was replaced with 0, 20 and 40% SDW. The water to binder ratio was 0.5. The binder consists of cement and SDW (by weight). After 90 d of curing, the porosity and pore size distribution tests were conducted on the pastes. Increasing the amount of SDW leads to an increase in the pore volume of the paste. There is no clear trend on the effect of SDW on the size of the pores.

1. Introduction

The porosity and pore size distribution of cement based materials have a major influence on their mechanical and durability properties. Mechanical and durability properties include strength, ingress of harmful substances and the attack on the actual material. This ingress is related to the volume of pores present as well as the size and distribution of such pores. The influence of porosity and pore size distribution on physical and mechanical [1,2] as well as durability properties [3,4] is well documented. Many attempts have been made to correlate the porosity and pore structure of cement based materials with their mechanical and durability characteristics [5,6]. The main relationships tend to indicate that strength is related to total porosity, whereas, durability tends to be influenced more by pore size distribution as it will affect the diffusion of ions and moisture [5,6].

The coal power industry is a major contributor to pollution which includes the emission of SO_x, NO_x and CO_2. The use of coal in developing countries such as China, India and Indonesia as well as developed countries such as Germany is not going to reduce in the foreseeable future. In fact the global consumption of coal has been continuously increasing. Over the past decades, there has been increasing pressure on governments in the world to reduce emissions caused by harmful gases. One such control is the reduction of SO_x from power stations. This can be achieved by installing desulphurisation systems to new and existing installations. These systems generally introduce alkaline sorbents such as limestone to the SO_x gases, which react and form solid residues. These residues are referred to as desulphurised waste and they can vary in composition from calcium sulphate to a combination of fly ash and calcium sulphite hemihydrate or calcium sulphate dehydrate [7–9]. This waste is normally sent to landfill. Attempts to use this waste in construction will enable its large scale utilisation. This paper will contribute to this effort.

There are many different desulphurisation processes available at present that produce a variety of wastes that vary in quality and quantity [10,11]. The type of waste is dependent on many factors including the process and the raw materials used. The majority of processes fit into three main categories, wet, semi dry and dry processes. However, other processes are available which are based on, or a combination of the three methods mentioned, such as circulating fluidised bed, gas suspension and absorption and fluidised bed combustion.

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The wet process is at present the most environmentally friendly in terms of purity and quantity of materials produced for exploitation. The wet processes uses an alkaline sorbent such as limestone, slaked lime or a mixture of slaked lime and fly ash, which is mixed into slurry and sprayed into the flue gasses. The most common method uses limestone as a sorbent, which reacts with the SO_2 gasses to form an insoluble calcium compound, which is then treated to produce some form of calcium sulphate ($CaSO_4 \cdot 2H_2O$-Gypsum) [10]. The gypsum purity of the wastes from wet processes normally exceeds 96%. This makes the wastes produced by the wet process suitable for use in the construction industry in areas such as the production of wallboard and cement. Wet processes are expensive to implement, operate and maintain, however, work has been carried out to improve the cost efficiency of such processes [12,13]. Even though installations are becoming more cost efficient, historically many smaller countries do not have the financial resources to install such processes, so more economically viable options are utilised, i.e., dry and semi-dry processes [10].

The semi-dry process (spray dry scrubbers) is the second most common desulphurisation method. An alkaline solution or slurry is introduced to the flue gasses in a reaction vessel. Once the reaction occurs the solution is evaporated, salts are precipitated, and the remaining solids are dried. Although the wastes are dried, the moisture content can still be as high as 2%, which is why the wastes are commonly referred to as semi-dry wastes. The general difference between the semi dry and wet process is that alkaline sorbent (slaked lime) and fly ash are entrained into the flue gasses. This makes the final wastes a mixture of calcium sulphite hemihydrate, calcium sulphate dihydrate and fly ash. In some installations the fly ash is sometimes separated from the calcium sulphate/sulphite wastes, therefore, the composition of wastes from semi dry processes can vary significantly [10]. Given that semi dry wastes are a mixture of calcium sulphate, sulphite and fly ash they have not been used into areas where wastes produced by the wet process are commonly used.

The least common processes is the dry method (sorbent injection), which introduces the alkaline sorbent in dry form to either/or a combination of, the fuel source, the furnace or the ductwork. Again, as with the semi-dry method the wastes produced is a combination of reacted and non-reacted sorbent along with fly ash. These types of systems are more likely to be fitted to older power stations, and their future use is limited due to their poor SO_2 removal (50–70%) and the type and quantity of wastes produced.

Recent studies have identified that the varied chemical composition of wastes yielded different types of reactions including; calcium-sulphate reactions, pozzolanic reactions, and gypsum-fly ash-lime reactions as well as more typical reactions occurring in plain cements [14]. Given the varied composition of the materials, it is important to identify test methods that best evaluate different reactions expected, which should allow desulphurised waste to be compared with more common cement replacement materials, such as fly ash, slag and silica-fume.

Selecting a suitable method to evaluate the reactivity of different materials is difficult due to the diverse nature of the different reactions that occur, however, many techniques have been developed over the years that evaluate chemical, physical and mechanical aspects. Investigations carried out during recent studies have focused on evaluating desulphurised wasters based on chemical [14,15] and physical method [16]. The chemical methods evaluate the presence of oxides and ions associated with pozzolanic activity, such as SiO_2, Al_2O_3, Si(IV), and Al(III), whereas the physical method involved measuring the compressive strength of mortar samples after the 28- and 90-d curing.

The degree of reactivity exhibited by materials tested using different chemical methods can give conflicting results because not all desulphurised wastes exhibit pozzolanic properties. Some desulphurised wastes exhibit cementitious reactions that are not identifiable by selected chemical methods. The tests also give no indication to how the materials will perform in cement-based materials, and thus may not be ideal for evaluating desulphurised wastes.

The activity index test defined in BS EN 450 [16], which is commonly used to determine the pozzolanicity of fly ash, has been used to measure the reactivity of desulphurised wastes [14]. The test is a measure of compressive strength, which is indirectly affected by the rate and degree of hydration and the reactivity of the materials used. The measurement of strength appears to provide a more useful method to distinguish the reactive properties of different desulphurised waste materials and allows comparisons to be made with other more common cement replacement materials such as fly ash, ground granulated blastfurnace slag and silica fume.

The evaluation of desulphurised wastes, based on activity index testing, during recent studies has led to classification of desulphurised wastes as follows [14]:

1. Non siliceous and deleteriously reactive (SO_3 content 35–50%).
2. Non siliceous and non-reactive (SO_3 content 20–30%).
3. Siliceous and non-pozzolanic active (SO_3 content 10–15%).
4. Siliceous and pozzolanic active (SO_3 content 10% or less).

These broad classifications are based on the known composition of each material and results of pozzolanicity tests carried out [14]. Only category 4 has truly beneficial influences on strength development, with some of the waste improving strength (relative strength − 110%) compared to a reference mixes of 100% cement.

There is a substantial volume of information available on the influence of mineral admixtures, such as fly ash, slag, silica fume and metakaolin, on porosity and pore structure of blended cement paste [17–22]. This paper reports some results on porosity and pore size distribution of cement paste incorporating simulated desulphurised waste (SDW) cured for 90 d. The SDW was prepared by mixing 85% fly ash and 15% gypsum and was used as cement replacement. This simulation was chosen to represent a typical desulphurised waste produced by a coal fired power station, while preventing the wide variability of desulphurised waste which would cause quality control problems in the research. Previous work was shown that simulation yields similar results of actual waste with the same chemical composition [7].

This work is part of a wide range investigation on the possible utilization of flue gas desulphurisation residues in construction applications instead of their disposal. Desulphurisation waste residues vary widely in terms of chemical compositions. It was shown that it is possible to simulate the real flue gas desulphurised products with synthetic waste which have similar SO_3 content [7,8]. Therefore, the novelty of this work lies in the simulation of this waste in order to assess their effects on the properties of cement based materials. The aim of this experimental investigation is to assess the porosity and pore size distribution of cement pastes containing SDW and cured for a relatively long period.

2. Experiment

Cement paste mixes consist of CEM-1 Portland cement (C), fly ash (FA), gypsum (G) and water. The oxide contents for C, FA and G are presented in Table 1. Mix P1 represents the reference paste containing 100% C. Pastes P2 to P3 contain different SDWs. The SDW is a blend of 85% fly ash and 15% gypsum and was used in this