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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

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 ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ -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 SO₂ removal (50 to 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 wastes 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 to 50%).
2. Non siliceous and non-reactive (SO_3 content 20 to 30%).
3. Siliceous and non-pozzolanic active (SO_3 content 10 to 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 work to provide high quality control. The cement was replaced with 0, 20 and 40% SDW. Table 2 shows the binder proportion of the mixes. The water/binder was kept constant at 0.5. The binder consists of cement and SDW.

The paste samples consisted of cubes of 50 mm size. This size is considered adequate for pastes which would provide a representative sample of a mix for mercury intrusion porosimetry (MIP) testing [23-25]. All samples were placed in a mist curing room at 20 ± 1 °C and $95 \pm 5\%$ relative humidity for 24 h after mixing. After that, the cubes were demoulded and placed in water at 20 °C for further 89-d curing (i.e., 90-d total curing). At 90-d, the cubes were tested for compressive strength and samples were taken from the middle of each crushed cube. A suitable sample size used for the pore size distribution analysis was between 0.9 and 1.2 g. The samples were dried in an oven at 70 °C to remove moisture. This usually took approximately 48 h. After drying, the samples were placed in an airtight bottle under silica gel until testing. MIP test was then used to determine total

porosity and pore size distribution.

The technique of using mercury intrusion is based on the mercury's ability to act as a non-wetting liquid. This allows the mercury to penetrate the pores of any given sample under pressure and not be absorbed by the solid pores because of surface tension. The pressure required to carry out the analysis depends on the pore sizes present within the sample. Assuming the pores of a material are cylindrical, the relationship between pore size and pressure can be expressed as in Eq. 1 below, more commonly known as the Washburn equation.

$$d = \frac{-4\gamma \cos \theta}{p} \quad (1)$$

where: p = absolute applied pressure; d = pore diameter; γ = mercury surface tension; θ = contact angle.

The derivation of the Eq. 1 is based on the fact that all pores are cylindrical, no deformation occurs, the mercury surface tension and contact angle remain constant and that intrusion pressure is in equilibrium. In the analysis the capillaries are assumed cylindrical, and having a circular cross section, therefore, the surface tension of the liquid is exerted in the contact area beyond a length equivalent to the pore circumference.

The contact angle depends on the nature of the sample, therefore, only an average value is used. The contact angle usually ranges from 125 to 152°. Normally an average value of 141.3° is used. The surface tension varies and is a function of the temperature. A range of 0.482 (25 °C) to 0.472 N m⁻¹ (50°) is known, however, a value of 0.48 N m⁻¹ is commonly used. By using the values 130° for the contact angle and 0.48 N m⁻¹ for surface tension the relationship can be simplified as follows:

$$d = \frac{1235}{p} \quad (2)$$

where: d = pore diameter in μm and p is the absolute applied pressure (kPa). Further information on the testing technique is given in previous investigations [24,25]. The effect of this drying technique on the loss of moisture from ettringite and the possible damage to the pore structure due to the MIP technique were not investigated.

3. Results and discussion

Figure 1 shows the total pore volume of paste containing 0, 20 and 40% SDW after curing for 90 d. The total pore volume of SDW blended paste is higher than that of the reference paste. The higher the SDW content the higher the volume. The increase is approximately 20 and 50% for paste containing 20 and 40% SDW respectively.

Figure 2 plots the cumulative pore volume (CPV) and the incremental pore volume (IPV) for pastes containing a) 0%, b) 20% and c) 40% SDW (P1-P3) respectively at 90-d of curing. The shape of the pore size curve for all pastes is somewhat similar. At 20% SDW (P2), there are higher amounts of large pores compared to pastes P1 and P3.

In order to gain a better idea about the size distribution of pores, the threshold diameter and percentage of small pores are plotted in Figs. 3a and 3b respectively for pastes containing 0, 20 and 40% SDW. The threshold diameter is obtained from the pore size distribution curve at the point before the pore volume rises sharply. Further information on the determination of the threshold diameter was reported elsewhere [24,25]. The reference paste (P1) and the paste containing 40% SDW (P3) exhibit a similar threshold diameter of 0.133 and 0.135 μm respectively. However, the threshold diameter is slightly increased to 0.158 μm at 20% SDW (P2). An increase in the threshold diameter indicates a coarser pore structure. This is further shown in Fig. 3b where the percentage of

small pores for the 20% SDW paste (P2) is about 66% compared with 71% for the reference paste, P1, and 84% for the 40% SDW paste. The 40% SDW paste showed a much greater percentage of small pores than pastes P1 and P2. It is worth noting that paste P2 exhibited slightly larger threshold diameter and lower proportion of small pores compared with pastes P1 and P2. The trend in the threshold diameter and the amount of small pores (Fig. 3) is not the same shown for the total pore volume (Fig. 1) where the change in pore volume increases systematically with the increase in the amount of SO_3 .

Manmohan and Mehta [26] reported that partial replacement of cement with fly ash increased porosity and increased pore refinement at 28-d, relative to pure cement paste. This was attributed to the pozzolanic reaction which occurs between the calcium hydroxide and the fly ash particles, leading to further production of C-S-H and C-A-H. These products fill the open capillary pores, resulting in an improved pore structure [27,28]. However, results on pore size distribution at early ages of curing showed different trends [29-31].

Other researchers [26,27] have reported that the reactivity of fly ash could be improved by adding sulphate, leading to the formation of sulphate containing C-A-S-H products around the fly ash particles. In the present study the 40% SDW paste seems to show more pozzolanic reaction compared with the 20% SDW paste.

4. Conclusions

The experimental results reported in this paper lead to the following conclusions:

Replacing 40% of cement with SDW containing 85% fly ash and 15% gypsum increases the percentage of small pores (i.e., pores of diameter less than $0.1 \mu\text{m}$) compared with pure cement paste (i.e., no SDW). An increase from 70% of the total pore volume for cement paste to 84% for the paste with 40% SDW replacement was observed. The lower percentage of small pores indicates a coarser pore structure. The total pore volume

increases with increasing SDW content of the cement paste. An increase of 50% is observed at 40% replacement of cement with SDW.

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Table 1. Chemical composition of binder

Material	Major Oxide (wt%)							
	CaO	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	MgO	K ₂ O	Na ₂ O	SO ₃
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

Table 2. Binder constituents of the pastes

Paste No.	Mix ID	Proportions (% weight of binder)	
		Cement (C)	SDW
P1	REF (100 _C)	100	0
P2	80 _C 20 _{SDW}	80	20
P3	60 _C 40 _{SDW}	60	40

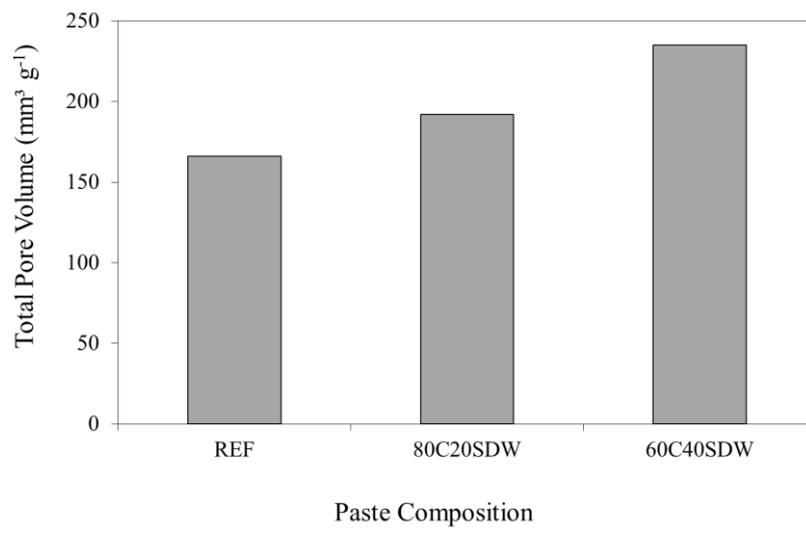


Fig. 1. Influence of SDW content on the total pore volume of pastes.

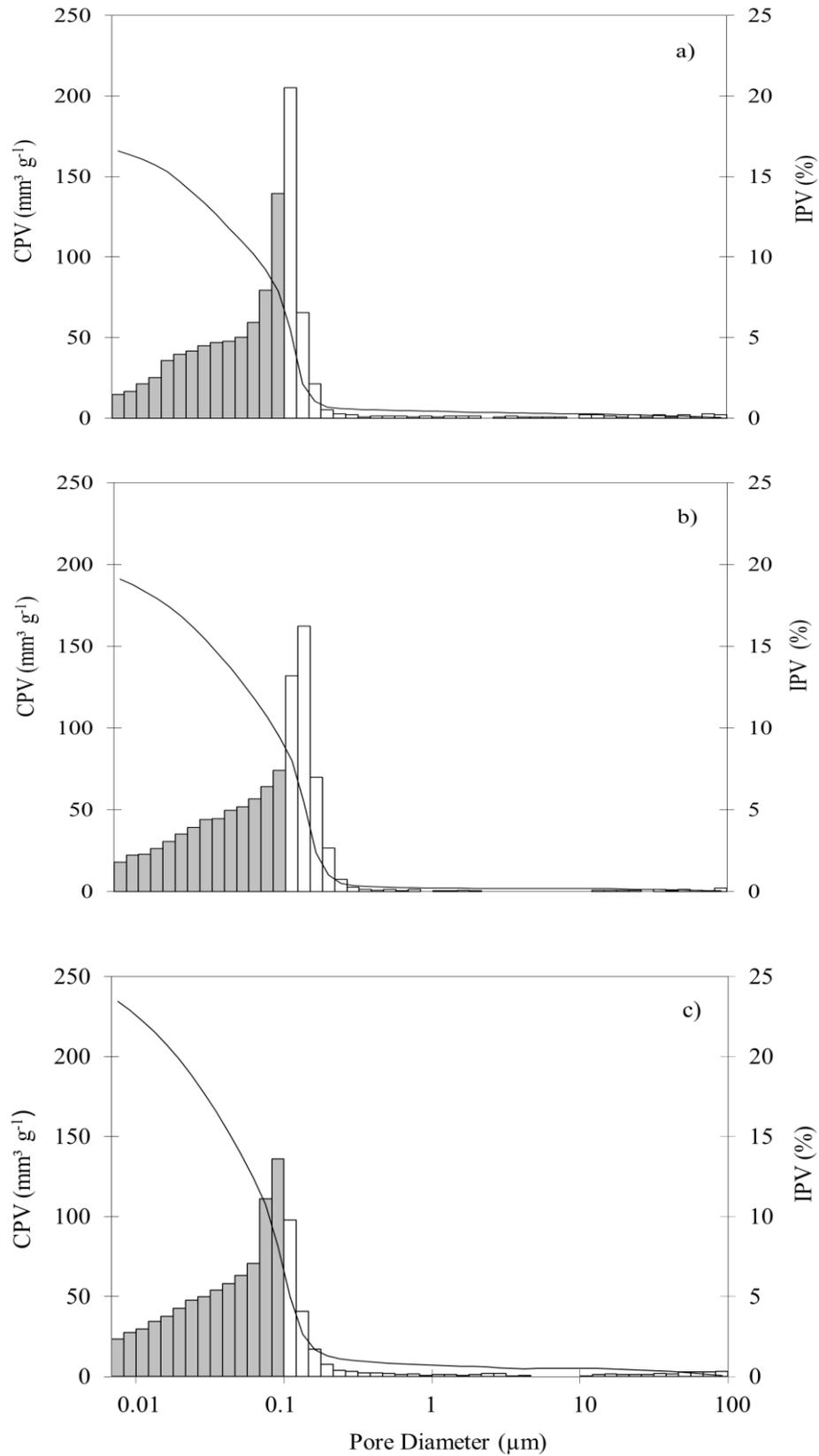


Fig. 2. Pore size distribution of pastes a) P1 (0% SDW), b) P2 (20% SDW) and c) P3 (40% SDW).

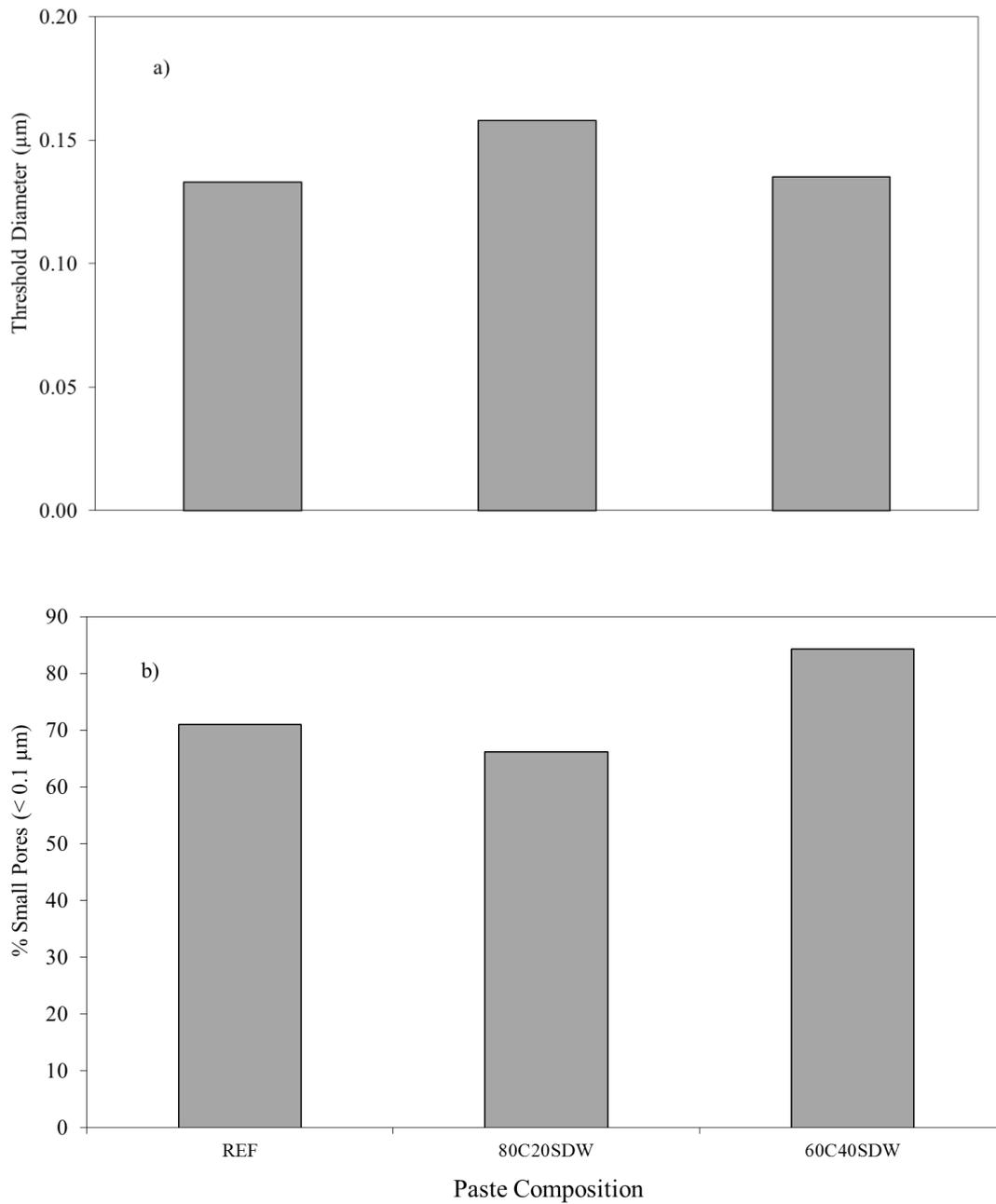


Fig. 3. Influence of SDW content on a) the threshold diameter (TD) and b) the percentage of small pores (< 0.1 μm) of pastes P1, P2 and P3.