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Microstructure studies on Portland cement pastes obtained in highly alkaline environments

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Abstract

For the last decade, the mechanism of the alkali activation process has been broadly studied. However, there still are some uncertainties in the understanding of the mentioned process. In order to improve the knowledge of the alkali activation process, some properties of a cement paste obtained through the hydration of an ordinary Portland cement with some high-alkaline solutions have been investigated. The flexural strengths of the pastes decrease as the alkalinity of the hydrating solution increases. The opposite behaviour is observed in the evolution of porosity. Microstructural analysis by scanning electron microscopy confirms the results obtained in a previous paper. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Portland cement hydration; NaOH; Na_2CO_3; Porosity; Mechanical strengths

1. Introduction

The alkali activation of materials is a chemical process by which the transformation of an amorphous or metastable structure in a dense skeleton with cementitious properties is carried out. A brief review of the bibliography related to the alkali activation process confirms that the mechanism governing the process is a widely reported subject [1–11]. However, there are significant uncertainties in the understanding of the process.

The alkali activation of materials in high-alkalinity media basically produces a polymeric gel with variable composition. The gel is produced when the starting material reacts with the alkaline solution. The good mechanical properties at the early stages are one of the most interesting properties of the materials prepared in these conditions.

It is remarkable to observe that it is not easy to find published papers related with the behaviour of ordinary Portland cement in high-alkalinity media.

In the hypothetical situation that a blended Portland cement (OPC + fly ash, slag, etc.) might be submitted to alkali activation with solutions of very high pH, it would be very interesting to know everything related with the hardening process of the cement pastes in the previously described alkaline media. In a previous paper [12], the chemical and mineralogical composition of the formed phases in the hydration process of the OPC with alkaline solutions has been described. The aim of this paper is to study the physical and mechanical, as well as the microstructural, characteristics of an OPC submitted to hydration under high-alkaline environment.

2. Experimental

2.1. Materials

Cement paste prisms of 1 × 1 × 6 cm were utilised. The chemical composition of the cement used in the preparation of the samples is presented in Table 1. The specific surface of the cement is 3622 cm^2/g.

The hydration of the samples was carried out with some different solutions (a water/cement ratio of 0.265 was used): NaOH 10 M, Na_2CO_3 3.8 M, and some other solutions resulting from the mixing of the former ones. In Table 2, the specific composition of the solutions used in the hydration process, as well as the weight percentage of Na in the solutions, is presented.

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Table 1
Chemical composition of the used cement

Oxide	Weight percentage
SiO_2	19.68
Fe_2O_3	3.42
Al_2O_3	5.38
CaO	63.50
MgO	1.86
K_2O	0.88
Na_2O	0.00
SO_3	3.46
LOI	1.77
IR	0.00

Deionized water was used as a blank hydrating solution in the study of the process of the cement (this solution is, namely, M00).

2.2. Method

The cement was hydrated with the solutions described above (Table 2) and the microstructure of the obtained pastes was studied by interpreting flexural strength data, porosity data (total porosity and pore size distribution) and scanning electron microscopy (SEM) images.

For the measurement of flexural strengths, rectangular prisms of 1 × 1 × 6 cm were prepared and cured at 22 °C and 100% RH. The breaking of the samples took place at 1, 3, 7 and 28 days.

Mercury porosimetry of those prisms of 1 × 1 × 6 cm was used to obtained the total porosity as well as the pore size distribution of the sample after 1, 3, 7 and 28 days of curing.

Finally, studying the morphology of the phases and their elemental composition by means of the SEM/EDX (energy-dispersive X-ray) completed the microstructural study of the pastes.

3. Results

3.1. Flexural strengths

Fig. 1 shows the results for the flexural strengths of the pastes after 1, 3, 7 and 28 days of curing. In this figure, it is clearly seen that the cement hydrated with deionized water shows the greatest values for the flexural strengths (generally speaking, the longer the time of curing, the higher the flexural strength of the samples). However, the hydration degree increment as a function of time is low in the case of the sample hydrated with deionized water when compared with those samples hydrated with the alkaline solutions. In fact, the following classification shows the order by which flexural strengths evolve (after 28 days of curing) as a function of the alkalinity of the hydrating water:

$$M01 < M28 \leq M55 < M82 \leq M10 < M00.$$

Table 2
Solutions used in the hydration process

Solution name	Na_2CO_3 (3.8 M) (%)	NaOH (10 M) (%)	% Na	pH
M01	0	100	57.6	14.0
M28	20	80	54.8	13.8
M55	50	50	49.4	13.8
M82	80	20	46.3	13.8
M10	100	0	43.5	11.7

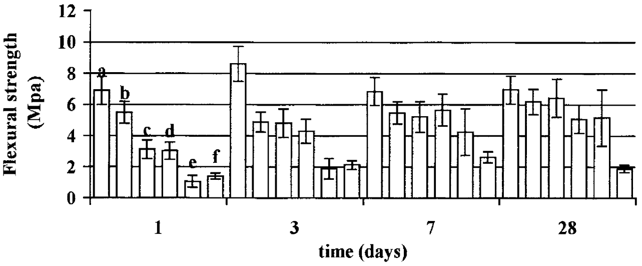

Fig. 1. Flexural strength evolution. (a) M00, (b) M10, (c) M82, (d) M55, (e) M28, (f) M01.

So, for those samples hydrated with M01 solution (100% NaOH; 10 M), it can be observed that flexural strengths values are always very low (2 MPa after 28 days of curing).

3.2. Porosity

Mercury porosimetry was applied for measuring total porosity and pore size distribution of samples after 1, 3, 7 and 28 days of hydration. The total porosity values are shown in Fig. 2. Generally speaking, the total porosity of the samples evolves in such a way that it decreases as curing time is longer (it can be clearly seen in those pastes obtained when hydrating our cement with deionized water).

After 28 days, the porosity of the pastes varies according to the following order:

$$M01 > M28 > M55 = M82 \geq M10 > M00.$$

The pore size distributions of the pastes obtained by hydrating the cement with deionized water (M00 solution),

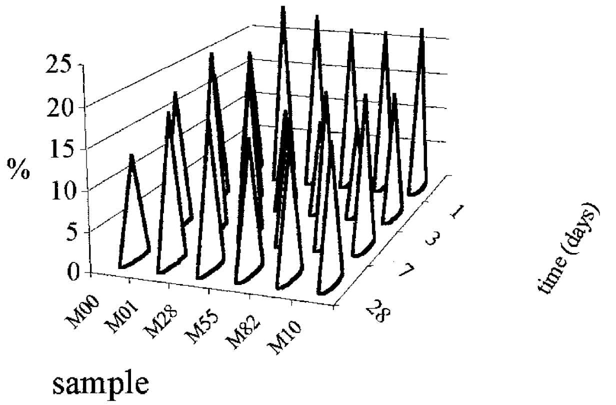

Fig. 2. Total porosity (%).

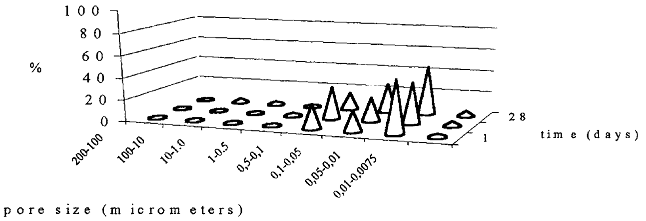

Fig. 3. Pore size distribution for the OPC hydrated with deionized water.

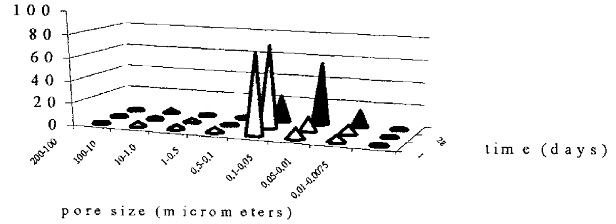

Fig. 4. Pore size distribution for the OPC hydrated with NaOH dissolution.

Na_2CO_3 (M10 solution) and NaOH (M01 solution) are, respectively, presented in Figs. 3–5. In all cases, pore size distribution is in the range between 0.50 and 0.01 μm.

In the particular case of the samples hydrated with deionized water (Fig. 3), the main group of pores is that sized in the range between 0.05 and 0.01 μm. It is remarkable to observe that the longer the hydration time, the smaller the diameter of the pores (0.01–0.0075 μm).

With regard to the samples hydrated with NaOH 10 M solution (Fig. 4), it can be observed that at the early stages of hydration (1 and 7 days), the pore size distribution falls within the range 0.1–0.5 μm. However, after 28 days of hydration, a refined structure is observed. That is to say: a decrease is observed in the pore fraction of 0.5–0.1 μm and an increase of the pore fraction in the range 0.05–0.01 μm. Something similar is observed for the pastes obtained with the M10 solution (Na_2CO_3 3.8 M) (Fig. 5). In this case, after 7 days of hydration, we have found a descent in the number of pores ranged between 0.5 and 0.1 μm and an increase in the low size pore fraction (0.1 and 0.05, and 0.05–0.01 μm).

For those materials hydrated in alkaline solutions, an increase in the lowest pore size fraction (0.01–0.0075 μm) is not observed.

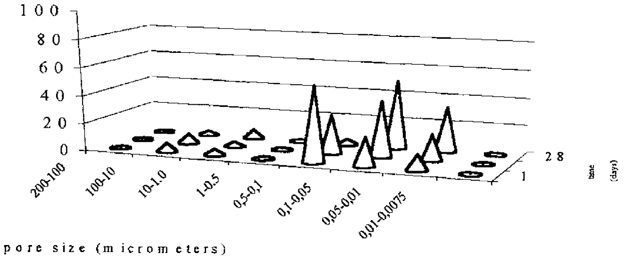

Fig. 5. Pore size distribution for the OPC hydrated with Na_2CO_3 dissolution.

3.3. SEM

Finally, those samples hydrated with different alkaline solutions for 28 days (as well as the samples hydrated with the blank, deionized water) were studied by means of the SEM as shown in Fig. 6. (a) to (e) show the most relevant microstructural aspects (compositional and morphological details) of the samples.

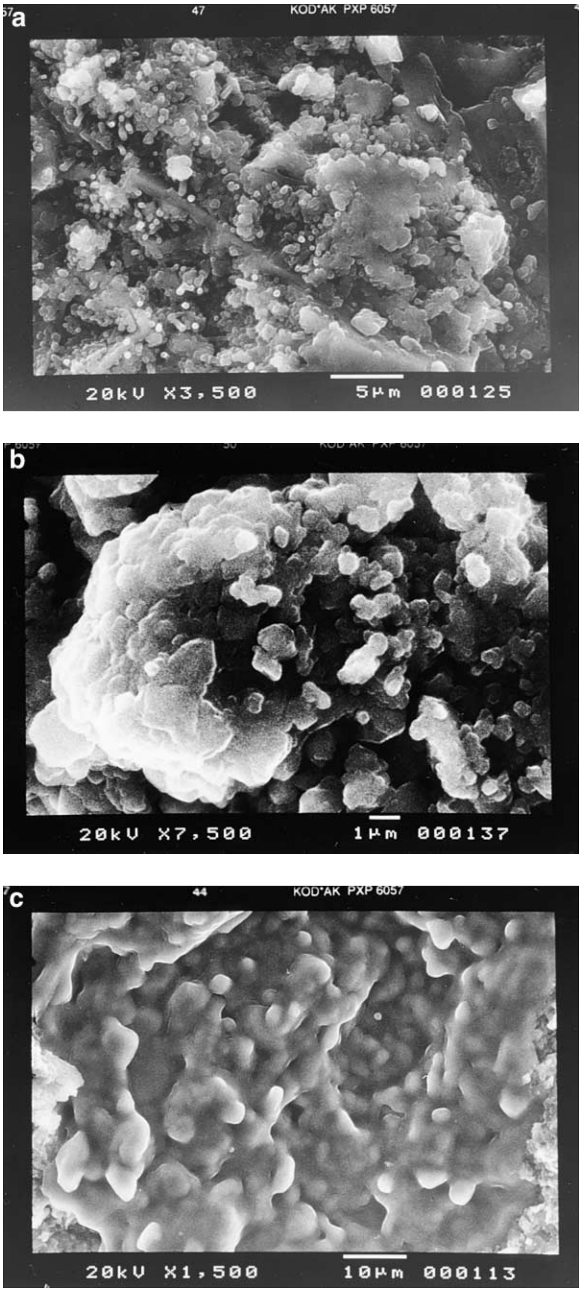

Fig. 6. SEM images of pastes at 28 days. (a) Cement paste hydrated with M00 solution. General view of the sample. CSH gel. (b) Cement paste hydrated with M01 solution. Sodium–calcium carbonate deposits are observed. (c) Cement paste hydrated with M01 solution. Sodium sulphate. (d) Cement paste hydrated with M01 solution. Hexagonal plates from $Ca(OH)_2$. (e) Cement paste hydrated with M10 solution. Carbonate deposits over the CSH gel.

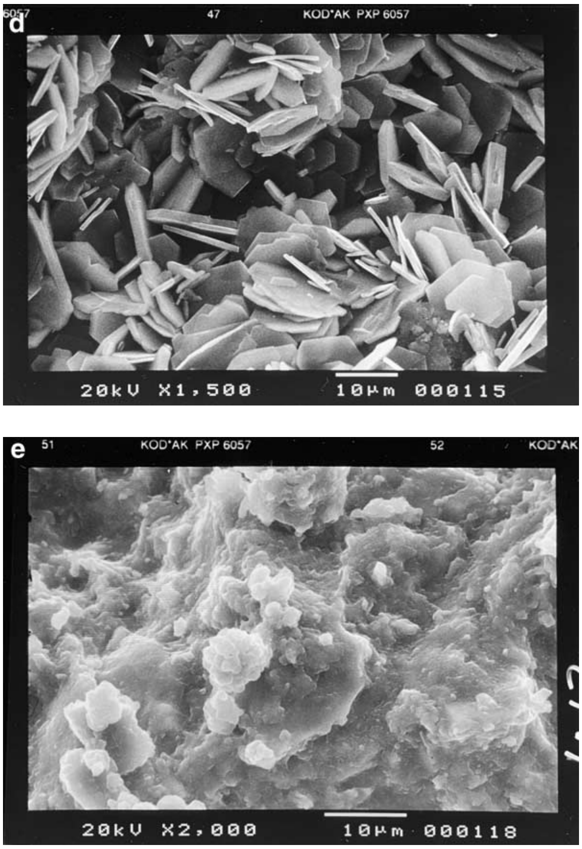

Fig. 6. (*continued*)

Thereby, (a) shows the CSH gel formed when cement was hydrated with deionized water and cured for a period of 28 days.

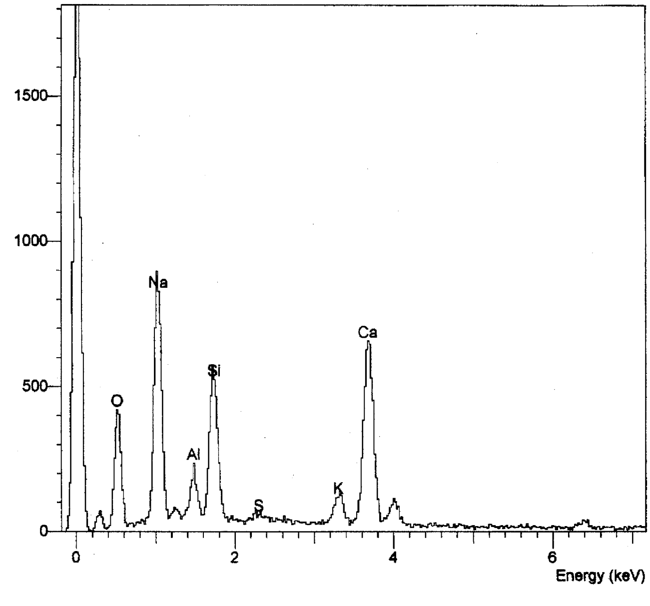

Fig. 7. EDX analysis of M01 sample.

(b) shows the general view of the cement paste resulting from the hydration of our cement with the NaOH solution (M01). Additionally, the EDX analysis of the small particles over the main phase formed in the hydration process reveals the presence of Na and Ca, which is strongly suggesting the formation of a sodium–calcium carbonate in the samples (see Fig. 7).

In that sample of cement hydrated with the NaOH solution, some other crystalline structures are observed. In (c), for example, sodium sulphate crystals can be seen (the elemental analysis by EDX shows S and Na), and in (d), the typical hexagonal plates of $Ca(OH)_2$ are shown.

The general aspect of the CSH gel formed after the hydration of the cement with Na_2CO_3 3.8 M (M10 solution) is shown in (e). The small deposits over the hydrated calcium silicate bulk correspond to a sodium–calcium carbonate formed during the curing process.

4. Discussion

From the flexural strength data (see Fig. 1), some different important conclusions can be extracted. Firstly, the hydration rate of Portland cement can be related to the alkalinity of the solution used in the hydration process in such a way that the higher the alkalinity of the hydrating water, the slower the reaction rate of hydration of the anhydrous cement phases. Consequently, the microstructure of the pastes obtained is different depending on the pH of the hydrating solution; so, the cement paste with the greatest flexural strength is the one obtained with deionized water. Finally, the other evident conclusion about the mechanical strength development is that the longer is the curing time, the lesser the difference of flexural strength between those samples hydrated with water and those with alkaline solutions.

These results are in good agreement with the date of Neville [13]. This author affirmed that when the cement was hydrated in presence of alkalis, and cured for periods of time lower than 28 days, the mechanical properties of the cement pastes were modified (the higher the alkali concentration, the lower the strengths).

Table 3 shows different ratios obtained by relating flexural strengths at 28 days and flexural strengths at 1, 3 and 7 days for our cement pastes. These values can assess the strength increase with time.

Table 3
Flexural strength ratio

Sample	FS_{28}/FS_1	FS_{28}/FS_3	FS_{28}/FS_7
M10	1.1	1.1	1.1
M82	2.0	1.3	1.2
M55	1.7	1.2	0.9
M28	4.8	2.7	1.2
M01	1.3	0.9	0.7

In our experimental work, with the alkaline solutions used, the following relationship can be observed: $S_{28}/S_1 \leq S_{28}/S_3 \leq S_{28}/S_7$. This indicates that the mechanical strength increases as curing time increases.

From the total porosity results (Fig. 2), a coherent relationship between porosity and mechanical strength can be assessed. For that cement paste with the highest percentage of total porosity, the lowest flexural strength is observed. Additionally, in Figs. 3–5, it is observed that the longer the curing time, the finer the pore system becomes; therefore, the amount of coarse pores decreases and the amount of small pores (between 0.05 and 0.0075 μm) increases.

The explanation of this microstructural changes has been attributed to the chemistry of this cement system. Mechanical strength, as well as porosity, is related to the hydration process of the unhydrated phases, and more directly, with the reaction rate of C_3S (main phase in the anhydrous system). Thus, it is normal for the process of hydration of a Portland cement in alkaline medium to be retarded due to the effect of the common ion: when the OH^- concentration of the system is increased, the equilibrium of the reactions of hydration of C_3S and also C_2S is displaced towards the left side, impeding the normal evolution of the hydration:

$$C_3S + H_2O \leftrightarrow CSH + Ca(OH)_2$$

Obviously, as the alkalinity of the hydrating solution increases, the degree of hydration of the anhydrous silicates decreases; therefore, the mechanical strength of the pastes decreases and the porosity of the system becomes higher (at least for the big pores).

The experimental results are in good agreement with this explanation since the mechanical strength of samples hydrated with NaOH 10 M solution is more drastically reduced than the strength of pastes obtained with Na_2CO_3 and deionized water.

Finally, the presence of some phases detected by SEM can be interpreted with the aid of the data published by us in a previous paper [12]. So, for instance, in that mentioned work, we showed that after 28 days, CSH gel decomposes under high-alkalinity conditions by forming quartz and $Ca(OH)_2$. In the samples M01 and M28, quartz was detected at early stages by XRD. Then, the presence of high amounts of hexagonal crystals of calcium hydroxide, detected by SEM in some samples (see Fig. 6c), should be mainly interpreted as a consequence of the mentioned decomposition of the CSH gel and not due to the hydration reaction of calcium silicates. The low mechanical strength of samples obtained when hydrating the cement with the NaOH solution confirm this fact.

In that cited paper [12], it was also proved that the normal formation of ettringite could not take place because gypsum reacts with alkalis producing sodium sulphate. It has been confirmed by the presence of Na_2SO_4 crystals (see Fig. 6d).

Finally, the presence of sodium–calcium carbonates (Fig. 6b and e) in the forms of pirsonite and gaylusite, too, confirms again the hydration mechanism described in Ref. [12] for cements submitted to very-high-alkaline environment.

5. Conclusions

The main conclusions extracted from this investigation can be summarised as follows. Flexural strengths and total porosity of cement paste are drastically affected by the alkalinity level of the hydrating water. For samples hydrated with NaOH 10 M solution, the flexural strengths are considerably lower than for samples hydrated with Na_2CO_3 3.8 M solution.

A coherent behaviour is observed when porosity is analysed (the higher the alkalinity of the system, the higher the porosity of the material obtained).

Microstructural analysis reveals that the hydration reaction of cement is retarded by the presence, in the system, of high-alkaline concentration.

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