The 4th International scientific Conference on Nanotechnology& Advanced Materials &Their Applications (ICNAMA 2013)3-4 Nov, 2013

SEM-Backscattered Imaging analysis of Cementitious Composite Matrix Incorporating Mineral Admixture

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ABSTRACT

Microstructure imaging interpretation of polished surface has become well established as a method for the study of cement and concrete microstructure. This paper is an attempt to provide micro-level examination to the microstructure of cement paste in concrete particularly the hydrated mineral admixture and interfacial transition zone, which received increasing attention due to their effect on the hardened concrete properties. Furthermore, illustrations are provided of the transition area of cement paste adjacent to the aggregate border as well as other cement paste areas. SEM images reveal that pozzolanic reaction is not the only benefit of using mineral admixture. Spherical shape of grains is important to improve the microstructure of cement paste particularly in the interfacial transition zone.

Keywords: Imaging Interpretation, Cement paste (CP), Microstructure, Interfacial Transition Zone (ITZ).

تحليل صور المجهر الالكتروني الماسح بتقنية التشتت الخلفي للمواد السمنتية المركبة الحاوية على المضافات المعدنية

الخلاصة

اصبحت طريقة تفسير الصور المجهرية للسطوح المعالجة، طريقة موثوقة لدراسة البنية المجهرية للسمنت والخرسانة. تركز هذه الدراسة على اختبار البنية المجهرية لعجينة السمنت في الخرسانة وبالخصوص اماهة المضاف المعدني وكذلك المسافة البينية التي يتزايد الاهتمام بها بسبب دورها المهم في صفات الخرسانة المتصلبة المنتجة. كما يركز البحث على اعطاء التوضيحات عن المسافة البينية قرب حافة حبيبات الركام وكذلك عجينة السمنت.

بينت صور المجهر الماسح الالكتروني ان التفاعل البوزولاني هو ليس الفائدة الوحيدة من استخدام المضاف المعدني بل ان الشكل الكروي للحبيبات يعتبر مهما في تحسين البنية المجهرية وخاصة في منطقة المسافة البينية.

https://doi.org/10.30684/etj.32.4B.9
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INTRODUCTION

During the past two to three decades the microscope imaging has become established as an essential tool in the study of materials related to the construction sector, such as concrete, cement paste, soils and rocks. It provides a useful complement to the traditional role of the microscope. The modern generation, named scanning electron microscope (SEM), is a versatile analytical work station, capable of providing several different types of images, quantitative data relating to porosity and cement paste composition and information about the microstructure of the matrix.

The microstructure of cement paste develops by hydration. The anhydrous cement grains react with water to produce hydrous grains. With time the solid volumes of the system increase. In Portland cement paste, the hydration reaction is dominated by the reaction of the clinker, which leads to the formation of calcium silicate hydrate (C-S-H) and calcium hydroxide (CH). In the microstructure, the characteristic of these phases is relatively distinctive. C-S-H creates mainly around the cement grains, while CH deposit in the water filled pores. This brief explanation of microstructural formation enables the important features of SEM images to be interpreted.

GREY LEVEL VARIATIONS IN C–S–H.

Variations in the grey level that may be observed in C–S–H phase, is a matter discussed previously in many papers [1–3]. The C–S–H component is a product of variable composition, particularly in terms of the ratio of calcium oxide to silica (C/S). Variations may also occur in the degree of micro porosity. Both these factors influence the grey level in SEM images. Decreasing the CH component will lead to redaction in C/S ratio. This occurs when calcium is leached from the cement paste, and/or when carbonation occurs, and also when there is a large amount of pozzolanic reaction, such as may occur in pastes containing silica fume or fly ash, both of which are used in this study. C–S–H with lower C/S ratio is darker in SEM images than that with higher C/S ratio. Variations in micro-porosity have been found to occur when the C–S–H forms at different temperatures, higher temperatures lead to ‘‘denser’’ C–S–H with lower micro- porosity and so a lighter appearance in SEM images. Famy, et al [3] mentioned that when the circumstances leading to grey level variation are not known, the two effects may be distinguished by combining SEM imaging with microanalyses as described above.

EXPERIMENTAL.

Different mixtures were used to provide various ranges of properties. Ordinary Portland cement conforms to BS EN 197-1; medium graded siliceous sand and quartz coarse aggregate (BS 882: 1992) were used to prepare the mixtures according to Table 1. The superplasticizer was used to maintain the approximately same flow of 125 ± 5 mm, and to allow the introduction of the cement replacement mineral admixtures (silica fume and fly ash) on 10% mass replacement in an attempt to improve the durability of the repairing material. The average particle sizes were 10 µm, 0.1 µm, and 50 µm for fly ash, silica fume, and cement particles respectively.

Table (1) Details of Experimental Program.

Mixture	Mix proportion by wt.	w/c ratio (wt.)	Type of admixture	
			Super plasticiser (% by wt. of cement)	Pozzolan (% replaced by wt. of cement)
Mortar	1: 2 (cement: sand)	0.42	-	-
Fly ash mortar		0.33	1	10% Fly ash
Silica Fume mortar		0.33	1	10% Silica fume
Concrete	1:2 :4 (cement: sand: gravel)	0.40	-	-

Specimen preparation for SEM images for this study is similar to that used by other researchers. A detailed description of all of the specific steps used has been published by Stutzman and Clifton [4], and another more recently, by Hassan [5]. It involved preparing of small 20mm cubed specimens using a cutting saw with a 1.1mm thick diamond blade. The samples were dried and hydration stopped by placing them into liquid nitrogen at -196OC for 15 minutes. This quick quenching process at very low temperature allows the generation of ice micro-crystals to form which do not affect the microstructure of the sample. The samples were then placed into a freeze drying machine at -55OC for 24 hours. This allows the ice formed within the pore system of the sample to be removed by sublimation.

After the drying stage, the samples were placed into a circular 30mm multiform mould and impregnated with epoxy-resin (Epofix, Struers). After 24hours curing, the hardened resin with embedded sample was demoulded and polished to a flat surface on a rotary grinding/polishing machine (Struers Rotopol-35) using silicon carbide paper of different grades (600-2400 grit). The samples were subsequently polished with diamond paste (3, 1 and 0.25µm) and polishing cloths using a hydrocarbon solution for lubrication. The surface of the polished samples was carbon coated in a vacuum coating unit and analyzed in an SEM (Cambridge Stereoscan 360) with a backscatter detector attached, at an accelerating voltage of 20kV and a working distance of 15mm.

MICROSTRUCTURE IMAGING INTERPRETATION

The available range of black to white in SEM images is usually divided according to its shades of darkness into 256 ‘gray levels’. The highest level, usually recorded as gray level 255, is fully white; the lowest level, usually recorded as gray level 0, is fully black. So, darker areas on the image are areas of lower gray levels, and equally, the brighter areas are areas of higher gray levels. In SEM images, light gray irregular shape areas show calcium hydroxide crystals, dark gray areas represent calcium silicate hydrate, and black areas indicate pores and cracks [1-3, 6].

In Figure (1) it is clear that the unhydrated cement grains exhibit higher gray levels than the hydrated components surrounding them.

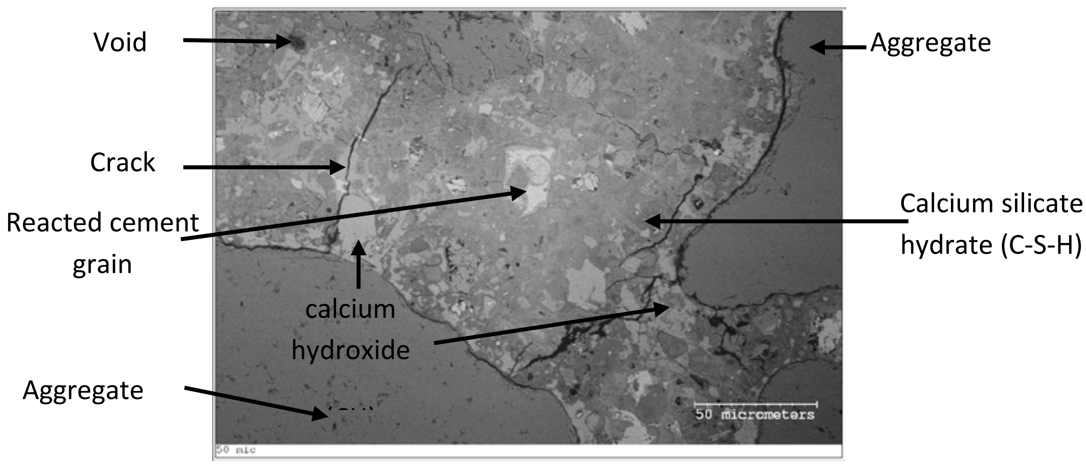


Figure (1) SEM image of a Portland cement concrete (14 weeks old, w/c=0.4), with the view of microstructural component.

Another shape featured in Figure (1), named calcium hydroxide (CH). It is less prominently, however it has a considerable importance. Their size ranged from 10 to 20 µm, and the outer shapes are irregular, and it is somewhat brighter appearance than the C-S-H. Figure (1) indicates two of them, and there are several others. Calcium hydroxide is an important product in cement paste. It can be notable and distinguished from other products in cement pastes by a gray level very little brighter than that of C–S–H gel. Even so, it requires sometimes close examination to be separated from other hydration products.

Pore space usually present in significant contents in the cement paste, and it can be detected by SEM images. The w: c ratio and degree of hydration are greatly affecting the total contents of pore spaces. Figure (1) shows an example of such pores. The low electron backscattering ability of the epoxy resin that fills the pore space in prepared specimens causes such areas to appear much darker than even the hydrated cement constituents. Image analysis can be used to quantify the content of detectable pore space in a given paste.

INTERFACIAL TRANSITION ZONE

The random packing of the cement grains is disturbed by the large aggregate particles to provide a zone next to the interface which has a deficit of cement grains. The size of this zone is corresponding with that of the cement grains, with the most significant differences occurring in excess of the first 15–20 µm from the interface. In an image such as in Figure(2), this 15–20 μm zone (indicated by the black line) appears to be small compared to the bulk paste, but it, referred to Scrivener KL [6], makes up a quantity of 20–30% of the total paste volume in a typical concrete. The shortage of cement grains in the ITZ means that initially there is effectively a higher water to cement ratio in this region, so for a given overall water to cement ratio the water to the cement ratio of the bulk cement paste is in the same way lower.

Figure (2) also illustrates a region where several cement grains are clustered together and there are marked differences in the paste density. Additionally, great deposits of calcium hydroxide can be seen along some aggregate surfaces, while others have very little calcium hydroxide in their surrounding area. These variations make it very difficult to characterize a specific gray level for the ITZ area. In contrast, recognition of area outlying around the aggregate surfaces of anhydrous cement, calcium hydroxide, other hydration products and pores is easier to quantify.

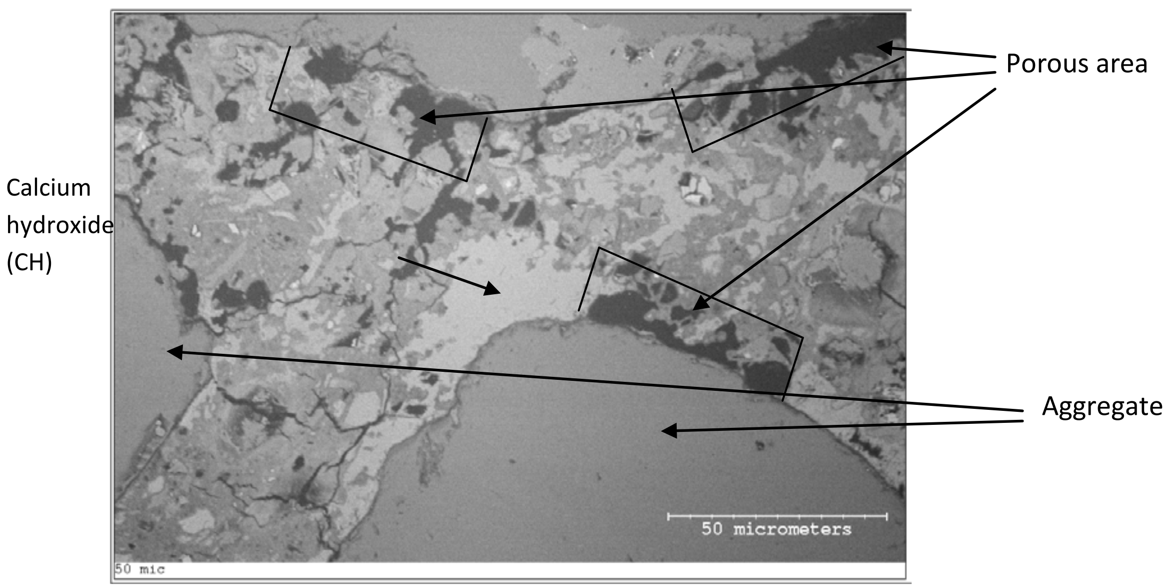
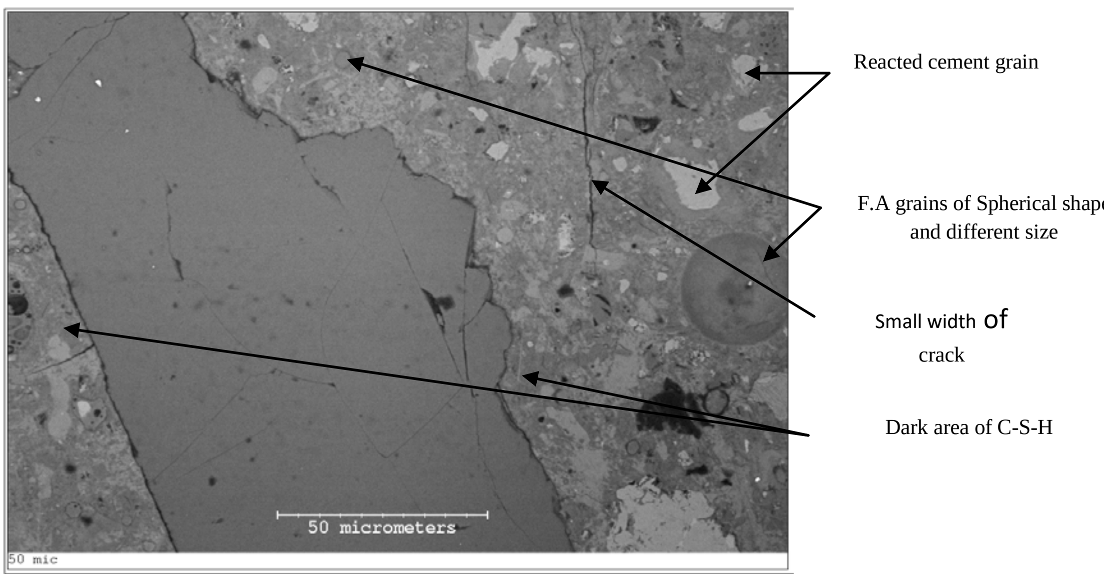


Figure (2) SEM image of a Portland cement mortar (28-day old, w/c=0.5), with the view of ITZ.

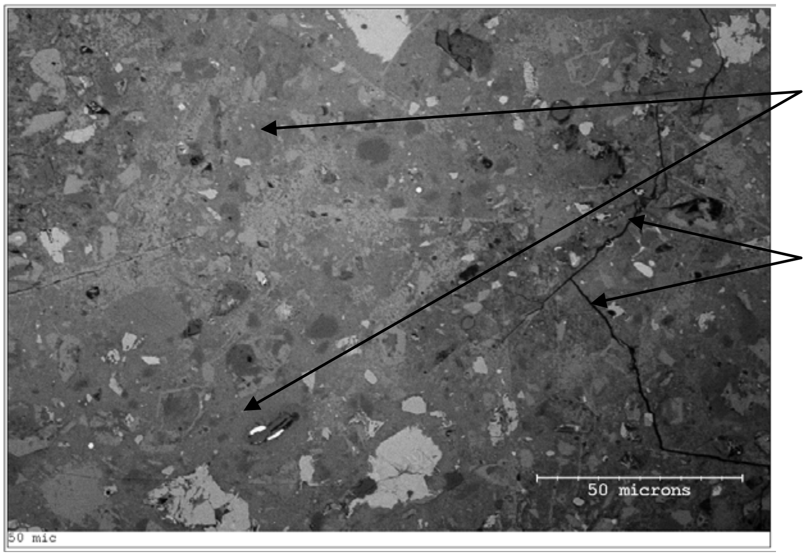
MATRIX PHASE CONTAINING MINERAL ADMIXTURE

Mineral admixtures, such as silica fume (SF) and fly ash (F.A) are finely divided siliceous materials that are added to concrete in relatively large amounts, generally, in a range more than 10 percent by mass of the total cementitious material [7]. The reaction between mineral admixture and calcium hydroxide is called the pozzolanic reaction. The technical advantage of using F.A or SF is derived mainly from that the reaction is lime-consuming instead of lime- producing, which leads to produce more C-S-H with time. Mehta and monteiro [7] mentioned that C-S-H produced by pozzolanic reactions at later age characterized by micro-porous and low density properties which lead to low gray level (dark color). The SEM images presented in Figure (3) also support this idea.

The second benefit of using mineral admixture is a physical effect of pore size refinement and filling up capillary pores and crack spaces, thus improving the microstructure of cement paste. The effects of mineral admixture addition on the resulting properties of cement paste were also reported by other researchers [8-10]. The SEM images of the F.A and SF cement paste samples presented in figure 3a,b also support this suggestion. As seen from the images, when compared to the conventional cement paste (i.e without any mineral admixture as in Figure 2), the cement paste with F.A or SF additives have much less pores areas and smaller crack widths. This is attributes to the later production of C-S-H caused by pozolanic reactions filling up pores and led to reduce the width and number of cracks.



a. SEM image of F.A mortar showing dense area of ITZ, and absence of wide cracks.
Figure. (3) To be continued.



b. SEM image of SF mortar showing dark and dense area of C-S-H, and absence of wide cracks.
Figure (3) SEM images of cement paste mortar with mineral Admixture (14-week old, w/c=0.4).

Figure (3) shows that the cement paste between aggregates is denser than that in Figure (2). The possible explanation of such that, a partial replacement of cement by F.A or SF results in higher volume of paste due to its lower density and this increase in the paste volume reduces the friction at the aggregate-paste interface and improve the plasticity and cohesive, and this leads to increase the homogeneity of the matrix producing more denser area.

Furthermore, the spherical shape of F.A and SF particles reduce the friction at the aggregate paste interface producing a “ball-bearing effect” at the point of contact [11, 12]. Therefore it can be concluded that pozolanic reaction is not the only parameter of a mineral admixture to improve the microstructure of cement paste, but some other factors such as particle shapes seem to be of great influence.

CONCLUSIONS

Examining the microstructure imaging of hydrated cement paste with mineral admixtures indicates the following:

1- The ITZ found at the cement paste / aggregate interface and the connectivity of these zones by microcracks within the paste may be significant in enhancing mass transport properties. It is necessary to determine practically this mechanism; which may provide a reliable guide.
2- Both the silica fume and fly ash admixture provide additional benefits to the microstructure homogeneity of the hydrated cement paste at later age.

3- Spherical shape of the fly ash and silica fume grains are important to improve the microstructure of cement paste particularly in the interfacial transition zone (ITZ).

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