

# In situ imaging of ground granulated blast furnace slag hydration

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**Abstract** Ground granulated blast furnace slag (GGBFS) reacts with water in the presence of calcium sulfates and alkalis and is frequently used as a partial replacement for portland cement in concrete. The hydration products are known to be slightly different compositionally and morphologically than those of pure portland cement hydration. In this study, a new technique, soft X-ray transmission microscopy, was used to image the hydration of slag in a variety of solutions to investigate the effects of alkali sulfate and hydroxide activators on the morphology of the resulting hydration products. This microscopy method is unique in that it enables high resolution in situ observation and documentation of the formation of hydration products over time in wet samples at atmospheric pressure.

## Introduction

Granulated or pelletized blast furnace slags (BFS) are byproducts of the steel industry which are sold for use as a partial replacement of portland cement in

concrete. They are often used to improve concrete properties and durability, and sometimes to lower concrete cost. BFS is formed in the blast furnace by reaction of limestone with silica and alumina present in the iron ore. When the liquid slag, created at 1350–1500 °C, is cooled quickly using water, granules or pellets with a predominantly glassy phase are produced which have hydraulic cementing properties when finely ground. The composition of the slag varies depending on the composition of the ore, but generally it falls in the range 27–42% SiO<sub>2</sub>, 30–50% CaO, 5–33% Al<sub>2</sub>O<sub>3</sub>, and 0–21% MgO [1]. Its hydraulic reactivity is dependent not only on composition but also on the glass content, particle size distribution, and surface characteristics [2].

Hydration of ground granulated blast furnace slag (GGBFS) is very slow in pure water. It is likely that an impermeable aluminosilicate coating forms on the surface of the grains soon after contact with water, preventing further reaction [2]. Therefore, GGBFS is usually blended or interground with portland cement, which serves to “activate” its hydration. Activation can also be achieved by adding calcium sulfates or alkali compounds to GGBFS-water mixtures. The primary hydration product, as with portland cement, is calcium silicate hydrate (C–S–H in cement chemistry notation<sup>1</sup>). The C–S–H formed by slag, however, has a lower CaO/SiO<sub>2</sub> ratio than that formed by portland cement; approximately 1.0 in slag [3, 4] compared to

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<sup>1</sup> In cement chemistry notation, single letters are used to represent oxides: C = CaO, S = SiO<sub>2</sub>, A = Al<sub>2</sub>O<sub>3</sub>, F = Fe<sub>2</sub>O<sub>3</sub>, H = H<sub>2</sub>O, and  $\bar{S}$  = SO<sub>3</sub>. Calcium silicate hydrate is abbreviated C–S–H because the stoichiometry is variable and numerical subscripts would be misleading.

1.5–2.0 in portland cement. Ettringite ( $\text{Ca}_6\text{Al}_2\text{S}_3\text{O}_{18}\cdot 32\text{H}_2\text{O}$ ), abbreviated AFt, is also a major early-age product of GGBFS hydration when it is activated either by portland cement or by gypsum.

Scanning electron microscopy shows little difference in the microstructure of C–S–H formed from slag grains compared to portland cement grains [5]. Both are characterized by a rim of “inner product” formed at and within the original boundaries of the grain, and “outer product” filling space between grains. The microstructure of slag pastes is notably different in that there is less calcium hydroxide [5] formed at the expense of platy monosulfoaluminate (AFm) phases,  $\text{Ca}_6\text{Al}_2\text{SO}_{10}\cdot 12\text{H}_2\text{O}$  [6]. Transmission electron microscopy differentiates between the microstructure of outer product C–S–H formed from slag and cement grains. Whereas outer product near cement grains is fibrillar in appearance, that forming around slag grains is foil-like [7–9].

Scanning electron microscopy and transmission electron microscopy give a good indication of the morphology of GGBFS hydration products at a given time, but cannot be used to document the continuous growth of the hydrated phases. Moreover, the results from both of these techniques are limited by artifacts induced by specimen drying prior to observation. Recently a novel technique, soft X-ray transmission microscopy, has been applied to the study of cementitious materials [10–12]. The microscope uses radiation in the soft X-ray regime, with wavelengths more than 100 times shorter than visible light. A resolution of 15 nm [13] is obtainable and samples can be viewed while wet and at atmospheric pressure. This enables observation and imaging of hydration products forming around cement grains in situ over time. This technique was applied to the study of slag hydration in solutions of varying composition and alkalinity in order to both characterize the hydration products and determine the effects of various activators on hydration.

## Experimental

The GGBFS sample used in this study came from Fos-sur-Mer, France. It has a chemical composition of

34.40%  $\text{SiO}_2$ , 10.44%  $\text{Al}_2\text{O}_3$ , 43.41%  $\text{CaO}$ , 8.60%  $\text{MgO}$ , 1.40%  $\text{FeO}$ , 0.17%  $\text{MnO}$ , and 0.54%  $\text{TiO}_2$ . This slag has a glass content of 75%, with an estimated 25% merwinite as the only crystalline phase detectable by X-ray diffraction (XRD). It was ground to a Blaine fineness [14] of  $450 \text{ m}^2/\text{kg}$ .

This slag was mixed with a variety of solutions in order to observe the effects of activators on its hydration. The matrix of solutions used is shown in Table 1, along with corresponding measured pH values. Distilled water was boiled in order to remove dissolved carbon dioxide and allowed to cool to room temperature. Solutions were mixed in polyethylene bottles either with neat water or with water saturated with respect to calcium hydroxide and/or gypsum. Saturation with respect to crystalline calcium hydroxide (portlandite) was achieved by adding 3.5 g  $\text{Ca}(\text{OH})_2$  (Sigma) for every 100 ml water. Saturation with respect to gypsum was achieved by adding 1 g  $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$  (Sigma) for every 100 ml water. Potassium hydroxide (Fisher) or potassium sulfate (Sigma) was then added in the concentrations listed in Table 1. The bottles were sealed, shaken vigorously, and the contents allowed to settle overnight. Aliquots of 14 ml were pipetted off the tops of the solutions and sealed in polystyrene bottles. Care was taken not to disturb the solids at the bottom of the bottle and to minimize exposure to air.

The soft X-ray transmission microscope used in this study (XM-1) is located at beam line 6.1.2 of the Advanced Light Source (ALS) at the E. O. Lawrence Berkeley National Laboratory (LBNL) in Berkeley, California and is operated by the Center for X-ray Optics (CXRO). Synchrotron radiation is filtered by a plane mirror into the soft X-ray regime (0.4–7 nm) and is focused on the sample using a condenser zone plate. A micro-zone plate is then used to focus the transmitted X-rays onto a CCD camera. Resolution for the images taken for this study is not the optimal 15 nm because of the zone plates used, sample thickness, magnification, exposure time, and number of photons captured per pixel. More information about the microscope can be found in Ref. [13, 15, 16].

**Table 1** Measured pH values of solutions used for slag hydration

	As is	Portlandite-saturated	Gypsum-saturated	Portlandite- and gypsum-saturated
Pure water	6.50	12.72	6.61	12.68
0.1 M KOH	13.00	13.08	n/a	12.88
0.4 M KOH	13.58	13.59	n/a	13.41
0.05 M $\text{K}_2\text{SO}_4$	6.43	n/a	6.29	12.88
0.2 M $\text{K}_2\text{SO}_4$	8.88	n/a	6.10	n/a

Images were taken at  $\sim 2000\times$  and have a circular field of view of approximately  $10\ \mu\text{m}$  in diameter. In order to observe larger areas, several images were taken over a grid in the area of interest. A custom autocorrelation process was then used to create a larger, composite image using montage alignment [17].

In order for sufficient soft X-rays to be transmitted through a water-based sample for imaging purposes, the sample must not be thicker than about  $10\ \mu\text{m}$ . This necessitates examining dilute systems of small grains of solid material suspended in solution. Slag was mixed with the solutions described in Table 1 at an initial water-to-slag ratio (w/s) of 50 by mass. After shaking the suspension for approximately 15 s, a 2 ml aliquot was removed and centrifuged briefly to ensure that only small grains ( $\ll 10\ \mu\text{m}$ ) remained in the supernatant. A drop of this supernatant was immediately sandwiched between two silicon nitride membranes, which were sealed between stainless steel plates. Rubber o-rings in the steel plates prevented evaporation and carbonation. The sample was then imaged immediately with the soft X-ray microscope, allowing observation of hydration as early as 5 min after mixing. Typically, a particular sample was kept in the sample cell and could be observed for approximately 2 h before the cell windows broke. The remaining suspension was rotated in a sealed bottle at 8 rpm. Aliquots of 2 ml were also removed at later times and examined in the microscope following the same procedure as for the first aliquot.

Further studies were performed on selected slag pastes made at a w/s of 0.5 by mass. These pastes were examined using environmental scanning electron microscopy (ESEM) to provide further images of early age hydration and by XRD to provide quantitative information on the hydrated phases present. ESEM samples were mixed briefly with a stainless steel spatula in a small dish before introduction into the chamber of the ESEM (Electrosan). Specimens were imaged at  $4\ ^\circ\text{C}$  with a vapor pressure of 5–6 Torr, which corresponds to a relative humidity inside the chamber of 90–100%; this prevented evaporation of water and allowed for hydration to proceed during imaging. Specimens for XRD were sealed in 2 ml polypropylene vials for 28 days after mixing. The samples were then dried under vacuum for 24 h, ground to a fine powder, then vacuum sealed and stored before testing. Samples for XRD were examined using a Philips X'pert diffractometer over a  $2\theta$  range of  $5^\circ$ – $80^\circ$ .

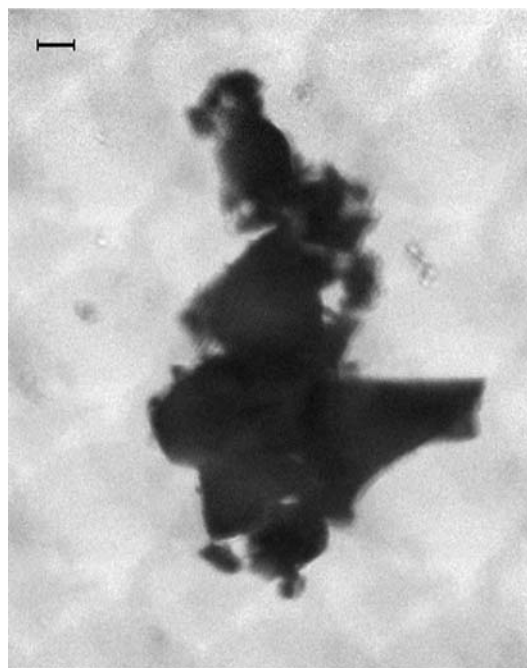
## Results and discussion

### Soft X-ray transmission microscopy

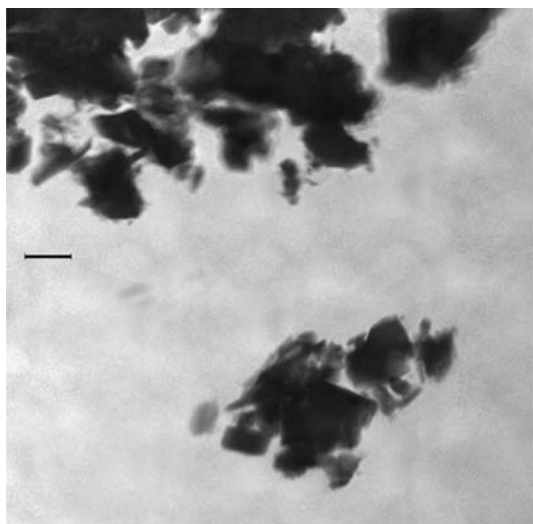
#### *Non-activated*

Figure 1 shows a soft X-ray transmission microscope image of a dry slag grain that was dusted on the silicon nitride membrane of the sample cell. The surfaces of the grain are rough and irregular.

The slag grains in Fig. 2 were in distilled water for 22 min prior to observation. It is possible that some hydration has occurred as there are some small features extending from and between the dark, solid grains that are more X-ray transparent, which could be hydration products. Although these features are absent in the dry slag sample, it is difficult to confirm that they are hydration products as they may instead be irregularities in the appearance of the slag grains. It is unlikely that these features represent the coating that is postulated to impede hydration in non-activated systems [2], as this layer is expected to be too thin to see using this technique. In any case, the morphology of slag grains in water remains static for at least 2 h after mixing, indicating that further hydration is not occurring during this time period.



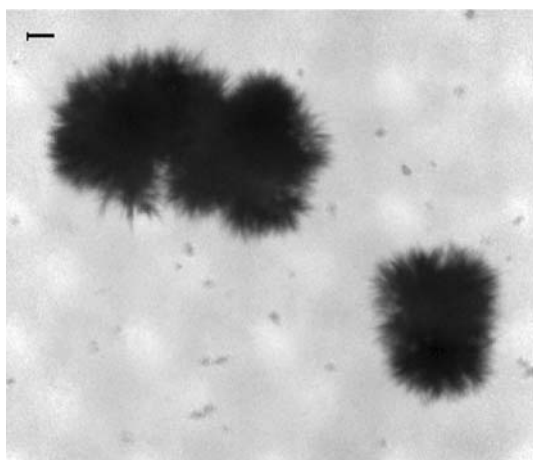
**Fig. 1** Dry slag, scale bar =  $1\ \mu\text{m}$



**Fig. 2** Slag in distilled water, 22 min. after mixing, scale bar = 1  $\mu\text{m}$

#### Activated

When slag is placed in 50:1 suspensions saturated in portlandite, with or without gypsum, hydration products appear immediately with a “sheaf-of-wheat” morphology as shown in Fig. 3. The sheaf-of-wheat hydration products are most likely a form of C–S–H or of silica-poisoned calcium hydroxide, and are also seen in samples of  $\text{C}_3\text{S}$  and portland cement under the same conditions [10, 12, 18–20]. After initial formation, the morphology of the hydration products does not change further within the first 2 h after mixing. Activation of slag by potassium hydroxide in a solution saturated with respect to portlandite and gypsum produces

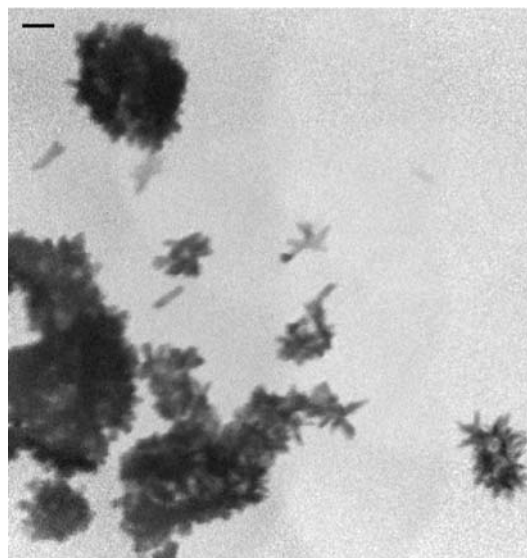


**Fig. 3** Slag in water saturated with  $\text{Ca}(\text{OH})_2$  and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , 23 min. after mixing, scale bar = 1  $\mu\text{m}$

similar hydration products, Fig. 4, but the fibrils are thicker in this case.

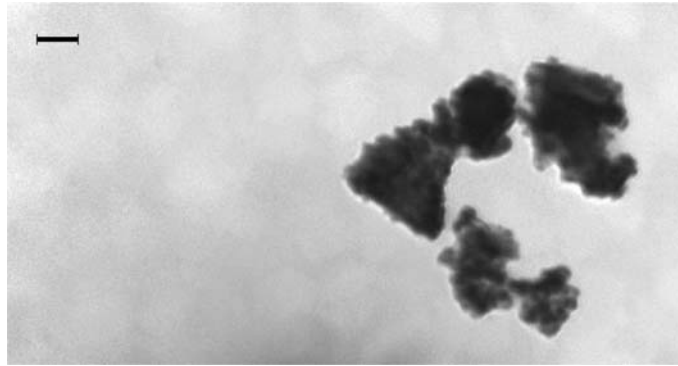
Figure 5 shows an image of slag grains suspended in a solution saturated with gypsum only. The hydration products around this grain have a strikingly different appearance than in portlandite-saturated solutions, exhibiting a “globular” morphology. As in the previous cases, there is no change in the first 2 h after mixing. After the 50:1 gypsum-saturated slag suspension had been rotated at 8 rpm for a total of 5 h, there appeared to be more globular hydration products, indicating continued hydration (Fig. 6a). However, these products quickly transform after approximately 30 minutes in the sample cell, leaving angular hydration products around unhydrated grains (Fig. 6b).

The hydration products of slag in solutions containing sulfates are known to be ettringite (AFt) and monosulfoaluminate (AFm) type phases [21], in addition to C–S–H. It is possible that the “globular” products in Figs. 5 and 6a are an amorphous hydrated phase with a chemical composition similar or identical to that of ettringite. An amorphous or colloidal form of ettringite has been postulated to grow in the presence of calcium, sulfate, and hydroxyl ions, such as in the environment of hydrating portland cement at early ages [22]. Globular hydration products were seen forming in this study in solutions saturated with gypsum alone, potassium hydroxide (with and without calcium hydroxide) and potassium sulfate with gypsum. That these globules transform to plate-like crystals further indicates that they may be a sulfate-containing phase and not a calcium silicate phase. The plate-like crystals are most likely monosulfoaluminate.

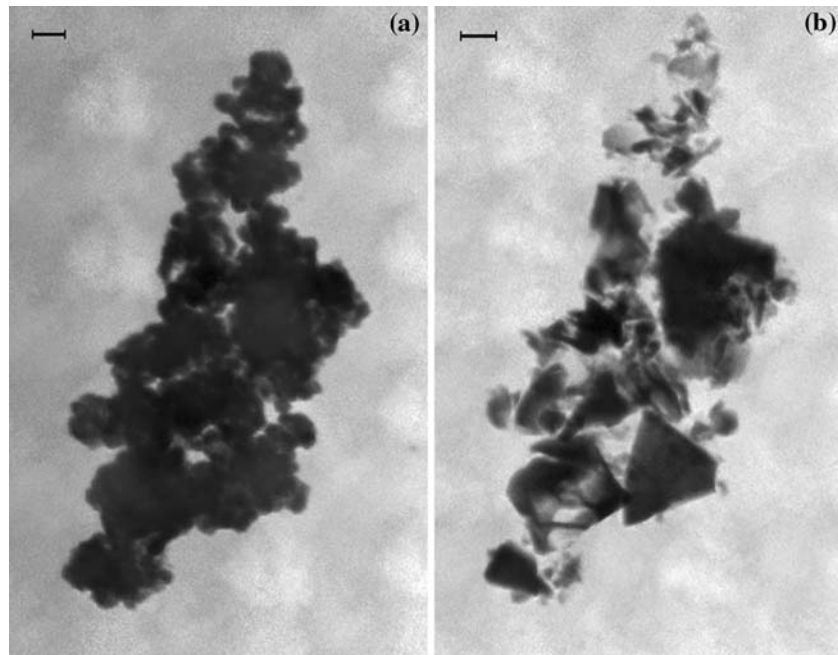


**Fig. 4** Slag in 0.4 M KOH solution saturated with  $\text{Ca}(\text{OH})_2$  and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , 77 min. after mixing, scale bar = 1  $\mu\text{m}$

**Fig. 5** Slag in water saturated with  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , 32 min. after mixing, scale bar =  $1 \mu\text{m}$



**Fig. 6** Slag in water saturated with  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , rotated continuously for 5 h, scale bar =  $1 \mu\text{m}$  (a) 5 h., 33 min. after mixing (b) 5 h., 56 min. after mixing



Crystalline ettringite is known to transform to monosulfoaluminate when the sulfate ion concentration in solution is low. It is possible that the growth of the “globular” ettringite consumed all of the available sulfate ions within the droplet in the sample cell, causing the ettringite to convert to monosulfoaluminate by reaction with more calcium and alumina dissolving from the slag. This transformation was observed only in water saturated with gypsum or potassium sulfate solutions saturated with gypsum. XRD studies were performed to determine the hydration products present in these systems; these results will be presented next.

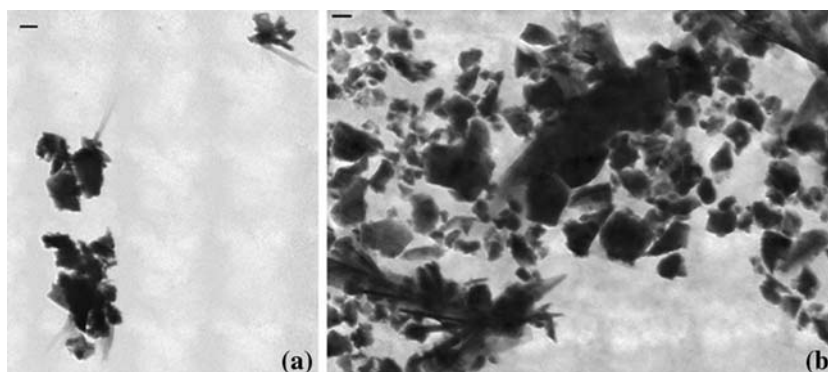
When the slag is hydrated in potassium sulfate solutions saturated with gypsum, crystalline needles, presumed to be ettringite, form in addition to the globular hydration products, Fig. 7. The amount of these needles increases with the concentration of potassium sulfate, Fig. 7b.

Figure 8 shows slag grains in a  $0.2 \text{ M K}_2\text{SO}_4$  solution. An amorphous layer of hydration products appears to form around the grains and remain unchanged for the first few hours after mixing. On the basis of images similar to that shown in Fig. 8, it was difficult to discern whether the amorphous regions represented hydration products or simply partial dissolution of the slag grain. ESEM and XRD studies were performed to address this uncertainty. A discussion of these results follows.

#### X-ray diffraction

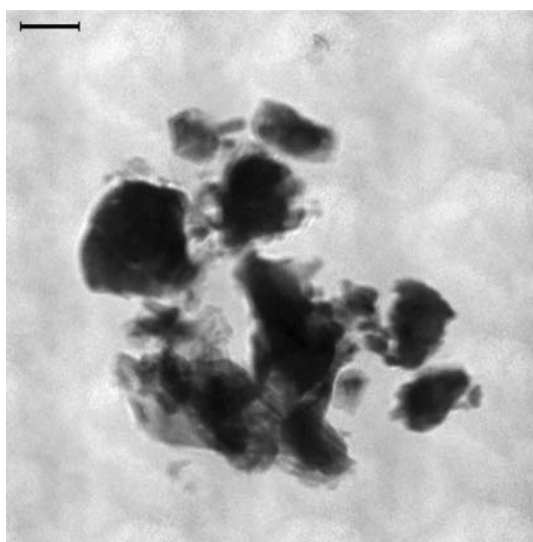
The microscopy studies have given only visual information on the development of hydrated phases in activated slag systems. These data were supplemented with X-ray diffraction analyses (XRD) in order to provide accurate phase identification. XRD was performed on 28-day old pastes of slag in solutions

**Fig. 7** Slag in  $K_2SO_4$  solution saturated with  $CaSO_4 \cdot 2H_2O$ , scale bar =  $1 \mu m$ , (a) 0.05 M  $K_2SO_4$ , 28 min. after mixing (b) 0.2 M  $K_2SO_4$ , 30 min. after mixing



saturated with gypsum or potassium sulfate with  $w/s = 0.5$ . The only detectable hydration product was ettringite, and this only in the sample made with a saturated gypsum solution. These results suggest that the hydration products seen by soft X-ray microscopy in gypsum-containing samples (Figs. 5–7) may indeed be a form of ettringite, as postulated earlier.

No crystalline hydration products were detectable in the sample made with saturated potassium sulfate solution. The absence of crystalline hydration products cannot be used to conclude that hydration has not occurred. The sample may have hydrated, but the hydration products could be amorphous, such as C–S–H, rather than crystalline; or crystalline phases may be present in such small amounts as to be undetectable by XRD. ESEM was then used to determine if the translucent regions surrounding the slag grains in Fig. 8 represent hydration products.



**Fig. 8** Slag in 0.2 M  $K_2SO_4$  solution, 1 h. after mixing, scale bar =  $1 \mu m$

### Environmental scanning electron microscopy

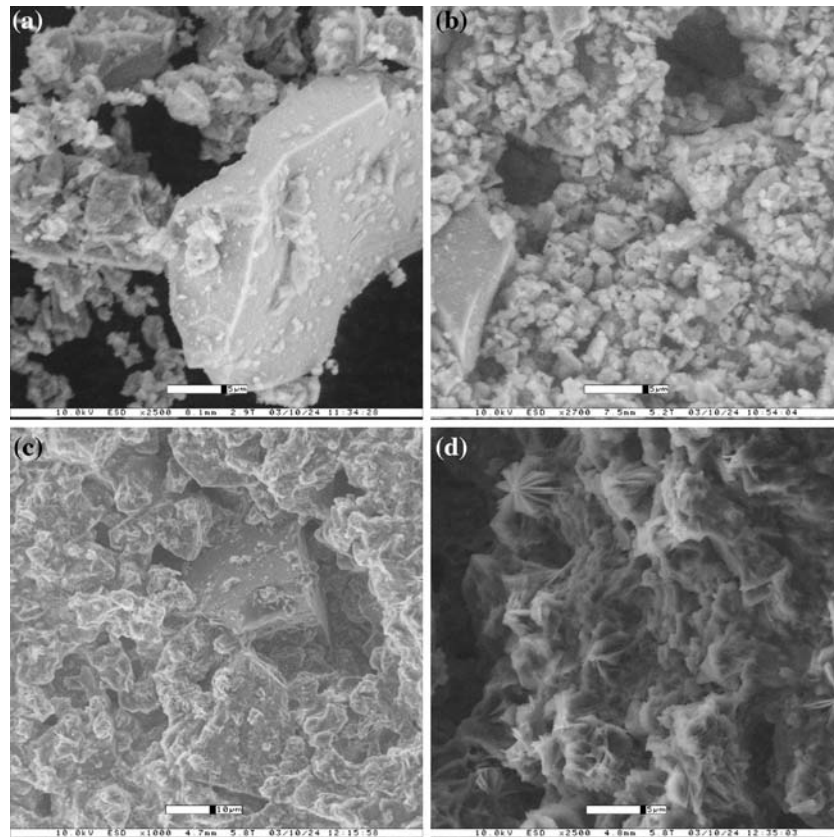
ESEM was performed on slag pastes ( $w/s = 0.5$ ) made with either de-ionized water or with a 0.2 M  $K_2SO_4$  solution to determine whether the soft-X-ray-translucent regions in Fig. 8 represent dissolution of slag grains or hydration products. Results are shown in Fig. 9. Dry slag dusted onto carbon tape (Fig. 9a) appears angular, with a wide distribution of particle sizes. When mixed with de-ionized water, no visible reaction occurs; Fig. 9b shows many small grains that settled on top of larger grains as the surface layer of water was evaporated. As with soft X-ray transmission microscopy, resolution is not sufficiently high to observe an aluminosilicate layer [2].

Potassium sulfate activates slag hydration as noted by the formation of a layer of amorphous hydration products, Fig. 9c and 9d. The amorphous layer confirms that seen by soft X-ray transmission microscopy, represented in Fig. 8. In addition to amorphous product, which is presumably an early-age form of C–S–H, rosette-shaped crystals, presumed to be monosulfoaluminate, appear quickly, Fig. 9d. The microscope was not equipped with energy dispersive spectroscopy, so the identification of the amorphous and crystalline products is based solely on morphology, not composition.

### Conclusions

Soft X-ray transmission microscopy has demonstrated that alkaline activators have a significant effect on the development of hydration products of GGBFS. Calcium hydroxide and potassium hydroxide encourage growth of C–S–H with a sheaf-of-wheat morphology, similar to that seen with portland cement and  $C_3S$ . Gypsum and potassium sulfate, in the absence of calcium hydroxide, result in the formation of globular hydration products that transform to a more angular

**Fig. 9** Environmental scanning electron microscope images: **(a)** dry slag **(b)** slag + de-ionized water, w/s = 0.5, 50 min **(c)** slag + 0.2 M  $K_2SO_4$ , w/s = 0.5, 15 min **(d)** slag + 0.2 M  $K_2SO_4$ , w/s = 0.5, 35 min



morphology with time. These may be an AFt-type phase that later transforms to an AFm-type phase when local supplies of gypsum are exhausted. Crystalline ettringite also forms when potassium sulfate is used as an activator. Potassium sulfate in the absence of gypsum results in the formation of a layer of amorphous hydration products surrounding the slag grains.

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