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# What causes differences of C-S-H gel grey levels in backscattered electron images?

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**Abstract**

Backscattered electron (BSE) images of heat-cured concretes show alite grains surrounded by inner C-S-H gel of two distinct grey levels (referred to as two-tone inner C-S-H gel). The lighter rim forms at elevated temperature whereas the darker rim develops during subsequent exposure to moisture at 20 °C. This microstructural feature can potentially be used as an indicator to assess the curing history of a concrete. However, microstructural examinations of room-temperature concretes containing silica fume or which have been exposed to severe conditions (external sulfate, carbonation) also show distinct rims of two-tone inner C-S-H gel. The chemical compositions of the rims were determined by EDX microanalysis in the scanning electron microscope (SEM). Our results show that for heat-cured samples, the different grey levels of the two-tone inner C-S-H are caused by relative differences in microporosity and water content and not by ones in chemical composition. However, in silica-fume blended concrete, sulfate attacked or carbonated specimens the different grey levels of the two-tone inner C-S-H gel were associated with significant differences in chemical composition. This difference allows two-tone inner C-S-H gel arising from heat curing to be distinguished from that arising from these other causes. © 2002 Elsevier Science Ltd. All rights reserved.

*Keywords:* Calcium-silicate-hydrate (C-S-H); SEM; Microstructure; Backscattered electron imaging; EDX

## 1. Introduction

Extensive laboratory and field studies on damaged concretes cured at elevated temperature have been carried out in the last 15 years [1–8]. This deterioration process, referred to as delayed ettringite formation (DEF), has led to investigations of the influence of high-temperature curing on concrete microstructure [3–15]. In polished sections of pastes hydrated at 80 °C for 16 h and subsequently stored in water at 20 °C, Scrivener [11] observed the presence of alite grains rimmed with two-tone inner C-S-H gel: a light rim formed at high temperature and a dark innermost rim developed during subsequent storage at 20 °C. This darker zone of inner C-S-H gel increases in thickness as the alite grains continue to hydrate. Quantitative X-ray microanalyses (EDX) of the two-tone inner C-S-H gel shows that the lighter zones have higher analysis totals (74–78%) than the darker zones (57–64%). Scrivener suggested that the differences in analysis totals were caused by different degrees of fine porosity in the material, which could be wholly or partly caused by different water contents of the C-S-H gel structure.

Famy et al. [7,16] further investigated different grey levels and corresponding backscattered electron (BSE) coefficients of distinct zones of inner C-S-H gel. Image analysis and EDX microanalysis were used. The mortar specimens were cured at 90 °C for 12 h following a precure period at 20 °C. Two precure periods were studied: 4 h and 28 days. Distinct rims of inner C-S-H gel formed with different grey levels corresponding to the temperatures at which they developed. For instance, immediately after heat curing, the BSE images of the 28-day precured mortars exhibited residual alite grains rimmed with two-tone inner C-S-H gel: a lighter rim of C-S-H gel formed at the higher temperature inside a darker one developed during the precure for 28 days at 20 °C. These two-tone rims exhibit a contrast which is the inverse of that observed in the 4-h precured mortars or in the mortars described earlier by Scrivener [11]. After a subsequent storage in water at 20 °C, the alite grains of the 28-day precured mortars hydrated further, producing a darker C-S-H zone, which developed inside the two rims previously discussed. The BSE images now presented a *three-tone inner C-S-H*

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*gel* (Fig. 1). In these cases, the occurrence of two or three-tone inner C-S-H gel corresponds to the curing history of the mortars and the only compositional difference between the C-S-H zones was found in the sulfate content. However, calculations of BSE coefficients showed that such changes in sulfate content would not result in a noticeable effect on grey level. The authors attributed the different grey levels to a difference in the pore structure and water content.

Since the work by Scrivener [11], the two-tone inner C-S-H gel feature has been widely reported in various investigations of heat-cured ordinary Portland cement (OPC) pastes, mortars and concretes [3–8,12]. However, there is some disagreement as to whether or not two-tone inner C-S-H gel forms in room-temperature-cured specimens. Scrivener and Taylor [3], Lewis [4], Yang et al. [5,6], Famy [7] and Clark et al. [12] observed two-tone inner C-S-H gel only in the heat-cured OPC samples whereas Diamond et al. [17] and Zhang [8] reported its presence in OPC pastes or mortars hydrated at ambient temperature. Diamond et al. [17] and Zhang [8] did not provide any explanation as to what causes this two-tone feature to form at ambient temperature.

Diamond et al. [17] also reported the occurrence of two-tone inner C-S-H gel in a silica fume OPC paste cured at room temperature for 100 days. The lighter and darker C-S-H gels were easier to distinguish than those observed in the ambient-temperature-cured OPC pastes due to a greater difference between the grey levels. No explanation for the occurrence of the two-tone C-S-H was given by the authors. However, it is known that hydration products of alite are affected by the addition of silica fume in silica fume blended concrete. The outer C-S-H gel has a significantly lower Ca/Si atom ratio than those of unblended OPC pastes [18]. It is also likely that silica fume addition can alter the composition of the inner C-S-H gel. In order to interpret the observations of two-tone C-S-H and those of Diamond et al. it is important to understand the origins of grey level contrast of inner C-S-H gel in BSE images.

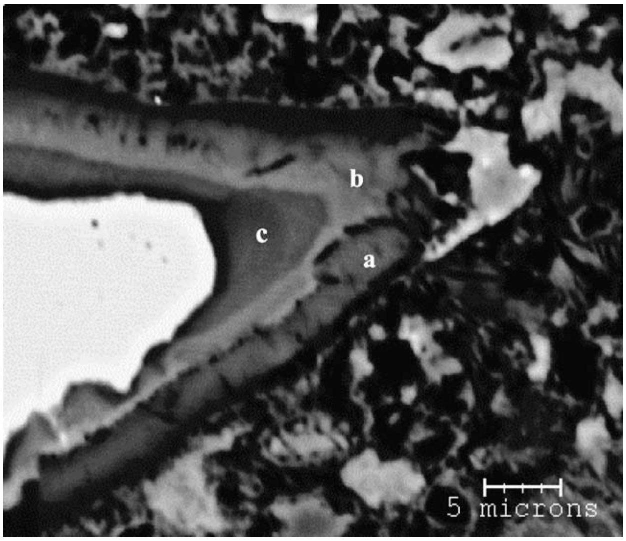

Fig. 1. BSE image of a laboratory OPC mortar precured for 28 days at 20 °C then heat cured at 90 °C for 12 h and finally stored in water for 300 days. Three-tone inner C-S-H rims are observed: an external rim of darker inner C-S-H formed during the 28-day precure at 20 °C (a), a rim of lighter inner C-S-H developed during heat curing at 90 °C for 12 h (b) and a rim of darker inner C-S-H formed during storage at 20 °C (c) [16].

Atomic number is the main factor determining grey level contrast in BSE images. Approximately, the phase with the highest weighted mean atomic number will have the highest BSE coefficient (and therefore the highest grey level) and will appear brightest in the BSE image. However, when other phases are intermixed with the analysed phase on a scale smaller than the interaction volume, these phases cannot be separately observed in the image and they will modify the BSE coefficient. The BSE coefficient is also affected by the microporosity if this is significantly finer than the interaction volume of somewhat below 1 $\mu m^3$ for the BSEs. This microporosity may be inherently present in the material (in its saturated state) and/or created by drying during the specimen preparation and in the high vacuum of the scanning electron microscope (SEM) [16,19,20]. This microporosity cannot be resolved in the BSE image and, depending on how much is present, may significantly decrease the BSE coefficient and therefore the grey level. X-ray microanalyses obtained in the SEM for phases present in anhydrous or hydrated cement phases are conventionally expressed in terms of oxide components. Assuming that standards have been properly used and matrix corrections applied, the totals thus obtained are normally close to 100% less the amounts corresponding to oxide components not determined, such as $H_2O$ or $CO_2$. They should thus be, for example, close to 100% for clinker phases, 76% for $Ca(OH)_2$ and 56% for $CaCO_3$. For C-S-H, values around 76% are commonly obtained [11,14,19,20]. The deficit of 24% is much more than can be reasonably attributed to the water present in the C-S-H exposed to the high vacuum of the instrument [20,21], and therefore microporosity, inherent to the C-S-H, must contribute to this deficit. A correlation between the analysis totals and the local capillary porosity showed that the analysis totals decreased as the local porosity increased [19]. The effects may be due to retardation of the incident electrons by fields resulting from internal charging on the surfaces of the pores [21], but further investigations about their origin are required.

This paper investigates the role of temperature, silica fume addition and exposure conditions (sulfate attack and natural weathering) on the appearance of two-tone inner C-S-H gel in four different samples.

## 2. Experimental

Four specimens were prepared for SEM examination:

- A laboratory OPC mortar cured at 90 °C for 12 h and then exposed to moisture for 500 days at 20 °C.
- A silica-fume blended OPC concrete exposed to moisture for 10 years at 20 °C.

Table 1
Mean atom ratios and analysis totals for the two zones of inner C-S-H gel

| Sample | EDX location | Al/Ca | S/Ca | Si/Ca | Ca/Si | % Analysis totals |
|---|---|---|---|---|---|---|
| A | Lighter inner C-S-H | 0.04 | 0.02 | 0.51 | 1.96 | 75 |
| | Darker inner C-S-H | 0.04 | 0.01 | 0.52 | 1.92 | 65 |
| B | Lighter inner C-S-H | 0.04 | – | 0.55 | 1.81 | 78 |
| | Darker inner C-S-H | 0.04 | – | 0.62 | 1.61 | 70 |
| C | Lighter inner C-S-H | 0.06 | 0.13 | 0.87 | 1.15 | 67 |
| | Darker inner C-S-H | 0.08 | 0.10 | 1.34 | 0.75 | 52 |
| D | Lighter inner C-S-H | – | – | 0.03 | 31.66 | 59 |
| | Darker inner C-S-H | 4.14 | – | 19.63 | 0.05 | 55 |

A, 90 °C-cured OPC mortar exposed to moisture for 500 days. B, A mature silica fume blended OPC concrete. C, 1-year-old OPC concrete exposed to external sulfate attack. D, A mature OPC concrete exposed to natural weathering. Standard errors are ±0.02 for atom ratios and ±1% for analysis totals.

- A 1-year-old OPC concrete damaged by an external sulfate attack at 20 °C.
- A 10-year-old OPC concrete subjected to natural weathering including carbonation.

The four samples were cut into thin slices, which were then freeze-dried to stop further hydration. They were then vacuum impregnated with epoxy resin, lapped to a flat surface with 9 μm alumina and polished successively with 3, 1 and 1/4 μm diamond paste. There was no exposure to heat at any time during the sample preparation. A carbon coating was applied to the polished sections for study by SEM and an EDX analyser. The microscope was operated at an accelerating voltage of 15 kV. The EDX system had been calibrated with oxide standards suitable for cement analyses. Matrix corrections were applied using the ZAF or phi–rho–zi methods. Oxygen was calculated by stoichiometry on the basis of the other elements present.

EDX microanalyses of the different two-tone zones were performed for 10 different hydrated alite grains and average values are reported in Table 1.

## 3. Results and discussion

### 3.1. Laboratory OPC mortar cured at 90 °C followed by a 500-day storage in water at 20 °C

Two-tone inner C-S-H gel has formed within the boundaries of the former alite grain (Fig. 2). The outermost rim of lighter inner C-S-H gel was formed during heat curing at 90 °C while the rim of darker inner C-S-H had developed during subsequent storage at 20 °C. Such two-tone appearance has been extensively reported in the literature [3–8,11,12]. EDX microanalyses of the lighter and darker inner C-S-H rims show that they exhibit similar chemical compositions (Table 1). The Ca/Si atom ratios are 1.92 (±0.02) and 1.96 (±0.02) for the darker and lighter rims, respectively. Such small differences cannot explain the difference in grey levels. The only significant difference is found between the analysis totals as previously reported by Scrivener [11]. The average analysis total for the lighter rims is 75% whereas that for the darker rims is significantly lower at 65% (Table 1). These results strongly suggest that the lighter inner C-S-H gel formed at 90 °C has a lower amount of fine porosity than the darker, inner C-S-H gel.

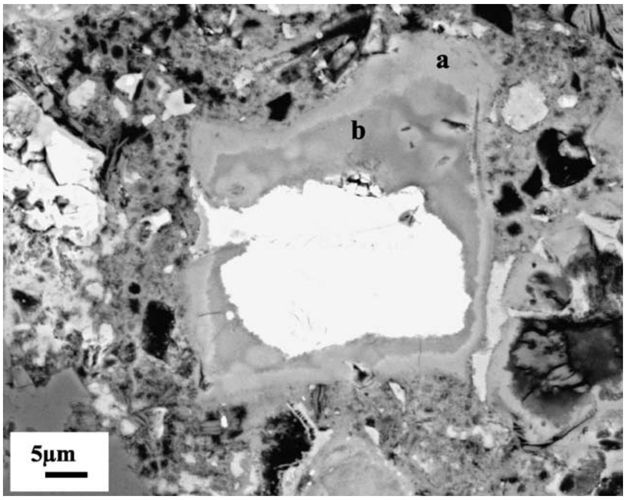

Fig. 2. BSE image of a polished section of a laboratory 90 °C-cured OPC mortar exposed to moisture for 500 days. Two-tone inner C-S-H gel has formed within the boundary of an alite grain. The outermost rim of lighter inner C-S-H gel formed during heat curing at 90 °C (a) while the rim of darker inner C-S-H developed during subsequent storage at 20 °C following heating (b). Residual alite is still present.

### 3.2. Mature silica-fume blended OPC concrete exposed to moisture at 20 °C

The microstructure of the mature silica-fume OPC concrete exposed to moisture at 20 °C exhibits two-tone inner C-S-H gel (Fig. 3). Most of the alite grains have totally

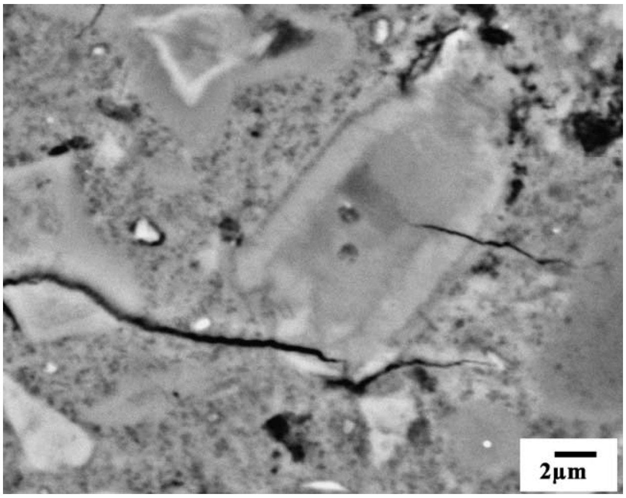

Fig. 3. BSE image of a polished section of a mature silica fume blended OPC concrete. A fully hydrated alite grain can be observed in which two-tone inner C-S-H gel has developed. The internal darker core is richer in silica than the outermost rim.

hydrated leaving an external rim of lighter inner C-S-H gel surrounding a core of darker inner C-S-H gel.

A significant difference is found between the Ca/Si atom ratios of the two C-S-H regions (Table 1). The light zone has a higher Ca/Si atom ratio (1.81 ± 0.02) than the darker one (1.61 ± 0.02), indicating that less calcium enters into the composition of the darker inner C-S-H gel. This difference may be explained by the presence of silica fume, which consumes calcium to form C-S-H. The lighter inner C-S-H, formed at early ages, mainly results from alite hydration while the darker C-S-H core, developed later in a more acid environment due to the presence of silica fume, has a composition appropriate to that environment. There is no significant difference between the Al/Ca atom ratios of the two zones. The analysis totals also show differences but this can be explained by the different Ca/Si atom ratios of the C-S-H zones. In this sample, the difference in grey levels is therefore attributed to a difference in chemical composition between the inner C-S-H zones.

### *3.3. One-year-old OPC concrete damaged by external sulfate attack at 20 °C*

After 1-year exposure to sulfate solution, microstructural features commonly found in concrete attacked by sulfate include the presence of gypsum and of ettringite, zones of dark C-S-H gel in the outer product from which most of the calcium has been lost, and the occurrence of two-tone inner C-S-H gel (Fig. 4).

The external rim of lighter inner C-S-H has a much higher Ca/Si atom ratio (1.15 ± 0.02) than the internal darker inner C-S-H gel (0.75 ± 0.02), which has formed later under different chemical conditions (Table 1). Even the Ca/Si atom ratio of the lighter rim is significantly lower than that typically found in inner C-S-H of $C_3S$ or OPC pastes [3–5,18,19]. This indicates that calcium has been leached out from the lighter inner C-S-H gel to the surrounding matrix where it reacts with the sulfate to form extensive deposits of gypsum and ettringite. Therefore the distinct grey levels observed result from different Ca and Si contents; however, the large difference in analysis totals suggests a contribution due to differences in microporosities within the inner C-S-H zones.

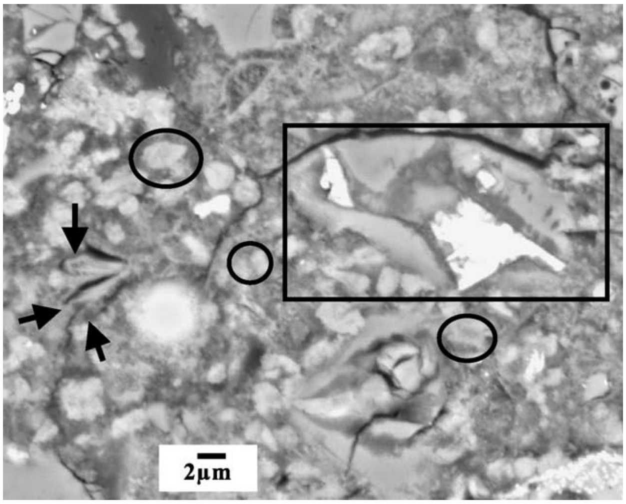

Fig. 4. BSE image of a polished section of a 1-year-old OPC concrete exposed to external sulfate attack showing two-tone inner C-S-H gel (rectangle). A large amount of calcium has been leached out from the inner zone of the C-S-H gel and participates in the formation of gypsum (circles) and ettringite (arrows) dispersed within the paste.

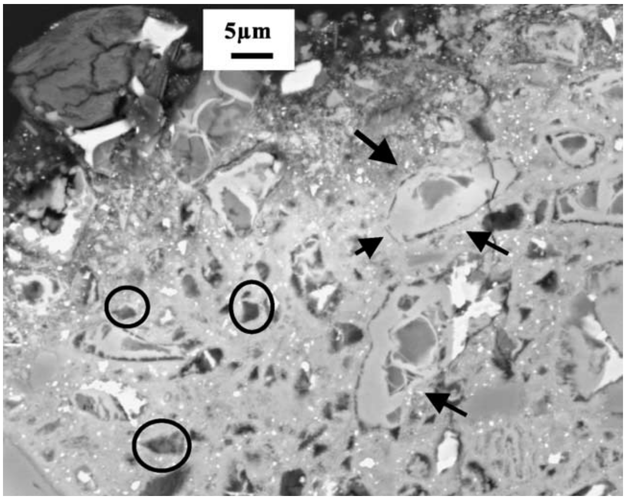

Fig. 5. Low magnification BSE image of a polished section of a mature OPC concrete exposed to natural weathering showing the depth of attack. The surface (top, left) forms a dark layer indicating that calcium has been heavily leached out from the hydration products as a result of severe carbonation. At greater depths, there is a large number of fully hydrated alite grains exhibiting either a totally dark core (circle) or a two-tone (arrows) inner C-S-H gel of different composition as a consequence of the attack.

### *3.4. OPC concrete subjected to natural weathering including carbonation*

In an examination of a mature OPC concrete exposed to natural weathering, a large number of grains consisting of two-tone inner C-S-H gel were observed (Figs. 5 and 6a). This concrete represents an extreme case of carbonation and shows extensive regions that have been damaged. The dark grey external surface shown in the top of the image of Fig. 5 has been seriously attacked and contains almost no calcium. At greater depths from the external surface, the outer C-S-H product has been replaced by calcium carbonate[1]. The smallest alite grains are completely hydrated and appear totally dark in the BSE images (regions circled in black in Fig. 5). X-ray microanalyses show that only traces of

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[1] Carbon, a light element, is difficult to quantify by EDX. However, a comparison of the carbon peaks of an alite grain with the phase studied allows one to determine if carbon, other than that coming from the carbon coating, is present in the given phase. Both analyses need to be made under identical conditions (kilovolts, current, time) [22].

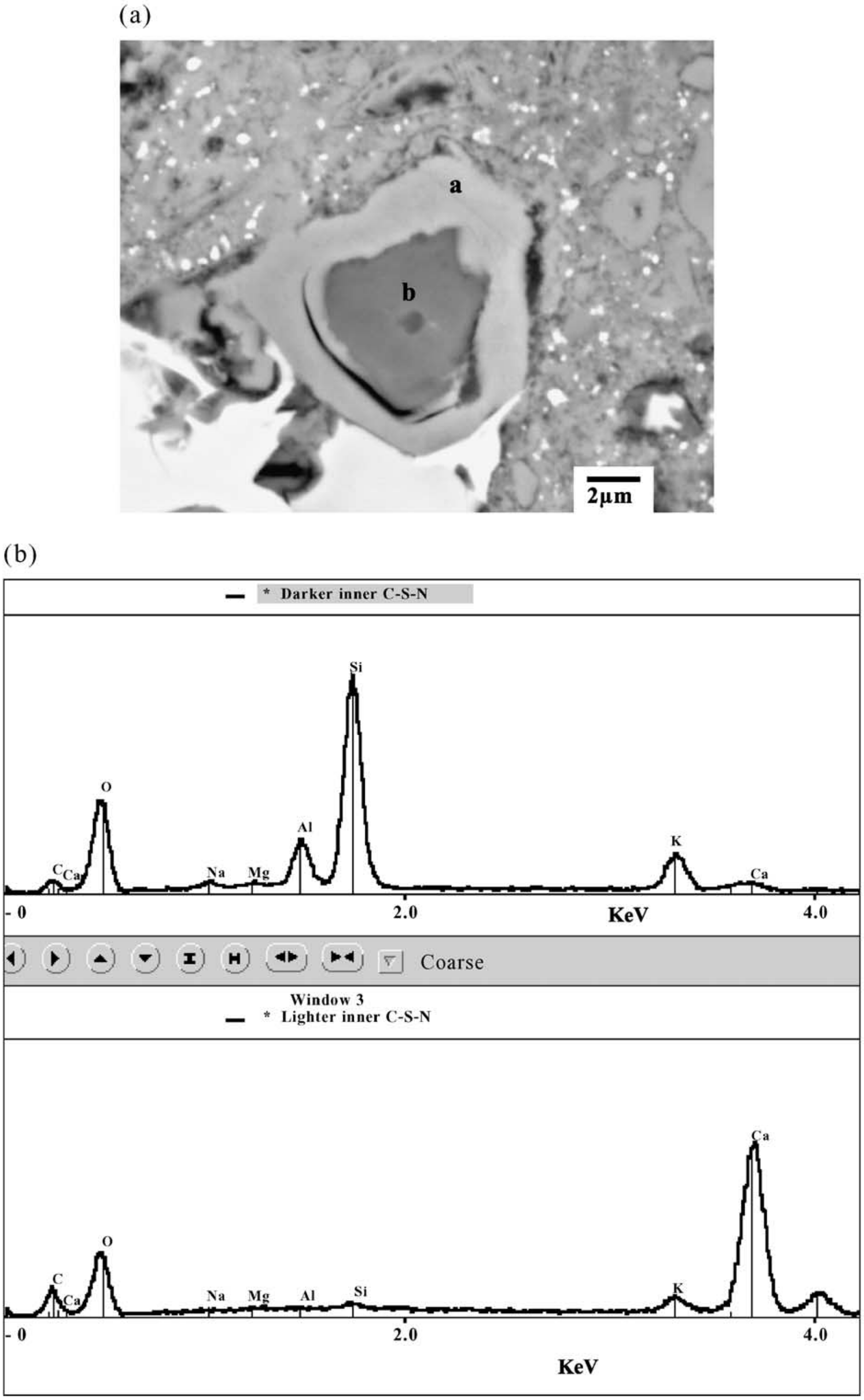

Fig. 6. (a) Higher magnification BSE image of a two-tone inner C-S-H gel present at greater depths in the mature OPC concrete exposed to natural weathering (Fig. 5). (b) X-ray microanalysis spectra of the lighter (a) and darker (b) inner C-S-H shown in Fig. 6a. Most of the calcium has been lost from the darker inner C-S-H gel leaving a darker core of silica gel. The lighter inner C-S-H is essentially calcium carbonate indicating that the sample has been severely carbonated.

calcium are detected in the dark zones, which are thus seen to consist of silica gel (Table 1).

The alite grains larger than 5 μm have also completely hydrated but these show light and dark zones (Figs. 5 and 6a). X-ray microanalyses of the two zones yielded two distinct spectra (Fig. 6b). The light zone corresponds to calcium carbonate while the darker core is silica gel containing significant amounts of potassium and aluminium. The silica gel has a strong tendency to sorb the potassium present in solution [23]. The carbonation, resulting in the dissolution of CH and the uptake of potassium ions by silica gel, strongly reduces the pH of the solution so that neither alite nor C-S-H is stable. Anhydrous or hydrated aluminate phases may not be stable either, resulting in the uptake of aluminium by the hydrous silica [23]. Again, in this case the difference in grey levels is mainly attributed to chemical changes.

### *3.5. General overview*

From the results discussed in the present paper, it is likely that the two-tone inner C-S-H gel features observed by Diamond et al. [17] in plain OPC or silica fume pastes and in plain OPC mortars hydrated at 20 °C are a consequence of chemical changes due to either the presence of silica fume or carbonation arising during specimen storage. Also, a closer examination of the experimental conditions which Diamond et al. used to prepare the sample shows that the specimens have undergone several stages involving drying and heating. They were also initially immersed in acetone for 6 h [17] or 3 days [8] before oven drying at 105 °C (for at least 8 h) to remove the free water. After being vacuum-resin impregnated, they were placed in an oven at 70 °C for 2 h [17] or between 8 and 10 h [8] to accelerate the polymerisation of the epoxy resin. These specimens have evidently been exposed to elevated temperature—with durations of curing and maximum temperatures similar to those of samples that have been deliberately heat treated. The possible effects of such treatments need further examination.

## 4. Conclusions

Hydration products showing zones of distinct grey levels have been observed in both heat-cured and ambient temperature-cured OPC mortars and concretes. The different grey levels in BSE images have been shown to result from different factors:

- In the heat-cured specimen, the two-tone inner C-S-H gel is mainly caused by a difference in microporosity and water content: the lighter inner C-S-H gel has a lower amount of fine pores than the darker inner C-S-H gel.
- In concrete containing silica fume and exposed to moisture at 20 °C, the light and dark grey levels are caused by different calcium contents: the lighter zone has a higher Ca/Si atom ratio than the darker one.
- In specimens damaged by external sulfate attack or carbonation the difference in grey levels results from large differences in the Ca and Si contents. In the extreme case of carbonation, all of the calcium in the darker zones has been leached leaving a silica gel; the lighter zones consist essentially of calcium carbonate.

These studies confirm that various factors can cause two-tone C-S-H features in OPC paste microstructures, but show that the effects in heat-cured samples can be distinguished by the absence of abnormally low Ca/Si ratios in the darker zones.

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