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CHLORIDE INGRESS PROFILES MEASURED BY ELECTRON PROBE MICRO ANALYSIS

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ABSTRACT

Traditional techniques for measuring chloride ingress profiles do not apply well to high performance cement paste systems; the geometric resolution of the traditional measuring techniques is too low. In this paper measurements by Electron Probe Micro Analysis (EPMA) are presented. EPMA is demonstated to determine chloride ingress in cement paste on a micrometer scale. Potential chloride ingress routes such as cracks or the paste-aggregate interface may also be characterized by EPMA. *Copyright © 1996 Elsevier Science Ltd*

Introduction

The durability of concrete is closely linked to its permeability, because detrimental processes normally require transport of the attacking agent: sulphate, oxygen, carbon dioxide, chloride, etc. For accelerated lifetime assesements of the concrete material, modelling of the transport process must be performed.

This paper describes some measurements of chloride ingress in cement paste. The chloride ingress has been followed with an untraditional measuring technique: Electron Probe Micro Analysis (EPMA). Chloride ingress profiles of three cement pastes were measured, ranging from a high water-cement ratio paste with a capillary continuous pore structure to a high-performance cement paste with a discontinuous pore structure.

Traditional measuring techniques and transport models used do not apply well to high performance cement pastes. However, this paper shows that EPMA is a valuable tool for following chloride ingress in such cement pastes. To our knowledge EPMA has not previously been used with success for this purpose. This paper emphasizes sample preparation and the application of the measuring technique.

Experimental Details

Materials and Mixing. Rapid-hardening white Portland cement with a Blaine fineness of 410 m^2/kg was used. Phase composition (weight%) measured by quantitative x-ray diffraction: C_3S: 75.0 ± 1.4, C_2S: 19.8 ± 1.2, C_3A: 3.4 ± 0.2, C_4AF: 0.0, $C\bar{S}$: 1.8 ± 0.5.

Silica fume with a specific surface of 21 m^2/g (determined by single-point N_2 sorption BET) was used. Chemical composition (weight%): SiO_2: 89.9, Fe_2O_3: 0.59, Al_2O_3: 1.17, MgO: 1.67, SO_3: 0.56. The silica fume was added as a dry powder.

The superplasticizer was a napthalene based dry powder, and was added at a rate of 1.0% by weight of cement + silica fume. No superplasticizer was added at w/c = 0.7: the water was demineralized.

The ingredients were mixed for three minutes in an epicyclic laboratory mixer.

Preparation of Samples. A total of nine samples were made: six for chloride ingress and three for reference.

Reference samples. Three different cement pastes were produced: 1) w/c = 0.7, 2) w/c = 0.3 with 20% silica fume addition and 3) w/c = 0.3 with 20% silica fume addition. The mix water of sample 1 and 2 contained 3 weight% NaCl, whereas sample 3 was not exposed to chloride at all. The pastes were hardened at room temperature for 1 month in Ø50 mm plastic bottles stored in a humidistat. During the first 24 hours after mixing the pastes were rotated in order to avoid bleeding.

Chloride ingress samples. Two sets of three different cement pastes were produced: 1) w/c = 0.7, 2) w/c = 0.3 and 3) w/c = 0.3 with 20% silica fume addition. The pastes were hardened at room temperature for 1 month in Ø50 mm plastic bottles stored in a humidistat. During the first 24 hours after mixing the pastes were rotated to avoid bleeding. Following prehardening for 1 month the plastic was removed and the samples transferred to humidistats with 3 weight% NaCl solutions at 5 and 40°C (synthetic seawater). The cement paste samples were kept in the solutions for 1 month. The solutions were renewed after 2, 5, 7, 14 and 23 days. The Na^+ and Cl^- concentration of the solutions were monitored by flame emission (Na^+) and by chromatography (Cl^-). Within the detection uncertainty (app. 10%) no change in the Na^+ and Cl^- concentrations of the solutions were observed.

Approximately 10 mm thick slices were cut from reference and chloride ingress samples. The slices were cut near the middle of the cylindrical samples, parallel to the direction of chloride ingress. The slices were dried over fresh silica gel for two weeks.

The slices were cast in epoxy resin and polished to a surface roughness of <1 μm. To minimize alteration to the chloride distribution of the samples, no water was used during sample preparation (cutting and polishing). Cleaning of the samples was done with trichloroethane spray followed by ultrasonic rinsing in acetone. The samples were finally sputter coated with a conductive carbon layer.

Instrumentation. A Cameca SX51 EPMA instrument equipped with four wavelength dispersive spectrometers was used for the chloride profile measurements. An accelerating voltage of 20 kV and a beam current of 20 nA was used. At these conditions the volume of sample analyzed is roughly 1-2 μm^3 for each point.

EPMA only measures the total amounts of selected elements. The EPMA technique does not give information about how the detected chlorine is chemically held. For cement paste systems chlorine, added as chloride, persists and that measured by EPMA can reasonably be referred to as chloride.

The EPMA measurements were performed in two different ways:

Qualitative measurements. Most of the measurements were performed as qualitative line scans, typically with 1000 analyzed points. The results from the qualitative measurements are given as x-ray "counts" of chlorine. The x-ray counting time is 1 second per point.

Quantitative measurements. Quantitative measurements are more time consuming than qualitative measurements, requiring 30 seconds per point. In order to perform quantitative measurements all significant elements present in the sample have to be analyzed. In the present study Cl, Ca, Si, Al, Fe, S, Na, Mg and Ti were included. The counts for each element are corrected with a complex formula which takes into consideration: 1) absorption of x-rays, 2) backscattering of electrons and 3) fluorescence. The corrected counts need to be calibrated with a standard of known composition. The results from the quantitative measurements are given as weight percent of chlorine.

Results

Application of EPMA. Quantitative measurements were performed on one chloride ingress sample and one reference sample with chloride in the mix water. These measurements were compared with the known amount of chloride in the reference sample as well as the qualitative measured profiles. As often observed, the weight percentages given by the quantitative measurements and the counts given by the qualitative measurements are close to proportional. This check shows that no major errors are introduced by using qualitative data. All data presented in the following are based on qualitative measurements: minor deviations from proportionality between uncorrected counts and quantitatively determined weight percentages are neglected. As demonstrated in the following figures inherent inhomogenities in the cement pastes have an overriding influence on the numerical values of individual determinations.

Paste Inhomogenities. The measured chloride profiles are not smooth curves; a number of different factors cause fluctuations on the profiles. Figure 1 shows an example of a measured chloride profile with EPMA.

Data in Figure 1 exhibit a large scatter. By performing a line scan (not shown) with 1 μm between each measured point it was noted that the scatter occurs on a micrometer scale. This type of short-range fluctuation is probably related to the very small volume of sample analyzed at every point, roughly 1-2 μm^3. The analyzed volume may accidentially include a precipitated NaCl crystal in a pore or may include unreacted cement clinker. Inhomogenities on a micrometer scale will inevitable exist in a cement paste. In order to smooth the curves, averaging is necessary: Figure 2 shows a measured EPMA line scan where a rolling mean ±0.25 mm around each point has been calculated. This averages out the mesoporosity and occluded precipitates, without losing detail.

In Figure 2, 1000 points have been measured from 0-4.2 mm and a further 1000 points from 4.2-25 mm. Thus calculated average counts in the range 0-4.2 mm are based on 5 times as many points as in the range 4.2-25 mm. Despite this, the average curve shows the same type of mm-scale fluctuations in the range 0-4.2 mm as in 4.2-25 mm. The observed long-range fluctuations are, therefore, not due to the same cause as the previous mentioned short-range fluctuations. Local variation in water-cement ratio is a possible explanation of mm-scale fluctuations. For the paste in Figure 2, w/c = 0.7 is only an average. A local zone with a low water-cement ratio will have a low chloride content because it is less porous; with a

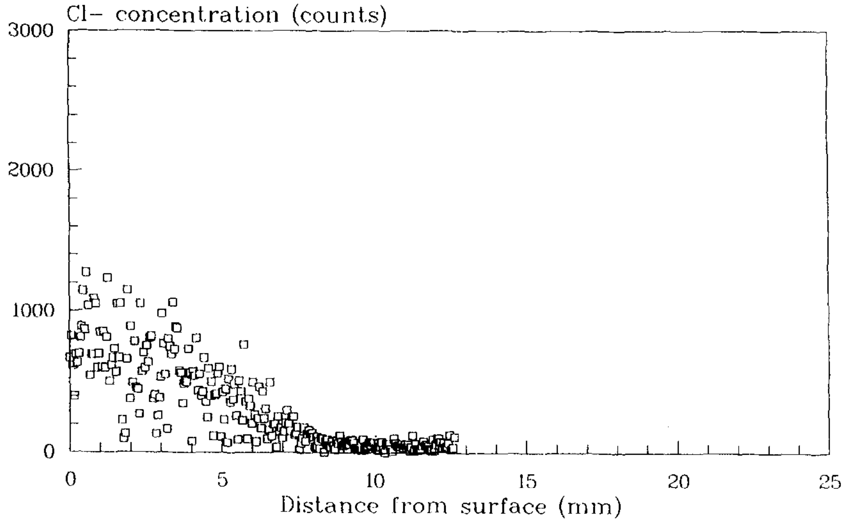

FIG. 1.
Chloride concentration profile as determined by an EPMA line scan with 250 measured points (app. 50 μm between each measured point). The cement paste has a water cement ratio of 0.30. It has been exposed to a 3% NaCl solution for 1 month at 40°C. The center of the cylindrical sample is situated 25 mm from the surface.

fixed chloride concentration in the pore water, the chloride count can change from 800 to 1200 if the water-cement ratio changes from 0.55 to 0.85, cf. Figure 2.

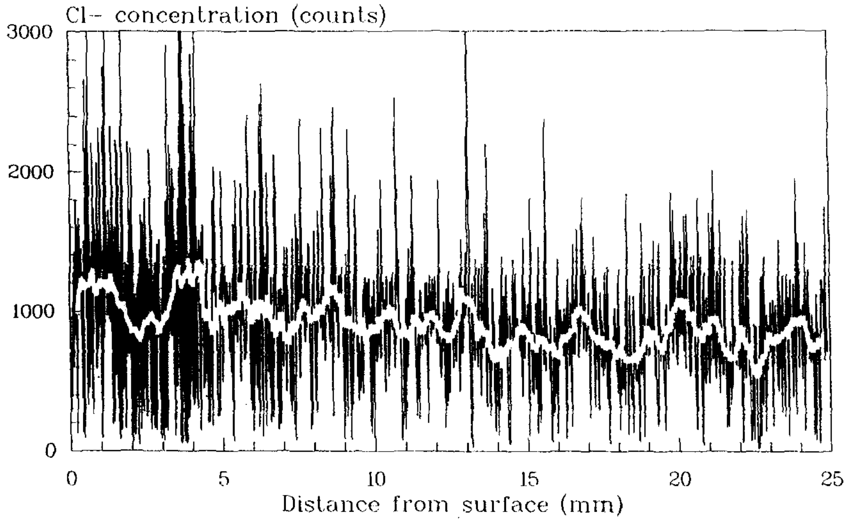

FIG. 2.
Chloride concentration profile as determined by an EPMA line scan. The broad line (white) is a calculated rolling mean ± 0.25 mm around each measuring point. The water cement ratio is 0.70. The paste has been exposed to a 3% NaCl solution for 1 month at 40°C.

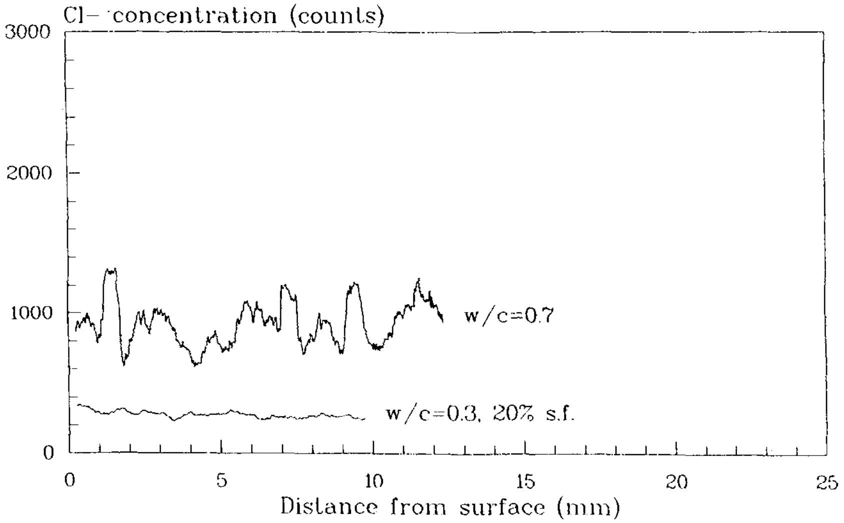

FIG. 3.

Chloride concentration profiles in the reference samples which contain 3% NaCl in the mix water. The graph for the paste at w/c = 0.7 is based on one line scan with 500 measuring points. The graph for the paste at w/c = 0.3 with 20% silica fume addition is an average of two line scans, each with 1000 measuring points.

An observation supports this hypothesis: The reference samples also showed mm-range fluctuations, even though the chloride is homogenously distributed beforehand in the pore water of these samples. Generally, paste inhomogenities are unwanted. By using, for example, a two stage mixing technique (1), a more homogenous paste can be produced.

Disturbance of Profiles. Surface roughness larger than 1 μm may lead to shadowing of emitted x-rays and thereby reduce the number of x-ray counts. Larger scratches may, furthermore, trap particles and polishing material which may be difficult to remove on subsequent cleaning. One of the pastes (w/c = 0.70, chloride exposed at 40°C) was heavily scratched, but the rest were well-polished. The scratches appeared at an early stage of polishing, but could not be removed due to softness of the sample. However, no major differences in fluctuations on the chloride profiles are observed between this sample and the rest.

Apart from ingressed chloride there are three additional sources of chloride detected by EPMA. These are:

1) *Chloride in epoxy filled pores.* The epoxy resin used for mounting the cement paste samples contains measurable amounts of chlorine. In some cases this slightly disturbs the profiles; some of the pores in the cement pastes were filled with epoxy resin during vacuum impregnation.

2) *The raw materials.* The cement contains approximately 0.01% chloride and the silica fume approximately 0.08%. A cement paste with 10% silica fume addition, therefore, contains approximately 0.02% chloride from the raw materials. This corresponds to a chloride concentration of approximately 20 counts.

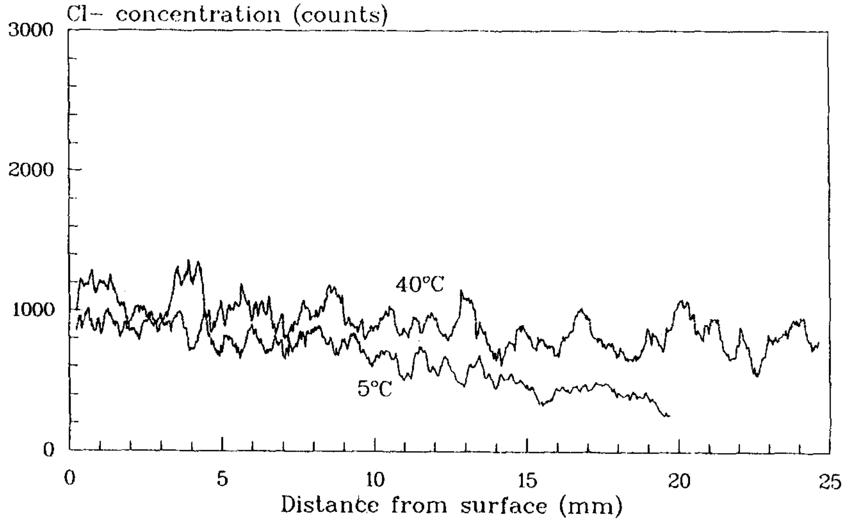

FIG. 4.

Chloride concentration profiles at w/c = 0.7. The paste has been exposed to a 3% NaCl solution for 1 month at either 5 or 40°C. The graph for the 40°C paste is based on two line scans, each with 1000 measuring points. The graph for the 5°C paste is based on one line scan with 1000 measuring points.

3) *Background noise on the EPMA measurements*. A detection noise around 20 counts for an EPMA line scan was encountered in this study. EPMA measurements on the reference cement-silica paste not exposed to chloride showed a chloride content around 50 counts. Half of this amount is due to the raw materials and the other half due to background noise.

Chloride in cement paste may move during sample preparation. The drying process which follows chloride exposure especially is a potential source of such errors. To examine this, three different drying techniques were tested: drying over fresh silica gel, vacuum drying and freeze drying. Two types of measurements were carried out:

1) EPMA line scans parallel to the direction of drying, i.e. perpendicular to the direction of chloride ingress.
2) EPMA line scans parallel to the direction of chloride ingress, but at different depths from the drying surface.

These tests did not show chloride removal due to the drying process. All three drying methods gave identical results.

The EPMA measurement itself may be another source of error. Potentially, chloride may migrate away from the volume analyzed during the EPMA measurement. This question was tested by repeating measurements in the same points; five consecutive measurements of 0.2 seconds were performed in a 1000 points line scan. No systematic change in chloride count was observed within the five measurements. Therefore, within the measuring conditions used in this study, the EPMA measurement does not seem to influence the chloride content in the volume analyzed.

The shorter measuring time did increase random fluctuations slightly. However, this was insignificant comparred to the µm- and mm-scale fluctuations previously described; the "geometric fluctuations" completely overrides the measuring fluctuations.

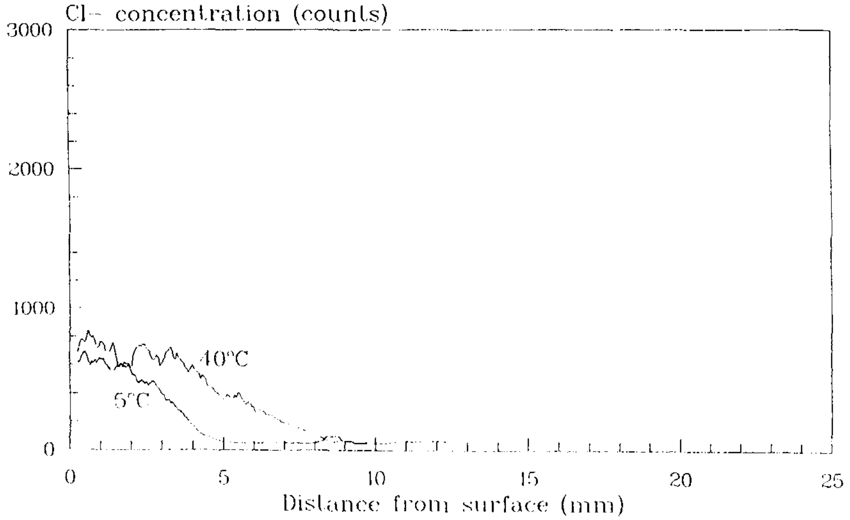

FIG. 5.

Chloride concentration profiles at w/c = 0.3. The paste has been exposed to a 3% NaCl solution for 1 month at either 5 or 40°C. The graph for the 40°C paste is an average of two parallel line scans, each with 250 measuring points. The graph for the 5°C paste is based on one line scan with 1000 measuring points.

Chloride Ingress Profiles and Discussion

The following figures show EPMA chloride profiles for the pastes examined. For the sake of visualisation all graphs have been put on a common scale and calculated as rolling mean ±0.25 mm around each point.

Figure 3 shows the two reference samples with 3% NaCl in the mix water. Figure 4 shows the cement paste at a water cement ratio of 0.7, Figure 5: w/c = 0.3 and Figure 6: w/c = 0.3 with 20% silica fume addition. Apart from the reference samples, two conditions are shown for each cement paste: 1) one month chloride exposure at 5°C and 2) one month chloride exposure at 40°C.

In principle, the profiles for the reference samples should be straight lines at a constant value. As seen in Figure 3 this expectation is achieved, apart from fluctuations, presumably caused by local variations in the water-cement ratio as previously discussed. The average chloride count is higher for the w/c = 0.7 paste than for the paste at w/c = 0.3 with 20% silica fume addition. The mix water of both pastes contained 3% NaCl, hence the paste at w/c = 0.7 contained more chloride.

The profiles for the chloride ingress samples depend very much on the type of cement paste, as shown in Figures 4, 5 and 6. At a water-cement ratio of 0.7, chloride has fully penetrated the sample (Figure 4), while the chloride has penetrated only 5 to 10 mm into the paste at w/c = 0.3 (Figure 5). This is not surprising since the capillary pores of a cement paste at water-cement ratio 0.7 are continuous whereas the degree of connectivity is low at w/c = 0.3 (2). None of the profiles in Figures 4 and 5 are completely controlled by the connectivity of the pore structure since an increased temperature during chloride exposure leads to a deeper chloride penetration: see Figure 5.

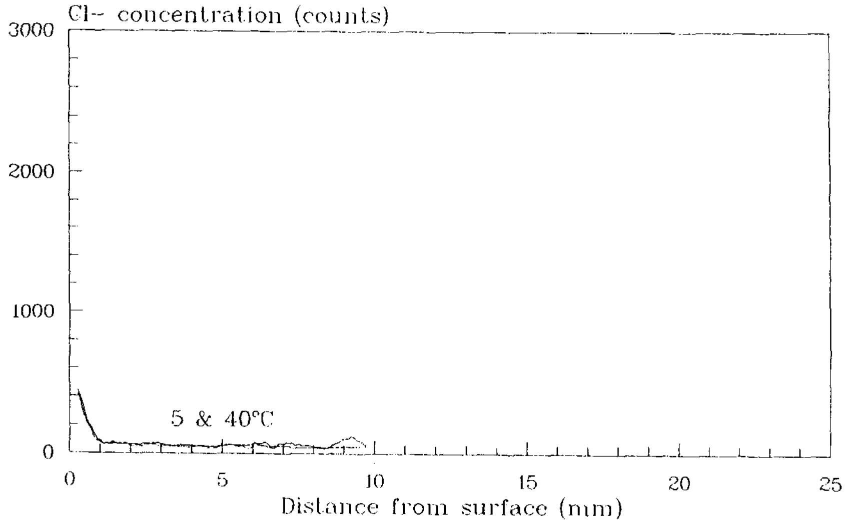

FIG. 6.
Chloride concentration profiles at w/c = 0.3 with 20% silica fume addition. The paste has been exposed to a 3% NaCl solution for 1 month at either 5 or 40°C. The two graphs shown are essentially coincident. Both graphs are based on one line scan each, with 1000 measuring points. The bump on the profile around 9 mm is caused by an epoxy filled pore.

When the pastes contain silica fume, a drastic reduction in chloride ingress is observed; see Figure 6. The chloride ingress is restricted to the outer approximately 1 mm of the cement pastes. Chloride detected at depths greater than approximately 1 mm can be accounted for by: background noise, raw materials and chloride in epoxy filled pores. Both profiles follow the same curve, i.e. the chloride profiles in Figure 6 are independent of temperature. This suggests that chloride penetration is completely controlled by the connectivity of the pore structure and not the transport process. At both temperatures the chloride may have fully penetrated all surface connective pores. For example 0.01 mm from the surface, most of the pores have connectivity to the surface, and are, therefore, chloride saturated. At a depth of 1.5 mm no pores have surface connectivity and chloride will not be able to reach these. For this high performance cement paste it seems that chloride is not able to penetrate deeper than approximately 1 mm from the surface. Probably the silica fume acts as a pore blocker thereby reducing the connectivity of the pore structure.

The chloride ingress in the samples is controlled by two transport processes: diffusion and capillary suction. The effect of capillary suction is most clearly seen in Figure 5. A temperature dependent change in curvature is observed in a depth of 2-4 mm on the two graphs. Capillary suction is a consequence of the pore system being only partly water saturated when chloride exposed; chemical shrinkage of the cement will partly empty the pore system during sealed hardening.

It must be emphasized that the chloride profiles have been measured in uncracked cement pastes, hardened without restraint. High performance cement pastes are known to have a high affinity for shrinkage during hardening (3). During fully restrained hardening such a paste may crack.

EPMA element mapping as shown in Figure 7 may also be an excellent tool for examining the influence of cracks on chloride ingress. The area shown is 1.5 mm^2 and starts from

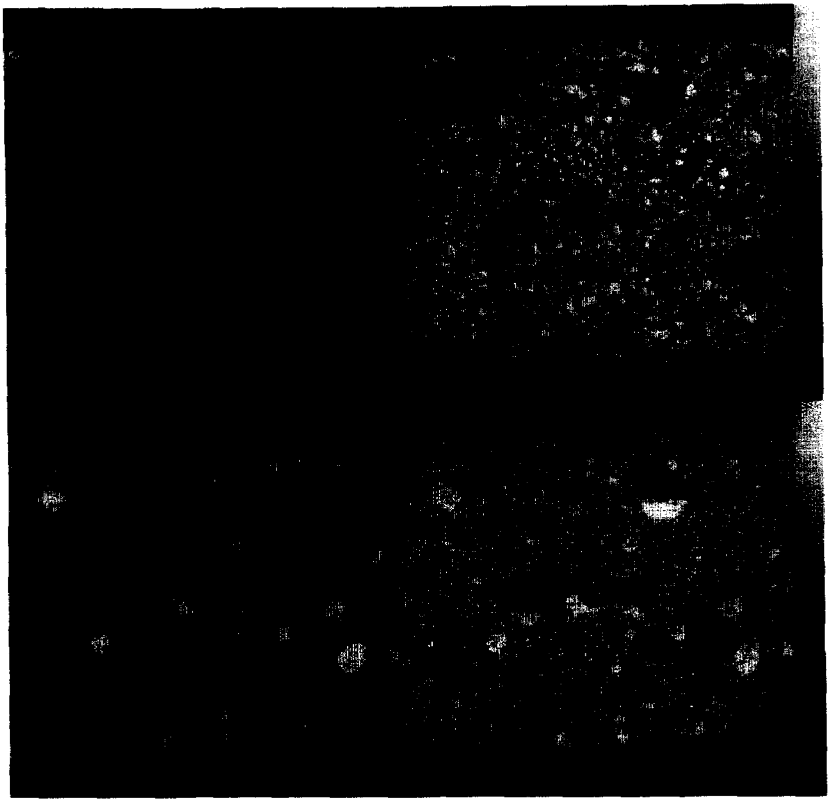

FIG. 7.

EPMA element map of a cement paste at w/c = 0.3 with 20% silica fume addition. The paste has been exposed to a 3% NaCl solution for one month at 40°C. A 1.3 by 1.3 mm area is shown. In clockwise direction from the top left corner each picture shows the concentration of the following elements: Cl, Ca, O and Si. The higher the concentration, the brighter the pixels (see bar scale at the right). The epoxy resin contains chloride as seen in the top of the chloride map. The map is created by measuring 256 by 256 points, each spaced 5 μm. The dimension of each measuring point is approximately 2 μm. The x-ray counting time is 25 ms for each point.

the surface (top) of a chloride exposed sample. In the chloride map it is clearly seen that the epoxy contains chloride, as previously mentioned. The chloride concentration in the cement paste is seen to diminish from the surface inwards.

Comparison of EPMA with Conventional Techniques. At present it is clear that the EPMA technique can give information about chloride ingress which cannot be gained by conventional methods. The EPMA method is especially suitable for studying chloride ingress in high performance cement pastes, where high spatial resolution is required.

Conventional methods for measuring chloride ingress profiles in cement paste systems are based on removing a macroscopic part of the original sample for analysis. The analytical sample can be removed, for example, by 1) drilling a hole and collecting the boremeal, 2) cutting a slice or 3) scraping off material with a lathe. The chloride may be extracted from the collected material with, for example, water or an acid, or by expressing pore fluid.

The analytical methods include titration with $AgNO_3$. Performed in this way it is possible to distinguish between different types of chloride; chloride in cement paste may exist as 1) free chloride, i.e. dissolved in the pore water or 2) bound chloride, either a) adsorbed on the surface of the cement gel or b) chemically combined. Chloride may be bound chemically by formation of new phases or by substitution into existing phases. Mainly the aluminate phases of the cement are able to combine with chloride into Friedel's salt, $3CaO{\cdot}Al_2O_3{\cdot}CaCl_2{\cdot}10H_2O$. The differentiation between free and bound chloride is important because only free chloride moves and actively depassivates steel. More than 50% of the total chloride content may exist as bound chloride (4).

For studying chloride ingress in cement paste systems the EPMA method has advantages as well as disadvantages compared to conventional techniques. Due to the sampling method the geometric resolution of the conventional method is of the order of size 1 mm. In some cases this resolution is insufficient. For example, in a high performance cement paste the chloride profile may level off within the first millimeter from the surface, see e.g. Figure 6. The geometric resolution of the EPMA method is roughly 1-2 μm, making it possible to follow chloride on a very small scale. Furthermore, chloride ingress routes such as cracks or mobility along paste-aggregate interfaces can be characterized by element mapping. This is not possible by the conventional technique. The EPMA method, therefore, is an important tool for studying high performance cement based materials.

As previously mentioned it is important to distinguish between free and bound chloride. This is not possible with the EPMA method, and constitutes a significant draw-back. However, the cement used in the present study has a very low alumina content: according to quantitative x-ray analysis it does not contain any C_4AF, and the C_3A content is 3.4%. The chloride binding capacity of this cement, therefore, is very low. Sample preparation is very laborious for the EPMA method. The process of cutting, drying, embedding in epoxy, grinding, polishing and rinsing is time consuming and all steps involve a risk of unintended chloride migration. However, data collection is very fast - several thousands points an hour - and, because it is non-destructive, the EPMA specimens can be reexamined in the case of errors or used for further studies. The chloride detection limit seems to be around 0.01 weight% for the EPMA method performed in the described way, about equal to the traditional method.

Conclusions

☐ The EPMA method is a very powerful technique for measuring chloride profiles in cement paste. The geometric resolution for the EPMA method is 100-1000 times better than for conventional techniques. This degree of resolution is required for studying high performance cement paste systems.

☐ The disadvantages of the EPMA method include laborious sample preparation and lack of distinction between free and bound chloride. The advantage is that it is non-destructive and selective, enabling short-circuit pathways, e.g. cracks, to be measured.

☐ Chloride profiles are given for three cement pastes which have hardened for 1 month followed by exposure to a 3% NaCl solution for a further month. Two exposure temperatures have been used: 5° and 40°C.

☐ For the cement paste at w/c = 0.7 the chloride penetration has reached the center of the sample, 25 mm from the surface. The capillary pore structure in such a cement paste is continuous and the chloride ingress may solely be controlled by the transport process.
☐ The chloride has only penetrated the first one mm of a high performance cement paste with w/c = 0.3 and 20% silica fume addition. The chloride profiles seem to be solely controlled by the connectivity of the pore structure.
☐ For the cement paste at a w/c = 0.3 without silica fume it is suggested that the chloride penetration is controlled partly by the transport process and partly by the connectivity of the pore structure.

Acknowledgement

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