A Review of Recent Applications of EPMA to Evaluate the Durability of Concrete

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Abstract

Electron probe microanalysis (EPMA) is a promising method for the evaluation of various kinds of material transport and phase changes. It can be used for the accurate estimation of the diffusion coefficient in concrete and for the verification of advanced models describing the material transport of various elements because of its ability to measure elemental distributions with a high spatial resolution. Recently, a quantification method of element concentration by EPMA was introduced and a standard for the methodology including sample preparation was established by the JSCE. However, the device and methodology are still under development. Therefore, it is worthy to review the application of EPMA for concrete. The basic configuration and principle of EPMA, characteristic examples of applications for the durability of concrete, techniques and problems related to methodology, and the future of this method are covered and discussed in this paper.

1. Introduction

With the change of design methods of concrete structures from standard specifications to performance based specifications, various advanced studies estimating the durability of concrete structures have been carried out. For example, steel corrosion in concrete by chloride in marine environments is now estimated by using Fick’s second law with an apparent diffusion coefficient (JSCE 2002, JSCE 2005-1). To improve accuracy in this field, complicated and advanced models have been proposed to simulate the movement of various elements in concrete (Tang and Nilsson 1997, Bentz and Garboczi 2001, Maekawa and Ishida 2001, Johannesson et al. 2005, etc.).

These advanced models can predict the movement of various elements theoretically. Measurement of the distribution of elements is important to verify the results of prediction, and electron probe microanalysis (EPMA) is an analysis method that allows the quantitative area analysis of elemental concentrations with a high spatial resolution and sensitivity on a solid surface.

Conventionally, element distribution measurement results have been displayed as color-mapped images using a color scale, giving users an excellent visual grasp of element distributions. The first application of color mapping in the field of concrete technology was a study by Kobayashi et al. (1988-1, 1988-2) displaying the movement and accumulation of sodium and chloride ions by carbonation at the carbonation front. After this excellent study, EPMA applications were developed, mainly in Japan. Rising computing power has enabled the use of numerical data for quantification in many ways. One example is the use of chloride concentration distribution data to estimate the diffusion coefficient. In order to make EPMA measurements reliable in the field of concrete engineering, a draft standard was established by the Japan Society of Civil Engineers (JSCE-G574-2005). This standard specifies the method of sample preparation, standard samples for quantification, measurement procedures, and the typical approach to numerical calculation (JSCE Standards 2005-1, JSCE 2006). An English version is currently under preparation by the JSCE.

The methodology of EPMA is still evolving. Mori et al. (2006) reported the scientific background of quantification of chloride in concrete for area analysis. There are some other advanced applications of EPMA based on EPMA performance and function improvements. However, there is no appropriate literature indicating the present state and the future trend of EPMA. This paper addresses this lack by reviewing a number of recent applications and explaining the basics of EPMA as well as various challenging aspects of EPMA. Referral to appropriate textbooks (JEOL 1983-1) or original papers for an understanding of the details of EPMA itself and quantitative information or analysis procedures is recommended.

2. Configuration and principle of EPMA

This chapter outlines the configuration of EPMA and describes the factors affecting the accuracy for quantification of elemental distribution in concrete from the principle of EPMA. There are intrinsic factors for concrete as well as common factors shared by all materials. The factors that are important for concrete analysis are explained mainly here. Other detailed principles, general remarks of EPMA and applications for materials other

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2.1 Configuration of EPMA and analyzing methods

EPMA was invented in France in 1956 and has a history of more than 50 years. Nowadays, the typical apparatus is equipped with 4 or 5 spectrometers for the simultaneous analysis of several elements. Repeated measurements are required in the case of a larger number of elements. There are two types of X-ray spectroscopy. Wavelength-dispersive spectroscopy (WDS) involves spectroscopic measurement of characteristic X-rays by diffraction using a dispersion element, and energy-dispersive spectroscopy (EDS) measures the energy of characteristic X-rays as electrical signals using a solid-state semiconductor detector. For EPMA, WDS is used because of its high sensitivity. The major differences between WDS and EDS are the energy resolution and peak-to-background (P/B) signal ratio in the detection of X-rays. WDS has a better energy resolution and P/B ratio and therefore is more suitable for the measurement of minor elements in concrete, such as chloride ions and alkalis, than EDS. WDS has a 10 to 100 times higher sensitivity than EDS, which enables much faster mapping to element distribution (SSSJ 1992-2). Usually, EDS does not have quantitativity for minor elements such as alkalis of less than 1 mass%. One reason of the poor quantitativity of EDS lies in its lower energy resolution for characteristic X-ray. EPMA is also equipped with an automated precise sample stage of 10 cm plate size. The accuracy of repositioning is on the order of 1 µm.

The basic configuration of EPMA is shown in Fig. 1 (JSCE Standards 2005-1, JSCE 2006). The figure may be complicated for general engineers and scientists in the field of concrete technology. It is difficult to explain the details in this review and referral to technical book (JEOL 1983-1) is recommended. Under vacuum, a convergent electron beam called an electron probe is irradiated on the surface of the specimen and a spectrum of characteristic X-ray corresponding to the kinds of elements composing the surface is generated. The spectrum is analyzed with a wavelength-dispersive spectrometer and the intensity of the peak of objective element is quantified by an X-ray detector. Accurate characteristic X-ray intensity can be measured by attaching an electron probe. By scanning the electron probe or moving the sample stage, line or map images of element concentration corresponding to the wavelength of characteristic X-ray can be obtained. In this case, because of limited measurement time and statistical variation of characteristic X-ray, the quantitative accuracy of each point is limited.

Map analysis of concrete is mainly carried out for a sample on the order of 1 cm. In this case, a stage scan method is used. For example, when the diameter of the electron probe is set to 0.1 mm and a sample of 40 x 40 mm is measured with an interval of 0.1 mm, X-ray intensity data from 400 x 400 pixels are obtained. Using up-to-date apparatus, this analysis takes a few hours. The data is sent to a data processor and a map image is displayed. In a data processor, the data of X-ray intensity are processed to the element concentration. The quantification for mapping is usually carried out by using a calibration curve. The details are described in an appendix of JSCE-G574-2005. When the area size of interest is less

![Fig. 1 Configuration of EPMA.](image-url)
than 100 µm, the beam scan method is used instead of the stage scan method. The spatial resolution of EPMA is 0.1 µm to 1 µm depending on the type of electron gun, accelerating voltage, and probe current. When an electron probe is attached at the same position, elemental composition in a small point can be quantified. When the sample is non-porous material, theoretical calculation methods such as ZAF method can be used. However, porous material and hydrates are unsuitable for these methods. Minor elements such as chloride or alkalis can be quantified by using appropriate calibration curves.

### 2.2 Factors affecting the accuracy of quantification of concrete

**Figure 2** shows a schematic diagram of spectrography of characteristic X-ray by WDS. At position S, where an electron probe is injected, characteristic X-ray is generated and analyzed by a dispersion element to the characteristic wavelength and is isolated only to the wavelength corresponding to the element of interest. Then, the intensity of isolated X-ray is quantified by an X-ray detector. S, a dispersion element, and an X-ray detector are arranged on a circumference with a radius of \( R \) called Roland circle. Assuming the distance between S and a dispersion element as \( l \) and the incidence and reflection angles of X-ray to the dispersion element as \( \theta \), the mutual correlation is described as Eq. (1) (JEOL 1983-2).

\[
\frac{d}{\sin \theta} = n\lambda
\]

where
- \( d \): lattice plane interval of a dispersion element
- \( n \): reflection index
- \( \lambda \): wavelength of X-ray.

By Eqs. (1) and (2), Eq. (3) is obtained.

\[
l = \frac{R}{d}n\lambda
\]

By Eq. (3), when \( n \) and \( d \) depend on the characteristics of a dispersion element and \( R \) is constant, \( l \) is determined by the wavelength \( \lambda \) of characteristic X-ray corresponding to the target element. Based on this theory of spectrography of WDS, the surface of sample must be controlled at position S. Usually, the sample stage moves horizontally and the surface of the sample must be set parallel to the moving plane. A sample of concrete has a size of several cm to 10 cm square and the surface must be ground to be flat. The difference in surface height and size of several cm to 10 cm square and the surface must be parallel to the moving plane. A sample of concrete has a horizontally and the surface of the sample must be set perpendicular to the moving plane.

Quantification by EPMA is based on a simple rule: the intensity of characteristic X-ray is proportional to the probe current. Furthermore, the intensity of characteristic X-ray is proportional to the probe current. Therefore, the stability of the probe current is very important for the quantification by EPMA because mapping requires several hours. Compared to scanning electron microscopes, special attention is required for the electron probe stability. The degree of vacuum in a sample chamber affects the electron probe stability. Because concrete samples are porous and contain volatiles, special attention should be paid to the reduction of gas emissions.

### 2.3 Recent EPMA trends

Recently, advanced electron guns using LaB\(_6\) crystal as the electron emitter or field emission (FE) type electron guns that enable brighter electron probes and dispersion elements with super lattices that enable brighter deflection have been developed. These devices enable higher spatial resolution and sensitivity analysis. As the nature of generation of characteristic X-ray by a convergence electron probe of 100 nm order, the generation volume of characteristic X-ray is a volume of approximately 2 µm diameter when the acceleration voltage is 15 kV, a typical value for the analysis of silicate. **Figure 3** shows 2D simulations of the generation area of characteristic X-ray in SiO\(_2\) at accelerating voltage at 15 and 5 kV. This means that a finer silicate texture with a volume less than approximately 1 µm diameter is difficult to analyze by typical EPMA. At a lower acceleration voltage such as 5 or 8 kV, the volume generating characteristic X-ray decreases. However, using conventional electron guns, it is difficult to obtain a fine electron probe of less than 100 nm and adequate probe current. By using one of the recent FE guns, a fine electron probe suitable for area analysis can be obtained at low acceleration voltage and the spatial resolution is improved to the 0.1 µm order. However, FE guns are sensitive to changes in the degree of vacuum. When a large size sample of concrete is used, it is not easy to maintain a high vacuum and the stability of the FE gun seems limited at this time for general concrete usage, although it is of course useful for analyzing submicrometer texture in a small sample.

Thanks to advances in computation techniques, for
each data point of map analysis, it has become possible to carry out ZAF calibration calculations for more accurate quantitative analysis of the distribution of element concentration. Another interesting technique is phase analysis. Mutual correlations of composing two or three elements are graphically displayed and it is possible to know the phase composing the sample visually.

One important progress in this field is the preparation technique of sample. Figure 4 shows a back scattered electron image (BEI) of the cross section of a particle of fly ash with an image of the Si distribution measured by FE-EPMA. It is not easy to analyze the cross section of fine particles in the range of 1 µm. Conventionally, powders are mixed with resin and hardened as a piece. Then this piece is ground and mechanically polished using abrasives. This method causes some damage to the edge of the particle, as shown in Fig. 4 (right). More recently, an ion beam is used to polish the sample. Although the size is limited to approximately 1 mm maximum, an extremely flat surface and sharp edge of each powder particle of less than 1 µm can be obtained, as shown in Fig. 4 (left). This method is suitable for the evaluation of submicron texture. In this case, a fine particle of fly ash of approximately 3 µm is successfully analyzed by FE-EPMA with a spatial resolution of the 0.1 µm order. A difference in the concentration of silica between mullite crystals and silica matrix was detected.

International activities for the establishment of an ISO standard for surface analysis are under way. ISO-TC202 is currently studying EPMA terminology, general guidelines for quantification and mapping, and applications for various materials.

3. Important points of analysis of concrete by EPMA and data interpretation

3.1 History of the application of EPMA for concrete

Early on in the application of EPMA for concrete, point analysis was a popular method. Kawamura et al. (1982) carried out point analysis for Na, K, Ca, and Si in order to study the reaction mechanism of the alkali silica reaction. Kobayashi et al. (1988-1, 1988-2) introduced area analysis and color mapping in the field of concrete. The redistribution of chlorine and alkalies by carbonation was clearly demonstrated. Later, more applications to analyze changes in elemental distribution have been carried out, e.g. distribution of chloride ions (Cl) and sulfur (S) (Kawahigashi et al. 1992), chemical attack by sulfate salt (Sasaki et al. 1994, Hironaga et al. 2001), dissolution of Ca (Saito et al. 1996), Cl penetration along a crack (Win et al. 2004), and Ca and S movement by sulfate attack (Maltaiz et al. 2004). These analyses are aimed at obtaining visual images of material transport and are effective for the investigation of the mechanisms related to the durability of concrete.

![Fig. 3 Simulation of area generating characteristic X-ray. Left: 15 kV, Right: 5 kV.](image1)

![Fig. 4 Cross section of fly ash by ion beam (FE-EPMA, accelerating voltage=8kV, particle size=3 µm). Left: BEI, center: Map image of Si, right: BEI of mechanically polished sample.](image2)
In some cases, measured numerical data are processed to obtain quantitative results. Kawahigashi et al. (1991) estimated the Cl concentration in concrete by averaging the data measured in the target area. In other cases, Cl concentration profiles have been calculated by averaging data of pixels vertical to the penetration direction of Cl after area analysis. Shiraki et al. (1990) carried out studies for normal concrete, Jensen et al. (1999) for cement paste, and Mori et al. (2002) for fiber-reinforced ultra-high strength mortar.

In order to achieve accuracy and repeatability at a certain level, a working group was organized in a sub-committee for JSCE standards to create a standard for area analysis of concrete by EPMA. The results of the activities of this working group were published as JSCE-G574-2005 “Area analysis method for chemical element distribution in concrete using EPMA (draft)” (JSCE Standards 2005-1, JSCE 2006). This standard regulates special matters that should be taken into account when EPMA is applied for concrete, including sample preparation, the setting procedure of measurement conditions, standard samples, data processing, and the method for obtaining concentration profiles.

### 3.2 Sample preparation

EPMA can measure the element distribution on the surface of material. Therefore, when material transport from the concrete surface is targeted for evaluation, a cutting sample is required. Water is usually used as the grinding solvent for slicing and grinding. However, a cement hardened body is composed of materials that are somewhat water soluble. Thus, when grinding is carried out by using water for an extremely long time, although Ca has low water solubility, unexpected inhomogeneous texture may be detected. Figure 5 shows mapping images of Ca of cement paste that is ground by using water or an organic solvent. When water is used, although the Ca concentration is expected to be homogeneous throughout the paste sample as shown in the case of organic solvent, inhomogeneous concentration of Ca is detected due to some leaching of Ca by water (JSCE 2005-2). This case is an extreme one. Usually, if sample preparation is quick enough, this kind of unexpected inhomogeneous texture is not detected. Regarding water-soluble elements such as alkalis and chloride, special caution is advisable. Alkalis are soluble in acetone and ethanol. Therefore, kerosene is a suitable grinding solvent (JSCE Standards 2005-1, JSCE 2006). When only the obtainment of a visual image is aimed for, a commercial aqueous grinding solvent can be useful for experts. However, if a precise concentration profile is aimed for, preliminary experiments are required to ensure the effect of sample preparation by measuring a sample whose concentration of the target element is known.

Another important point of sample preparation is resin impregnation. Resin strengthens the porous brittle cement paste and reduces gas emission in a high vacuum. Appropriate resin impregnation may be required. One point is the contamination of some elements by the resin. When Cl in concrete is targeted for measurement, Cl free epoxy should be selected. Another point is homogeneous impregnation. For resin impregnation, a sample is set usually in a vacuum and resin is impregnated under some pressure. However, the resin impregnation is occasionally insufficient and inhomogeneous. Wong and Buenfeld (2006) reported on the BEI detection of a patch microstructure caused by inhomogeneous impregnation of resin. This effect has not been evaluated by EPMA quantitatively and further investigation is required.

The minimum requirements for the procedure of sample preparation are regulated by JSCE standard 2005-1. In order to check the effectiveness of this regulation, a round-robin test was carried out by four different institutes. Table 1 summarizes the details of sample preparation (JSCE 2005-3). The measurement results are shown in Fig. 6 (JSCE 2005-4, Mori et al. 2005-1). A concrete block having a water-to-cement ratio of 0.50 was immersed into a 3 mass%-NaCl solution for 3 months. Sliced samples were cut from the same concrete bar and distributed to each institute, where they were processed to samples appropriate for EPMA measurement. As shown in Fig. 6, similar profiles were obtained.
for Cl. When the thickness of the carbon deposited for electric conductivity is too thin, a significant differences from the other institutes were detected, as shown in Fig. 6 (Inst. 1*). This factor is one of the important points mentioned in JSCE 2005-5.

### 3.3 Measurement condition
Concrete material, especially cement paste, is highly susceptible to electron probe irradiation. During electron probe irradiation, some elements, chloride, sodium, and sulfur, suffer damage and the intensity of characteristic X-ray decreases (JEOL 1983-3, JSCE Standard 2005-1, JSCE 2006). Simultaneously, BEI changes as the result of irradiation. Figure 7 shows the same position of cement paste before and after area analysis. BEI after EPMA measurement suggests some damage by electron beam irradiation.

It is not easy to specify the quantitative value of the damage. However, it is worthy to point out the fundamental way to reduce damage in this section. In order to reduce damage, the electron density should be controlled to be the minimum required value. Figure 8 shows the effect of continuous electron probe irradiation on Friedel’s salt (Mori et al. 2006). Time variations of rela-

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<td>Dry sanding by waterproof abrasive paper of SiC, finesses of SiC for final sanding is #2000</td>
<td>Wet polishing by diamond slurry, finesses of diamond for final polishing is about #8000</td>
<td>Impregnation by polyester resin, dry sanding by waterproof abrasive paper of SiC, diamond disk and diamond lapping sheet, finesses of diamond for final sanding is about #4000</td>
<td>Impregnation by methacrylate resin, wet polishing by SiC abrasive powder, finesses of SiC abrasive powder for final polishing is #1000</td>
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Fig. 6 Round-Robin test for Cl concentration profile measurement (JSCE 2005-4, Mori et al. 2005-1).

Fig. 7 Damage of sample by irradiation of electron probe. Fly ash cement paste. Left: BEI photograph before area analysis. Right: BEI photograph after area analysis for one hour. 8 kV 2 nA.
tive intensity of characteristic X-ray of Cl are shown for various electron probe diameters, keeping the probe current constant. The smaller the electron probe diameter, the higher the current density and the sample damage, and the lower the detected intensity of characteristic X-ray. As the result of irradiation, Cl ions scatter out from the sample or are kicked deeper inside the sample.

Another problem of high current density is contamination of the apparatus. When the probe current becomes higher, the intensity of X-ray detected increases and the measurement time becomes shorter. However, too high a current may result in EPMA staining. Many X-ray detectors are protected by thin films. These films suffer staining and the sensitivity of X-ray detectors decreases quickly.

3.4 Area analysis
Area analysis by EPMA is usually carried out as follows. An electron probe is attached. The electron probe diameter is typically 0.1 mm. A sample is continuously scanned by moving the sample stage keeping the position of the sample surface at the same height. An X-ray detector starts to count the intensity of characteristic X-ray corresponding to the target element as a discrete event in cumulative fashion. The stage moves in one direction for 0.1 mm during 30 ms for example. A value of 0.1 mm is typical for evaluating material transport in concrete in many cases judging from the size of the texture of cement hydrate. The aim of this analysis is not the evaluation of each cement hydrate but the overall movement of elements in concrete passing through cement paste. A 10 cm square sample can be measured in several hours in this condition. After 30 ms, the accumulated X-ray intensity in the X-ray detector is transferred to a computer and the value is canceled to zero and to the count starts again. An electron probe scans the all surface of the sample and digital data for a 0.1 mm square area are obtained. Each data set consists of the position information and characteristic X-ray intensities such as Ca, Si, S, Na, and Cl.

Because the electron probe diameter is larger than the microtexture of concrete, some contamination of data from different phases such as paste and aggregate is difficult to avoid. Although it may be possible to achieve higher spatial resolution by decreasing the electron probe diameter, both the electron probe diameter and scanning step of the stage would have to be decreased. Doubling of the resolution would require a four-fold increase in length of time. If 10 µm is required as the spatial resolution, a 100 times larger period of time, which is hundreds of hours, is required, which is unrealistic. Instead, a method like point counting by optical microscope could be used. With this method, the stage is fixed for 30 ms during counting of the intensity of X-ray, and then moves to the next point. The interval can be set arbitrarily. With this mode, a continuous graphical image is not obtained when the interval is too large. However, phase analysis with high spatial resolution is possible.

3.5 Methods for quantification
From the intensity data of characteristic X-ray transferred from an X-ray detector to a computer, element concentration is calculated based on some theory. For metals and silicate minerals without pores and water, a theoretical calibration method called the ZAF method is popular and is reasonably accurate. Periodical measurement of standard samples including the target element is required for ZAF calibration. However, for porous cement paste, this theoretical calibration is difficult to apply. In the case of rough semi-quantitative analysis called ratio method (JSCE Standard 2005-1), the intensity of characteristic X-ray of the target element in sample is assumed to be simply proportional to the element concentration in samples, and the element concentration is calculated from the information of characteristic X-ray intensities from the target sample and the standard sample, and the element concentration in standard sample. Although this method is simple and used widely, this assumption is wrong when chemical compositions of the standard samples and the target sample are very different. ZAF is the abbreviation of atomic number Z, absorption, and fluorescence excitation. When an electron beam irradiates a solid surface, characteristic X-ray is generated under these effects and for accurate quantification, these effects should be canceled by some method. One method is theoretical calibration called ZAF calibration. However, because ZAF calibration requires measurement results of every element component, porous material and hydrates are beyond the scope of this method.

For the ratio method and theoretical calibration method, standard samples are important because the difference in standard samples may cause some scattering of quantification. Therefore, in JSCE-G574-2005, several standard samples corresponding to target elements are regulated. There is still room for investigation from the viewpoint of chemical stability, homogeneity, and appropriateness for concrete (JSCE 2005-6).
The other method is using a calibration curve by using appropriate standard samples having a chemical composition similar to that of the samples. This method is theoretically correct and also the most reliable. For example, when Cl is measured in cement paste, several samples of cement paste having different Cl concentration levels covering the concentration range of the sample whose Cl concentration was determined by chemical analysis are used to make a calibration curve. By using these standards, every factor affecting the intensity of characteristic X-ray is automatically canceled. One example for Cl is shown in Fig. 9.

For point analysis, it is possible to accumulate characteristic X-ray by an X-ray detector for tens seconds to reduce the statistic scatter adequately. However, for area analysis, only some tens of milliseconds can be used for each pixel. Instead of a longer measurement time, a large number of data points is used to reduce statistic scatter. Figure 10 shows the relationship between the number of data averaged and the relative error of the average value of Cl concentration in cement paste (Mori et al. 2006). With more than 750 pixels, the relative error of concentration can be reduced to less than 2%. Although the accuracy of each data point is low because of the limited measurement time, adequate accuracy can be achieved by increasing the number of data.

3.6 Concentration profile

In JSCE-G574-2005, a method to obtain the concentration profile from numerical data of area analysis is regulated. The orientation of the required concentration distribution in the area of analysis is determined and the concentration in each pixel in the direction perpendicular to the concentration distribution is averaged. An example of Cl concentration profile of 1 mm interval is shown in Fig. 11 (Mori et al. 2006). The profile shows coincidence with measurement data obtained by the conventional method of slicing and chemical analysis after acid dissolution (JSCE Standards 2003, 2005-2). The data by the conventional method are the average value for a 7 mm interval.

One important procedure to obtain a smooth concentration profile is the discrimination of the paste part and the aggregate. In general, material transport takes place through the cement paste only. Because EPMA can use information only on the surface, the inhomogeneous content of aggregate affects the shape of the concentration profile significantly. However, if the concentration data only from cement paste was used, a smooth profile can be obtained. Figure 12 shows the Cl concentration profile in cement paste calculated from the same data shown in Fig. 11 (Mori et al. 2006). The discrimination of cement paste was carried out by the difference of chemical composition between paste and aggregate. Usually, Ca, Si and S are appropriate indicators for discrimination between paste and aggregate (JSCE Standards 2005-1, JSCE 2006, JSCE-7 2005, Mori et al. 2006). The absolute values of Cl concentrations obtained.
by this method show a perfect match with the conventional method.

The establishment of JSCE-G574-2005 unifies important factors affecting the quantitativity by EPMA for concrete and improves the data reliability. One comment that the authors wish to make regards consideration of the aim of analysis. This standard specifies the minimum requirement for area analysis of concrete by EPMA. However, the method for sample preparation and measurement conditions should be determined appropriately according to the aim. The quality of data depends on an understanding of and experience with materials and EPMA. It is difficult to show general conditions for sample preparation and measurement conditions and trial and error is required to obtain good data. This is always true for the most advanced analytical techniques. EPMA is an expensive apparatus (JSCE 2005-8). When this kind of analysis is requested from an outside firm, the client must be able to precisely explain the characteristics of the sample and the aim of the analysis to the analyst (Kobayashi 2006-2).

4. Recent applications

4.1 Apparent chloride diffusion coefficient

Using EPMA, much higher spatial resolution can be achieved compared to the conventional method, and precise estimation of the chloride diffusion coefficient is possible (Hosokawa et al. 2003-1). Figure 13 shows the estimated apparent Cl diffusion coefficients, $D_a$, from the Cl profiles obtained by the round-robin test by the JSCE, along with the results obtained by the conventional slicing method (Mori et al. 2005-1, JSCE 2005-9). The error bars in Fig. 13 indicate the estimation errors of corresponding $D_a$. $D_a$ obtained by the EPMA method for concrete has relatively bigger estimation error but that for paste has only small one. For the estimation value of $D_a$ for paste in each laboratory, $D_a$ is equivalent with that of the conventional method but has less estimation error. This shows that EPMA method is an effective method to estimate apparent diffusion coefficient.

High spatial resolution is very effective for the evaluation of durable concrete against material transport such as ultra-high strength concrete including silica fume. Figure 14 shows the area analysis of Cl concentration of ultra-high-strength concrete. A concrete specimen showing 130 MPa at 28 days was immersed into 10 mass%-NaCl solution for 28 days. Figure 15 shows the Cl concentration profile calculated from Fig. 14. Even in the case of limited depth of Cl penetration on the order of a few mm, the Cl concentration profile was clearly evaluated and $D_a$ could be estimated (Hosokawa et al. 2003-2). Another interesting point of this evaluation is the Cl distribution around aggregate. Before immersion of the concrete specimen into a NaCl solution, when concrete is water saturated, this kind of preferred penetration around aggregate was not detected. This characteristic behavior was detected only when the sample was cured in a dried condition of 60%RH at 20°C for half a year in the study and then immersed into a NaCl solution. Although the reason of this preferred penetration is not clear, this result suggest the existence of a more permeable zone around aggregate even in this kind of ultra-high-strength concrete at least after drying. The interfacial transitional zone or small cracks caused by drying are assumed to be possible reasons.
4.2 Reverse analysis of parameters related to Cl diffusion

Cl penetration into concrete is accompanied by partial binding by cement hydrates. The binding behavior is a non-linear function to the Cl concentration in aqueous phase in cement paste (Tang and Nilsson 1997). The Cl binding isotherm is known to differ depending on the composition of the cement. Assuming Fick’s second law with non-linear Cl binding of Freundlich-type, three parameters used in this function can be numerically determined through reverse analysis. One is $D_a$ and the others are constants used in the Freundlich binding isotherm equation. In order to calculate these parameters numerically, a sufficient number of data points is required and the EPMA method with high spatial resolution is an appropriate method for measuring Cl profiles. One example is shown in Fig. 16. In this example, three kinds of cement and two levels of water-to-cement ratio concrete were evaluated. By reverse analysis, Cl concentration profiles were successfully reproduced by using estimated constants. Furthermore, the estimated parameter describing binding behavior has a reasonable positive correlation with the alumina content of cement as expected theoretically.

4.3 Multi-element measurement

In many cases, only Cl penetration is considered for chloride damage. However, in actual marine and coastal environments, many other elements are involved. A stringent model of material transport is based on the Nernst-Plank equation but not on the simple Fick’s second law (Johannesson et al. 2005, Samson et al. 2005). In this model, many kinds of ions and solid phases are considered. In order to verify the model, measurement of the distribution of various ions is desirable. For this purpose, EPMA is suitable. Figure 17 shows the concentration distributions of various element of concrete core from a marine structure exposed to seawater for 10 years (Sato et al. 2004). EPMA measured 9 elements: Ca, Si, Cl, S, Na, Ma, Al, K and C. Complicated mutual interactions of ion and hydrate phases near the surface were successfully indicated.

4.4 Phase analysis

Through advanced computing power, not only the 2D distribution of various element concentrations, but also their phase distribution can be analyzed. Figure 18 shows an example of analysis of the phases composing basalt (Fujii et al. 2005). The main phases of basalt, such as two kinds of pyroxene, plagioclase, glass phase, can be distinguished clearly with the scatter map of silica and alumina. The areas corresponding to each phase are selected by encircling them with a line on the scatter map and the selected pixels are plotted with some color corresponding to each phase. A 2D map of the composing phases is then obtained.

The information obtained by EPMA in this case is equivalent to or less than that obtained through optical microscope observation of a thin section. The interest of information yielded by EPMA lies in its resolution, chemical composition and the quantitative area ratio of each phase. When a thin section is observed through an optical microscope, the information contains some thickness because a thin section has 20 µm thickness. The spatial resolution of EPMA is on the order of 1 or 2 µm, which is equivalent to that of an optical microscope, but the information yielded by EPMA comes only from
near the surface and each grain composing a rock can be distinguished more clearly.

Of course, the information yielded by EPMA includes the elemental composition. In the case of basalt, potassium mainly exists in the glass phase. Figure 18 (upper right and lower left) shows a perfect match of the existing area of glass phase and the potassium concentration distribution. Another characteristic point of EPMA is the
quantitative phase composition information. The area ratio of each phase is calculated by a computer. This measurement is a kind of point counting usually carried out by optical microscope observation. However, the area of analysis is too small compared to the texture in this case. To find out the phase composition, a larger area must be analyzed. Standard area analysis by EPMA is inappropriate for this purpose because in order to analyze a larger area with high resolution, an extremely long period of time is required, as mentioned before. Recent EPMA has a function to analyze multi-points discretely but not continuously. Figure 18 (lower right) is composed of 160,000 pixels at 5 µm intervals. The electron probe size was approximately 0.1 µm. Using this method, precise phase composition data can be obtained.

6. Summary

(1) The outline of EPMA and the procedure of analysis are explained. The important points for obtaining reliable data of concrete are indicated. Sample preparation, standard samples, measurement condition to avoid sample damage, procedure of area analysis and quantification are described briefly.

(2) Conventional and recent advanced applications are introduced. From conventional point analysis and 2D visual image of concentration distribution, quantitative area analysis has become available. A concentration profile with high spatial resolution can be obtained by using quantitative EPMA data and numerical data processing.

(3) The JSCE standard for EPMA is introduced and the method for estimating the apparent Cl diffusion coefficient is explained. The activity of round-robin test shows the adequate repeatability of this method when the measurement follows the procedure indicated in the JSCE standard.

(4) Characteristic applications of recent EPMA are introduced. A large number of data points enables the accurate estimation of apparent Cl diffusion coefficient $D_a$. Taking advantage of EPMA, an apparent Cl diffusion can be analyzed even in the case of ultra-high-strength concrete. Some examples of numerical data processing such as phase analysis are introduced.

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Fig. 18 Phase analysis of andesite (Fujii et al. 2005). From scatter diagram of SiO$_2$-Al$_2$O$_3$ (left), isolated phase are selected (center), and the location of each phase is displayed (right). Opx: Orthorhombic pyroxene, cpx: Clinopyroxene, pl: Plagioclase, gl: Glass. Lower left: Map image of potassium. Analyzed area was 0.2 mm square. Lower right: Map image of each phase. Analyzed area was 2.0 mm square.
References


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