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Determination of Kind of Cement in Hardened Concrete by Electron Probe Microanalyser

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ABSTRACT

A method for estimation of the chemical composition of cement in hardened concrete by an electron probe microanalyzer was studied in order to specify the kind of cement in it. Concrete was prepared with ordinary Portland cement. Square area of 400 micrometer by 400 micrometer in it was subjected to mapping analysis to quantify nine major elements of cement. Quantified values of elements in each pixel were converted treating their sum as 97% and retaining their relative ratios (converted composition). Pixels corresponding to aggregate were excluded based on values of CaO. The average of converted composition for residual pixels corresponding to cement and hydrates was calculated, and it was regarded as the estimated composition of cement. It was close to the chemical composition of the cement analysed by fluoresecent X-ray method. This method was applied to the concrete of actual structure, and the kind of cement in it was specified.

Keywords. Kind of cement, Hardened Concrete, Chemical composition, Electron probe microanalyser (EPMA), Mapping analysis

INTRODUCTION

The kind of cement used in concrete is an important factor intimately related to the performance characteristics of concrete. Determining the kind of a cement prior to its use is done relatively easily by measuring its chemical composition and fineness, as long as no significant degradation of the cement, owing to weathering for example, has occurred. On the other hand, it is not easy to determine the kind of cement used in hardened concrete.

However, in practice, cases where one needs to know the kind of cement used in concrete that has been placed and hardened arise far more often than the need to know the kind of some unused cement. A case in point is when quality, such as the strength and color tone of concrete, far deviates from expectations, casting doubt as to whether the specified kind of cement was indeed used, giving rise to the need for scientific verification (Sawaki, 2009).

In light of the above, the author studied methods to estimate the chemical composition of cement used in hardened concrete through mapping analysis using an electron probe microanalyzer (hereafter, "EPMA") (Sawaki, 2010a) (Sawaki, 2010b) (Sawaki, 2010c) .

Chemical composition is one of the defining characteristics of cement, and thus is a major clue for determining the kind of cement. This paper presents in detail this new method and introduces examples of the application of this method to concrete sampled from an actual structure.

THEORETICAL OVERVIEW

EPMA and mapping analysis. Figure 1 shows the appearance of the EPMA equipment and a schematic diagram of mapping analysis. EPMA consists in projecting an electron beam under vacuum conditions on the mirror polished surface of a sample, and detecting characteristic X-rays from among the signals emitted from the sample under excitation. The wavelengths or energies of these X-rays are analyzed to determine the elements present in the X-rayed area and their concentration. As the area irradiated by the electron beam can be made extremely small, on the order of micrometers (μm), the chemical composition of a pinpointed area can be obtained. The depth at which specific X-rays are generated is considered to be at the μm or lower (sub-micron) level.

The execution of this analysis on a single pinpoint area is called point analysis. On the other hand, the concentration of elements can be analyzed in terms of one-dimension or two-dimension distribution by analyzing numerous pinpoint areas while changing the irradation

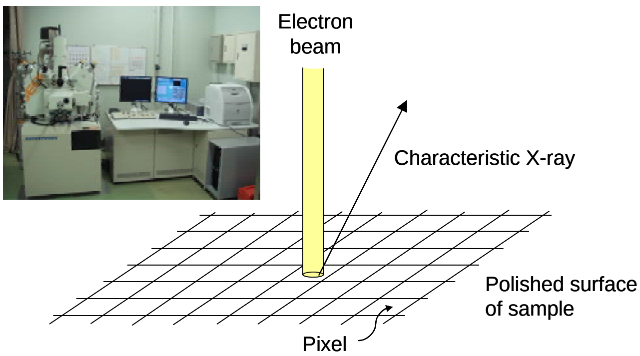


Figure 1. Appearance of EPMA and schematic diagram of mapping analysis

area by moving either the sample or the electron beam. One-dimensional analysis, in other words evaluation along a line, is called line analysis, and two-dimensional analysis, in other words evaluation across a plane, is called area analysis. The results of area analysis being presented in the form of a map that represents concentration with colors or light and dark areas, this type of analysis is also called mapping analysis. In this paper, the various pinpoint areas used in mapping analysis are referred to as pixels.

Method for estimation of chemical composition of cement in hardened concrete.

As described above, mapping analysis is used to obtain the chemical composition per pixel on the μm order. Analysis is usually done for several hundred pixels in both the horizontal and vertical directions, resulting in the collection of chemical composition data for several tens of thousands to several hundreds of thousands of pixels for a single analysis. The approach to estimating the chemical composition of the cement in the hardened concrete based on the data thus obtained is explained below using Figure 2.

In the case of hardened concrete, some pixels correspond to cement and cement hydrates, some to blending components such as blast furnace slag, some to aggregate, and some others to a mix of the above. The author thought it would be possible to estimate the chemical composition of the original cement by selecting cement, cement hydrates, and blending component areas and obtaining the average chemical composition of several tens of thousands to several hundreds of thousands of points in these areas. However, in the case of cement hydrates, conversion to the composition excluding the bound moisture would be required.

The procedure employed is as follows. First, the nine major components that make up cement as elements, i.e. Ca, Si, Al, Fe, Mg, S, Na, K, and Ti, are analyzed for each pixel. The results are expressed as mass percentage values for the respective oxides of each element, such as SiO_2 and CaO. The sum of these values is on the order of 97% to 98% for pixels of unhydrated cement, but in the case of hydrated cement pixels, that value is expected to be lower (Sawaki, 2010a), owing to the water, carbon dioxide, and so on, that are bound in the cement. However, even when water and carbon dioxide coexist in cement, the cement is only downblended by them, unless some chemical change such as significant progress of carbonation, has occurred, and relations of relative magnitude among the elements of the original cement should not have substantially changed. In other words, all the elements are downblended equally. Thus, it is considered possible to obtain the chemical composition approximating that of the unhydrated cement by converting the results so as to make the total sum of the values about 97% to 98%, which is the sum value for unhydrated cement, while retaining the relative ratios of the various elements. Hereafter, the composition thus obtained is referred to as “converted composition.”

Next, the pixels corresponding mainly to the aggregate are excluded from the analyzed pixels. This exclusion focuses on elements for which there is a large difference in content between the cement and aggregate. A threshold is set for content, based on which the cement and aggregate are told apart. For example, since the content of Ca, which is the most abundant element in cement, is lower in most kinds of rocks used as aggregate, a threshold is set for the CaO value, and pixels that exceed this value are judged to be cement, whereas those that do not are considered to be aggregate. Selecting the types of elements and their thresholds so as to exclude pixels of aggregate as much as possible is considered to be one of the key points in this method.

Lastly, the average of the converted compositions is calculated for the pixels from which aggregate pixels have been removed, and this is regarded as the estimated composition of the cement.

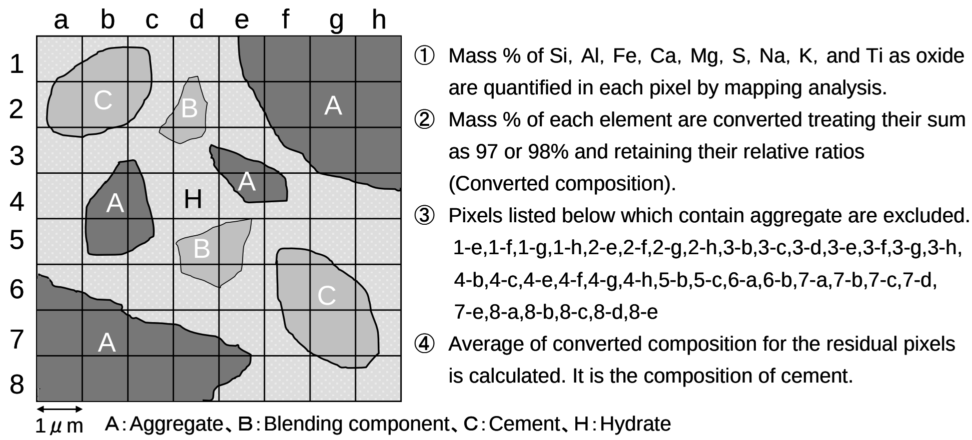


Figure 2. Schematic explanation for estimation of chemical composition of cement in hardened specimen by EPMA mapping analysis

To determine whether the above approach is valid, cement whose chemical composition was already known through preliminary analysis was used to make concrete, then the chemical composition of the cement was estimated using the above-described method, and whether the results of the analysis approximated the known chemical composition was determined, as detailed below.

EXAMINATION OF ESTIMATION METHOD ON CONCRETE SAMPLE

Preparation of hardened concrete. Using ordinary Portland cement, water-cement ratio of 0.5, aggregate-cement ratio of 5.83, and the addition of super plasticizer, concrete was mixed and molded to form cylinders 100 mm in diameter and 200 mm in height. The cylinders were demolded one day after mixing and cured under water at 20°C for 28 days. The chemical composition of the ordinary Portland cement was obtained beforehand using the fluorescent X-ray method. The mix proportion of the concrete is given in Table 1, and the chemical composition of the cement is shown in Table 2.

Table 1. Mix proportion of concrete (kg/m^3)

Water	Cement	Fine aggregate[*1]	Coarse aggregate[*2]	Chemical admixture[*3]
165	330	924	1001	2.64

*1: Marine sand (Yobiko, Saga) and Crushed sand (Yobino, Fukuoka),
*2: Crushed stone (Kajiki, Fukuoka), *3: Rheobuild SP8SE

Table 2. Chemical composition of cement used for preparation of concrete (%)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	Sum
19.33	5.11	2.85	63.94	2.38	2.10	0.26	0.40	0.27	96.64

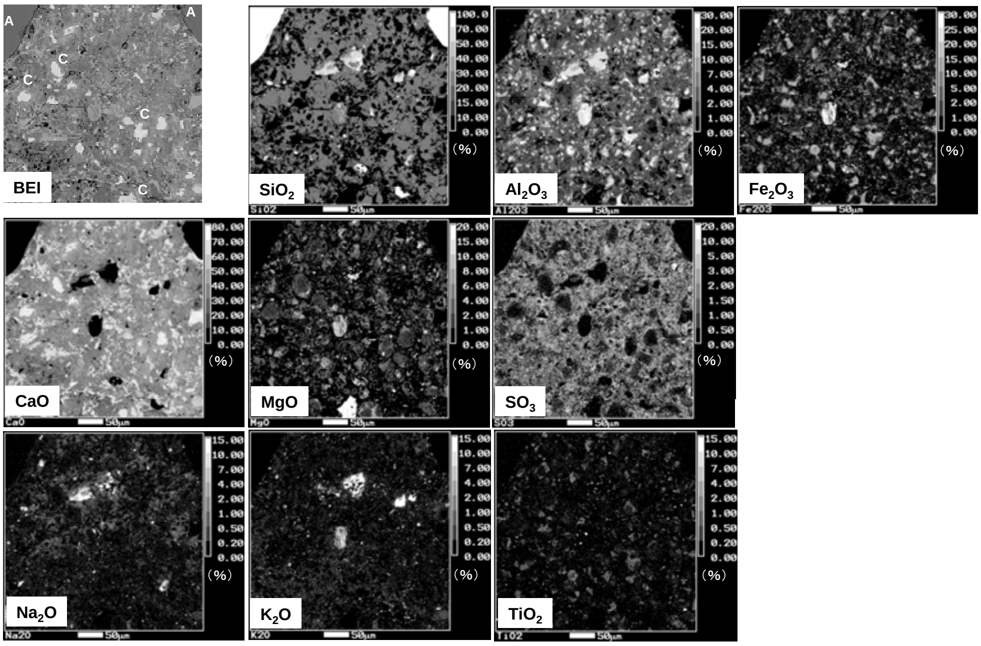
Mapping analysis procedure. The cylindrical specimens were crushed in a direction perpendicular to the long axis of the cylinder, in the vicinity of the center of the cylinder in the longitudinal direction, and small pieces of crushed concrete measuring approximately 10 mm were collected. These pieces were immersed in acetone for several days and then dried at room temperature to remove the free water inside.

The pieces of concrete were then embedded in epoxy resin and one side was mirror polished. Carbon was vapor deposited on this side and element mapping analysis was carried out. The analysis looked at the nine elements of Si, Al, Fe, Ca, Mg, S, Na, K, and Ti, and the results indicated the mass percentage of each element as oxides. The EPMA equipment used was an electron probe microanalyzer made by JEOL (product name: JXA-8200 X-ray microanalyzer). The mapping analysis conditions, which were based on those commonly applied for concrete, are listed in Table 3. The size of a pixel was fixed as 1 μm × 1 μm, and the number of pixels to be used for the analysis was set to 400 × 400 pixels, or 160,000 pixels. Thus the area for analysis measured 400 μm x 400 μm.

Mapping analysis results. The results of the mapping analysis are shown in Figure 3. The mass percentage of the oxides of the nine elements obtained for each pixel is indicated

Table 3. Condition of mapping analysis by EPMA

Accelerating voltage	15kV
Current	5×10^{-8}A
Diameter of probe	0.5μm>
Size of each pixel	1μm by 1μm
Number of pixels for measurement	160,000 (400 by 400)
Time of measurement for each pixel	40msec
Standard sample	Ca, Si: Wollastonite (CaO=48.00%, SiO_2=50.94%) Al, Na, K: K-Feldspar (Al_2O_3=20.44%, Na_2O=7.07%, K_2O=5.62%) Fe, Mg: Forsterite (Fe_2O_3=9.75%, MgO=50.83%) S: Anhydrite (SO_3=58.81%) Ti: $KTiOPO_4$ (TiO_2=40.33%)
Analytical crystal	Ca, S, Ti: PETJ Si, Al, Mg: TAP Fe: LiFH Na: TAPH K: PETH



BEI: Backscattered electron image, A: Aggregate, C: Cement particle

Figure 3. Resuts of mapping analysis for hardened concrete sample (Area for analysis: 400 μ m by 400 μ m)

by light and dark areas. The light and dark parts indicate high and low mass percentages, respectively. The mass percentage range as it applies to the light-dark scale is shown to the right of the mapping image of each element. Each of the mapping images could be said to be a collection of the chemical composition data of 160,000 pixels.

The BEI image at the top left is the backscattered electron image of the same area as that used for mapping analysis. The particles that appear dark gray in the BEI (symbol A) are aggregate, those that appear light gray (symbol C) are cement, and the material that fills in the spaces in between is hydrated cement.

Pixels corresponding to cement paste. Table 4 shows the analysis results for twenty contiguous pixels selected out of the 160,000 pixels. The measured chemical composition shown on the left side is the analysis result. For pixels No. 1 to No. 11, CaO accounts for the highest value, followed by SiO_2 and Al_2O_3. Since this order of magnitude is the same for the chemical composition of ordinary Portland cement, these pixels can be considered to correspond mainly to cement paste. However, calculation of the sum of the nine elements (as oxides) gives percentages that are just in the 60s and 70s range, which is lower than the normal sum value of about 97% for unhydrated cement. As mentioned earlier, this is considered to be due to the moisture bound in the concrete.

In order to obtain the composition of the cement, the measured values were converted to obtain the sum value of 97% while retaining their relative ratios. The results are shown as the converted chemical composition on the right side of Table 4. Comparing the converted chemical composition with the measured chemical composition, each of the elements has a higher mass percentage, and there are pixels that closely approximate the actual compositionof cement. However, there is a large degree of variation among the pixels, and pixels that differ greatly from the composition of cement are still observed. In this experiment, the size of one pixel is set as 1 μm, but assuming a cube with a 1 μm side, the volume is 10^{-18} m^3, and given a cement paste density on the order of 2 g/cm^3, this equates a mass value no greater than about 10^{-12} g. Considering that macro analysis using for example the fluorescent X-ray method is carried out on samples whose weight is on the order of grams, one can see that analysis of individual pixels with EPMA is done on extremely minute parts. Bearing this in mind, variations in composition among pixels is only a natural consequence of the fact that cement paste is an aggregation of various minerals, and thus estimating the composition of cement requires averaging of the compositions of a large number of pixels.

Pixels corresponding to aggregate. The pixels from No. 13 to No. 20 can be considered to correspond mainly to aggregate because SiO_2 and Al_2O_3 account for the highest values. (No. 12 is thought to comprise both cement paste and aggregate.) As the compositions of these pixels and the cement paste pixels differ greatly, they are considered to be unsuitable for estimating the composition of the cement. Therefore it is believed necessary to distinguish between the pixels that correspond to cement paste and those that correspond to the aggregate, in order to exclude the aggregate pixels and collect only the information of the pixels that correspond to the cement paste.

Table 4. Chemical composition and converted composition of contiguous twenty pixels

No.	Chemical composition of each pixel obtained by mapping analysis (%)										Converted chemical composition*1 (%)								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2	Sum	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2
1	18.6	3.8	1.2	35.0	0.8	2.1	1.1	0.0	0.0	62.5	28.8	5.9	1.8	54.2	1.3	3.3	1.7	0.0	0.0
2	17.0	5.6	0.3	37.5	0.6	1.4	0.5	0.0	0.0	62.9	26.3	8.6	0.4	57.8	0.9	2.1	0.8	0.1	0.0
3	19.0	4.5	0.3	35.8	0.6	0.6	0.5	0.2	0.0	61.5	30.0	7.1	0.4	56.5	0.9	1.0	0.8	0.2	0.0
4	18.6	4.5	0.4	40.2	0.2	1.7	0.3	0.1	0.0	66.0	27.3	6.6	0.6	59.0	0.3	2.6	0.4	0.1	0.0
5	16.2	3.2	0.3	50.0	0.4	1.4	0.5	0.2	0.1	72.2	21.8	4.3	0.4	67.2	0.5	1.8	0.7	0.3	0.1
6	10.7	2.2	0.4	55.4	0.2	2.5	0.4	0.3	0.0	72.1	14.3	3.0	0.5	74.6	0.2	3.3	0.5	0.5	0.0
7	9.1	3.5	0.3	54.4	0.5	0.0	0.5	0.3	0.4	69.1	12.8	4.9	0.4	76.4	0.8	0.0	0.7	0.5	0.6
8	7.6	1.6	0.1	59.2	0.1	1.4	0.3	0.3	0.2	70.8	10.3	2.2	0.2	81.1	0.2	1.9	0.4	0.5	0.3
9	10.0	1.8	0.8	60.7	0.3	1.4	0.3	0.5	0.2	76.0	12.7	2.4	1.0	77.5	0.4	1.8	0.3	0.7	0.3
10	11.4	1.7	0.7	51.9	1.3	2.5	0.5	1.3	0.0	71.2	15.5	2.3	0.9	70.7	1.8	3.4	0.7	1.7	0.0
11	16.5	4.0	0.4	40.2	5.0	1.4	0.9	1.3	0.0	69.5	23.0	5.5	0.6	56.0	6.9	1.9	1.3	1.8	0.0
12	27.5	9.7	5.2	26.5	5.1	0.0	4.8	2.3	0.0	81.0	32.9	11.6	6.3	31.7	6.1	0.0	5.7	2.7	0.0
13	45.6	16.9	3.8	6.6	8.9	0.0	4.0	1.7	0.0	87.5	50.6	18.7	4.2	7.3	9.9	0.0	4.4	1.9	0.0
14	40.7	17.2	9.4	5.2	12.1	0.3	1.7	1.8	0.0	88.3	44.7	18.9	10.3	5.7	13.3	0.3	1.8	2.0	0.0
15	30.1	17.8	23.2	2.1	7.4	0.0	3.5	2.1	0.0	86.4	33.8	20.0	26.1	2.4	8.3	0.0	4.0	2.4	0.0
16	33.2	15.8	16.5	1.4	1.2	0.0	8.7	0.7	0.1	77.5	41.6	19.8	20.6	1.7	1.5	0.0	10.9	0.8	0.1
17	51.6	17.5	2.7	1.7	0.1	0.0	8.4	0.3	0.0	82.2	60.8	20.6	3.2	2.0	0.1	0.0	9.9	0.3	0.0
18	58.7	18.0	0.7	0.5	0.4	0.0	8.2	0.4	0.1	87.0	65.5	20.1	0.7	0.6	0.4	0.0	9.1	0.4	0.1
19	58.1	18.4	0.0	2.0	0.1	0.0	10.7	0.6	0.0	89.8	62.7	19.9	0.0	2.1	0.1	0.0	11.5	0.7	0.0
20	57.8	18.8	0.4	1.2	0.0	0.0	10.4	0.5	0.0	89.2	62.8	20.5	0.4	1.3	0.0	0.0	11.4	0.6	0.0

*1: Contents of nine components (SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, SO_3, Na_2O, K_2O, TiO_2) in the left column were converted treating their sum as 97% and retaining their relative ratios.

Estimation of the composition of cement through the identification of pixels. Focusing on elements for which there is a large difference in content between cement paste and aggregate, the author sought to identify the respective pixels of cement paste and aggregate. Based on the fact that in ordinary Portland cement, the CaO content is highest, while aggregate only has low CaO content, it was considered appropriate to set a minimum value for CaO, judge all pixels recording CaO values below this limit to be aggregate, and exclude them. Table 5 lists the number of pixels left over after excluding those pixels whose CaO value was below the minimum value for CaO, which was set in 10% increments from 0%, and the estimated chemical compositions obtained by averaging the converted chemical compositions of these pixels.

The minimum value of CaO of 0% means that the information of all 160,000 pixels is collected to obtain their average chemical composition. As is clear in Table 5, the estimated chemical composition in this case has high content of SiO_2, Al_2O_3 , and Fe_2O_3 compared with the composition obtained with the fluorescent X-ray method, while CaO is low. Obviously, this is because the aggregate pixels were included in the calculation of the composition. On the other hand, by setting a minimum value for CaO, the number of pixels was reduced, and as the minimum value rose, the estimated chemical composition increasingly approximated that obtained with the fluorescent X-ray method. The chemical composition obtained with the fluorescent X-ray method was most closely approximated when the minimum value was set to 50%. This indicates that by excluding the aggregate pixels based on the minimum value of CaO and obtaining the average composition of the more than 100,000 remaining pixels, the chemical composition of the cement can be estimated with a considerable degree of accuracy. When the minimum CaO value was set to 60%, the CaO content was high compared with the value obtained using the fluorescent X-ray method, while the SiO_2, Al_2O_3 , and Fe_2O_3 contents were low, but this is attributed to the higher ratio of pixels corresponding to materials of high CaO content such as $Ca(OH)_2$ and $CaCO_3$.

Table 5. Variation of estimated chemical composition of cement in the concrete sample with the minimum value of CaO

Minimum value of CaO (%)	Number of pixels used for estimation	Estimated chemical composition of cement (%)								
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2
0	160000	25.9	5.9	3.0	56.9	2.3	2.0	0.4	0.4	0.2
10	146820	21.7	5.8	3.0	61.1	2.3	2.2	0.3	0.3	0.2
20	147514	21.5	5.7	3.0	61.5	2.3	2.2	0.3	0.3	0.2
30	146271	21.3	5.6	3.0	61.8	2.3	2.2	0.3	0.3	0.2
40	144186	21.1	5.5	2.9	62.2	2.3	2.2	0.3	0.3	0.2
50	130943	20.9	5.1	2.3	63.7	2.0	2.1	0.3	0.3	0.2
60	62581	15.1	4.3	1.4	72.6	1.5	1.6	0.2	0.2	0.1
Actual composition (%) *		19.33	5.11	2.85	63.94	2.38	2.10	0.26	0.40	0.27

* : Determined by X-ray fluorescent

This paper states that the best estimation results can be obtained by setting to 50% the minimum value for CaO for concrete that uses ordinary Portland cement and natural crushed stone aggregate, but the fact that the matter of which elements should be provided with a minimum or maximum value, and the magnitude of this value, depend to some extent on the compositions of the cement and aggregate, has been confirmed through other experiments not described in this paper (Sawaki, 2010a) (Sawaki, 2010b). For example, if crushed stone, which includes only a very small amount of SiO_2 like limestone, is used, a minimum value for SiO_2 could be set in order to exclude as aggregate pixels that fall below this value. It has also been confirmed that in the case of concrete that uses blast furnace slag cement and natural crushed stone aggregate, setting the minimum value of CaO to 30%, which is lower than in the case of ordinary Portland cement, yields the best estimation result (Sawaki, 2010b). Thus it is advisable to select the optimum conditions based on the mapping analysis results.

APPLICATION TO CONCRETE COLLECTED FROM ACTUAL STRUCTURE

Estimation of the composition of the cement used in concrete specimens obtained from a dam built over thirty years ago and still in service was conducted. A small piece measuring approximately 10 mm was collected from a fist-sized chunk of concrete, prepared with the procedure described above, and subjected to mapping analysis. Considering the possibility that chemical changes, such as carbonation, over time might affect the estimation, analysis and estimation were carried out for four distinct areas. Based on the fact that the CaO concentration in aggregate is lower than in cement paste, a minimum value of CaO was set as before to exclude the aggregate. The estimated chemical composition of the cement obtained as a result is given in Table 6, along with the numbers of pixels used for the estimation. The chemical compositions of ordinary Portland cement and moderate heat Portland cement are also listed as reference.

The estimated chemical compositions of the four areas show only a slight amount of variation, with CaO on the order of 60% to 61%, SiO_2 on the order of 24% to 25%, Al_2O_3 on the order of 5.4%, and Fe_2O_3 on the order of 2.8%. CaO values are lower than for ordinary Portland cement and moderate heat Portland cement, while the SiO_2 values are higher. Al_2O_3 and Fe_2O_3 values are close to those of ordinary Portland cement. MgO and SO_3 values also do not differ greatly from those of ordinary Portland cement. Based on the above, it is considered highly likely that the cement used in this concrete is ordinary Portland cement.

The CaO and SiO_2 values recorded were low and high, respectively, but this is known to generally agree with estimations of concrete of comparatively advanced ages done until now. Determination of the exact causes requires further study, but at present the explanation is thought to lie in the fact that as time passes, the properties of the concrete itself change, owing to dissolution of the cement for CaO, and progression of the alkali-silica reaction in the aggregate for SiO_2, which affects the estimation results.

Table 6. Estimated chemical composition of cement in the concrete collected from the actual structure

Number of area of mapping analysis	Number of pixels used for estimation	Estimated chemical composition of cement (%)								
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	TiO_2
1	130562	23.9	5.5	2.8	61.1	1.2	1.8	0.1	0.3	0.2
2	130475	25.1	5.4	2.7	60.3	1.2	1.7	0.1	0.2	0.2
3	140568	24.7	5.5	2.9	60.4	1.3	1.7	0.1	0.2	0.2
4	144552	24.2	5.3	2.8	61.2	1.3	1.8	0.1	0.2	0.2
Example of chemical composition of Portland cement	OPC	21.3	5.1	2.9	64.2	1.5	2.0	0.30	0.50	0.30
	MPC	23.8	3.7	3.9	63.8	1.1	1.9	0.26	0.32	0.18
OPC: Ordinary Portland cement, MPC: Moderate heat Portland cement										

CONCLUSION

The need to determine the kind of cement used in concrete based on analysis of hardened concrete frequently arises in actual practice. This paper demonstrates with actual cases the feasibility of determining the kind of cement employed in concrete by using the proposed method for estimating the chemical composition of the cement in hardened concrete through EPMA mapping analysis. Further, it has been determined that the chemical composition estimation results for concrete of advanced age may be prone to a certain kind of error. The estimation of the chemical composition of the cement in hardened concrete is traditionally done by dissolving the cement in hydrochloric acid or the like, but this approach presents issues such as limitations depending on the kind of cement and aggregate, and the fact that the obtained results simply have to be taken on faith owing to the absence of other, validating, methods. The hereby proposed method using EPMA resolves these issues.

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