Structure analysis of cement and concrete materials using X-ray powder diffraction technique

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1. Introduction

In order to solve various problems in materials, there are very high demands for crystal structure analysis. However, most materials used in industries are in powdery or polycrystalline states, and it is often quite hard to obtain single crystals for some materials. Structure analysis from X-ray powder diffraction can be applied not only for crystal structure analysis of a material which is hard to obtain suitable single crystals, but also can be used for structure analysis under special conditions and/or *in-situ* observations that are difficult for single crystal structure analysis.

In recent years, to overcome the hurdles of structure analysis from X-ray powder diffraction, researchers in universities and X-ray instrument manufactures have developed experimental hardware and application software. They have improved the performances of hardware such as a reduction of measurement time by increasing the brightness of an X-ray source and enhancing the sensitivity of a detector, and a reduction of calculation time by enhancing the performance of the application software. Structure analysis from X-ray powder diffraction is now treated as a routine work, where research of powder diffractometry is active. In the beam line ID31 of ESRF that is managed by Prof. Andy Fitch, it is possible to automatically take up to 50 diffraction data of samples sealed in capillaries for structure determination using a special robot sample changer in one night. As a result of the improvements in research environment, the number of reported crystal structure analyses using powder diffractometry has been greatly increased.

In what follows, we would like to show examples of successful complicated crystal structure analysis using powder diffraction technique.

2. Sorel cement and concrete

A high quality cement, which is formed by mixing magnesium oxide MgO and magnesium chloride $MgCl_2 \cdot 6H_2O$, was discovered in 1867. This cement (magnesia cement) is also called Sorel cement(1) after its discoverer, and it has a feature that it can well bind with not only inorganic compounds but also organic compounds. It has also other features, such as higher fire resistant, lower thermal conductivity, and better corrosive resistant than commonly used the Portland cement. On the other hand, the Sorel cement has a drawback that it becomes eroded when exposed to water for a long period of time. In the process of forming concrete in Sore cement, it is believed that Sore cement forms some kind of magnesium compounds, and these compounds greatly affect the quality of the concrete.

Bilinsky *et al.* reported a phase diagram of magnesium compounds that are formed by the reaction of $MgO–MgCl_2–H_2O$ system(2). According to the phase diagram, the following magnesium compounds, which are called F3 form and F5 form, respectively, are expected to be formed in the process of concrete.

$$3MgO + MgCl_2 + 11H_2O \rightarrow 3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O \text{ (F3 form)}$$

$$5MgO + MgCl_2 + 13H_2O \rightarrow 5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O \text{ (F5 form)}$$

Crystal structure of the F3 form was determined by de Wolff *et al.* from a powder sample in 1953(3). It is amazing that the crystal structure for F3 was successfully determined from a powder diffraction pattern for more than 50 years ago. At that time, they measured the powder diffraction using the camera method, furthermore, the crystalline system for the F3 form is triclinic, and the reported crystal structure is excellent and still applicable today. On the other hand, the F5 form is discovered by Matkovic *et al.*, and its powder diffraction pattern and lattice constants are registered in the Powder Diffraction File database (PDF). However, its crystal structure has not been reported(4).

In addition, it is known that a trace amount of a magnesium compound called chlorartinite ($Mg_2CO_3(OH)Cl \cdot 3H_2O$) is formed in the concrete. Chlorartinite is a compound found by Vergasova *et al.* in 1998 as a mineral that is created by a volcano, and only its diffraction pattern and lattice constants are registered in PDF(5).

Figure 1 shows the process that forms the magnesium compounds in the concrete. Usually, the composition ratio of chlorartinite in the concrete is less than 1%, and only weak peaks are observable in the powder diffraction pattern of concrete as shown in Fig. 2. However, it is revealed that a large amount of chlorartinite is formed in cracked concrete (Fig. 3), as a result of measuring its powder diffraction pattern. If based on the reaction process shown in Fig. 1, it is considered that cracks were created because of the formations of the F3 form and/or chlorartinite.

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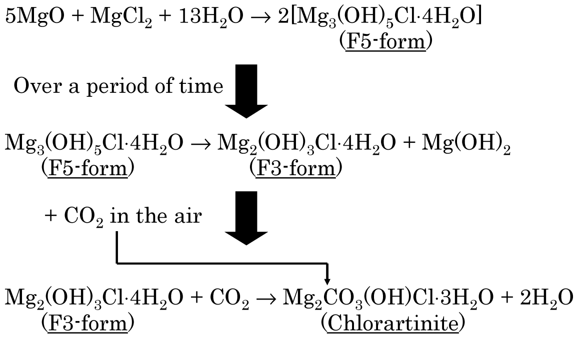
In this paper, in order to approach this cracking problem from the viewpoint of variations in crystal structures, we determined the crystal structures of the F5-form and chlorartinite from powdery state(6)–(8). Furthermore, by using the respective crystal structure data, we performed quantitative phase analysis by means of the Rietveld method, and studied the relevance of the ratio of the crystalline components in the concrete to the cracking problem. The followings show a series of the processes.

3. Experimental

Because both F5 form and chlorartinite are substances of low solubility, not only they are difficult to obtain single crystals that are suited for single crystal structure analysis. However, single-phase F5 form is very difficult to obtain. Therefore, we used a grinded powder sample of concrete, for the X-ray diffraction analysis of F5. On the other hand, for chlorartinite, we used a powder sample as it is, which is commercially available as an industrial product for X-ray diffraction analysis.



$5MgO + MgCl_2 + 13H_2O \rightarrow 2[Mg_3(OH)_5Cl{\cdot}4H_2O]$ (F5-form)

Over a period of time

$Mg_3(OH)_5Cl{\cdot}4H_2O \rightarrow Mg_2(OH)_3Cl{\cdot}4H_2O + Mg(OH)_2$ (F5-form) (F3-form)

+ CO_2 in the air

$Mg_2(OH)_3Cl{\cdot}4H_2O + CO_2 \rightarrow Mg_2CO_3(OH)Cl{\cdot}3H_2O + 2H_2O$ (F3-form) (Chlorartinite)

Fig. 1. Reaction scheme for the magnesium compounds formed in concrete.

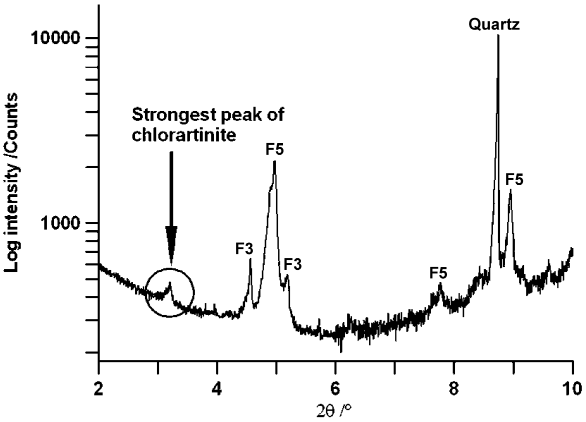


Fig. 2. Powder diffraction pattern of a normal concrete.

Fig. 3. Cracked concrete.

We used beam line X3B1 at National Synchrotron Light Source (NSLS) in Brookhaven USA and beam line ID31 at European Synchrotron Radiation facility (ESRF) in Grenoble France to measure powder diffraction data. Because experiments in the synchrotron radiation facilities make it possible to select a wavelength of the incident X-ray beam, to make the divergence angle of the beam very small, and to obtain high-resolution data, we can obtain diffraction data that are suited to index and for phase determination. Even so, in order to obtain high quality data, we made the particle sizes of the powders sample as uniform as possible, fused the sample in a capillary, and employed the transmission geometry to measure diffraction intensities. In addition, to enhance the precision of the phase determination, we tried to increase the statistical precision by using long measurement times.

4. Crystal structure analysis

When we perform the search/match to find a powder diffraction pattern, if the crystallographic information is registered in the PDF document or the Inorganic Crystal Structure Database (ICSD), we can use its lattice constants, crystalline system and crystal space group as initial values for crystal structure refinement. Fortunately, for both the F5 form and chlorartinite, their crystalline systems and lattice constants are reported in the PDF files, we used these values. If these data are not available, we need to determine their lattice constants and crystal space groups by using an indexing program (for example, DICVOL04(9)) after a peak position determination.

In the case of the F5 form, because we used an actual concrete as a sample, multiple phases are presented in the diffraction pattern. In this case, we must first identify all phases presented in the sample using search/match, and then extract crystallographic information (including the atomic coordination) from the ICSD and/or CSD (Cambridge Structural Database).

Before determining the initial structure, we refined the lattice constant and the profile function of the powder diffraction pattern of each sample using the Le Bail method(10) (Table 1). By applying these values to an initial structure analysis, we can expect to determine a more precise initial structure. (If we extract the diffraction reflection intensities using the total pattern decomposition of the Le Bail method or Pawley method(11), we can analyze an initial structure in the direct method used in single crystal structure analysis. We did try, but unfortunately, we could not obtain an initial structure.)

In the crystal structure analysis of the F5 form and chlorartinite, we used FOX(12) (Parallel Tempering is used for the direct space method) for the unknown struc-

Table 1. Crystallographic data of $Mg_2(OH)_5Cl \cdot 4H_2O$ (F5 phase) and $Mg_2CO_3(OH)Cl \cdot 3H_2O$ (Chlorartinite).

Compound	F5-form	chlorartinite
Formula (idealized)	$H_{13}ClMg_3O_9$	$CH_7ClMg_2O_7$
Formula weight (in g/mol)	265.47	215.11
Space group	*P2/m*	*R3c*
Z	1	18
a (in Å)	9.6412(5)	23.14422(16)
b (in Å)	3.1506(2)	-
c (in Å)	8.3035(5)	7.22333(5)
β (in °)	113.986(6)	-
V (in Å^3)	230.43(3)	3350.84(5)
D-calc (in g/cm^3)	1.913	1.758
R-p (in %)	4.19	5.23
R-wp (in %))	5.98	6.56
No. of reflections	186	205
No. of variables	16	45

ture analysis program. In the FOX, we can input the crystalline systems, lattice constants and atomic coordinations of the known compounds beforehand, and determine the structure of an unknown phase even though multiple phases are presented in the powder diffraction pattern. We estimated the composition from the elemental analysis, thermal analysis, crystalline lattice volume, and the density of general magnesium compound. It is known that the magnesium atom contained in the F5 form and chlorartinite takes six coordinations; so we incorporated MgO_6 octahedron as the rigid molecular model to execute the program. If the coordination number of a metal ion is uncertain, it is also possible to confirm the coordination number by using an NMR or an EPR. We have finally been able to obtain the initial structure from the FOX (Fig. 4).

In the next step, we refined each initial structure by using the Rietveld analysis(13). For the F5 form, because multiple phases are refined at the same time, we constrained the analysis so that the temperature factors take the same value for each phase. On the other hand, for chlorartinite, because CO_3 groups were un-stabilized, we refined the analysis by constraining C–O atomic distances and bond angles. Figures 5 and 6 show the Rietveld plots of the F5 form and chlorartinite, respectively. In addition, Table 1 gives the respective final R values. Figures 7 and 8 show the determined crystal structures of the F5 form and chlorartinite, respectively.

The molecular structure of the F5 form (Fig. 7) consists one-dimensional chains by means of three-strand MgO_6 octahedrons along the *b*-axis; and between one-dimensional chains, the counter anion Cl^- and H_2O are randomly allocated at the ratio of 1 : 1. In addition, OH and H_2O are allocated at both ends of the one-dimensional chains at the ratio of 1 : 1.

Figure 9 shows the molecular structure of the F3 form. This structure consists of one-dimensional chains by means of two-strand MgO_6 octahedrons along the *b*-axis, revealing that the F5 form has a similar crystal structure as that of the F3 form.

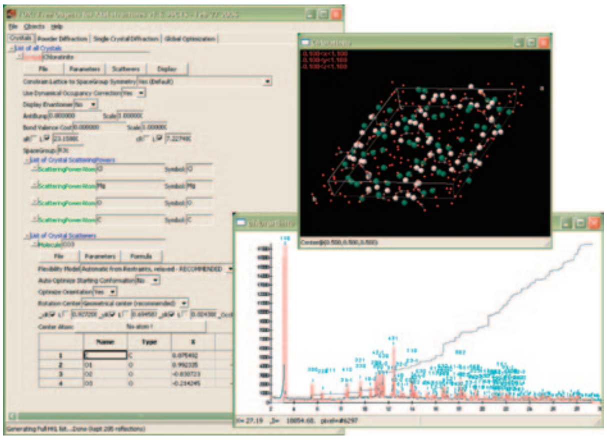


Fig. 4. Initial structure analysis program FOX.

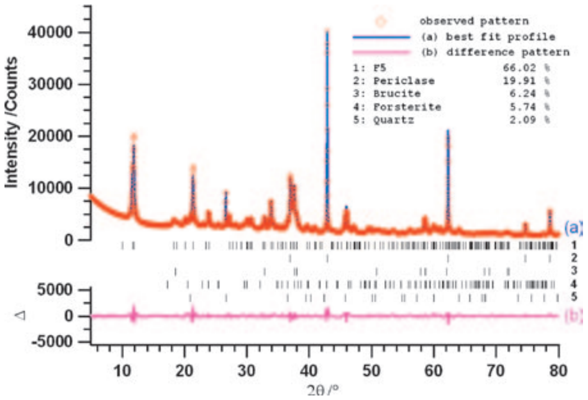


Fig. 5. Rietveld plot of F5 form.

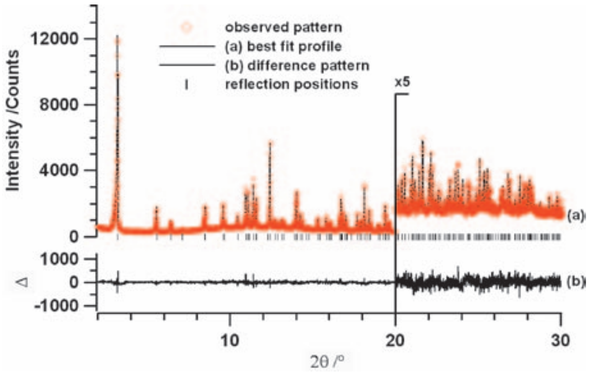


Fig. 6. Rietveld plot of chlorartinite.

The molecular structure of chlorartinite (Fig. 8) forms a skeleton like a complex zeolite. Fifteen-membered puckered rings, which is formed by the MgO_6 octahedrons, exist along the *c*-axis, in which the counter anion Cl^- and the randomly allocated H_2O are present.

When we leave chlorartinite in vacuum, we found that the H_2O molecules located in the vacancies are desorbed while keeping the skeleton like zeolite. The powder diffraction pattern has revealed that this dehydration process occurs reversibly. The structural expansion and contraction accompanied with such dehydration and ad-

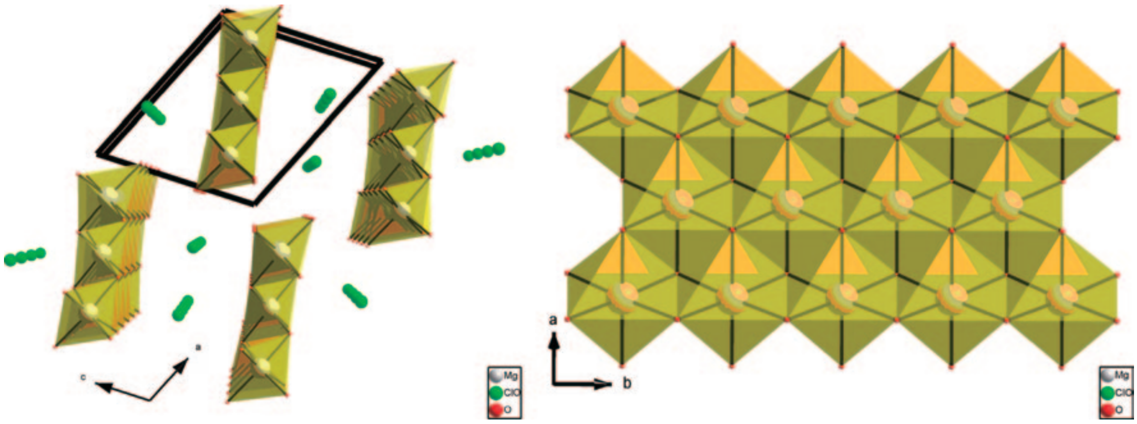


Fig. 7. Molecular structure diagrams of the F5 form (The left is viewed down the *b*-axis, and the right is viewed down the *c*-axis.).

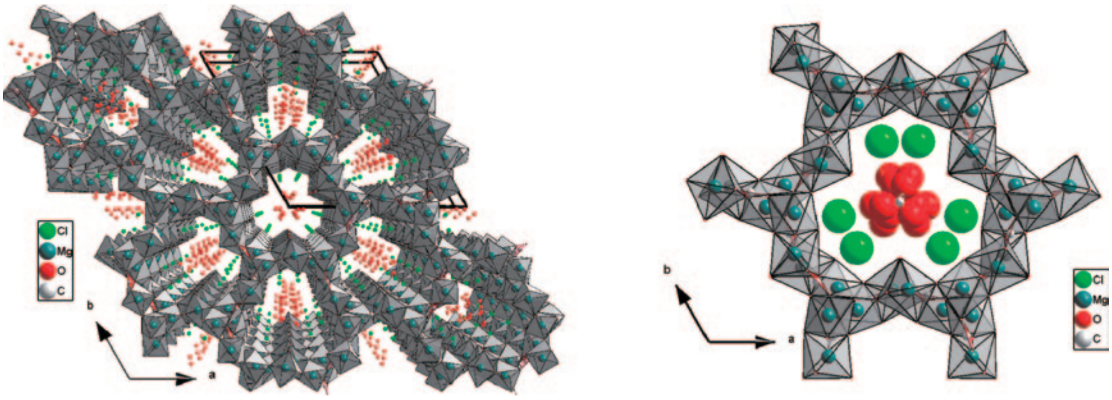


Fig. 8. Packing diagram (left) and molecular structure diagram (right) of chlorartinite.

sorption are considered to be one of the causes that lead the concrete to crack.

5. Quantitative analysis of cracked concrete

After drilling a part of a cracked concrete shown in Fig. 3, and milling it, we measured the powder diffraction pattern. The result of a qualitative analysis shows that quartz (PDF 83-539), chlorartinite (PDF 7-278), calcite (PDF 83-577), microcline (PDF 76-1239), and clinotobermorite (PDF 88-1328) are contained in the concrete sample as the crystalline phases. By searching the ICSD database, we obtained the crystalline information (such as the crystal system, space group, lattice constant and the atomic coordinate) of these components. Using the information, we performed a quantitative analysis by means of the Rietveld method. Figure 10 shows the final qualitative analysis Rietveld plot. The result of the quantitative analysis shows that compositions are quartz: 52.3 wt%, chlorartinite: 28.9 wt%, microcline: 9.9 wt%, calcite: 8.8 wt%, and clinotobermorite: 0.13 wt %, and that the composition ratio of filler and binder is 71% : 29%.

6. Summary

According to the reaction scheme shown in Fig. 1, the F5 form in the concrete dissolved into the F3 form over a long period of time in an environment having a large amount of water. Furthermore, the F3 form formed chlorartinite by reacting with carbon dioxide in air. The F5 form, whose crystal structure was determined in this study, is a major phase presented in the concrete; and the production of chlorartinite greatly affects the property of the concrete; so both substances are considered to give the important information for clarifying the mechanism on forming the concrete.

To perform the quantitative analysis using the Rietveld method, the information on the crystal structures is indispensable. The successful determination of the crystal structures of F5 and chlorartinite makings it possible to quantify the crystalline phases presented in the concrete.

Because chlorartinite is found to have large channels in which the trapped water molecules easily moving in and out, the water molecules are believed to have a buffer action. Furthermore, because excessive chlorartinite more than a normal amount was found from the cracked concrete, it is anticipated that the chlorartinite can be used as a reference material for evaluating the state of the concrete.

7. Concluding remark

Up until a few years ago, powder structure analysis tends to be avoided by many crystallographers. However, as it is now, powder structure analysis is becoming a

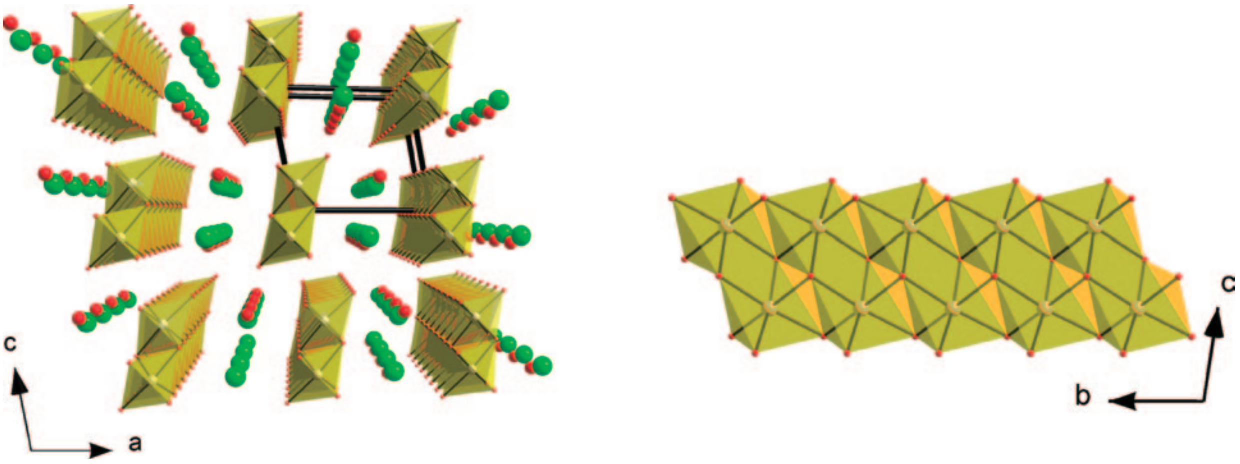


Fig. 9. Molecular structure diagrams of the F3 form (The left is viewed down the *b*-axis, and the right is viewed down the *a*-axis.).

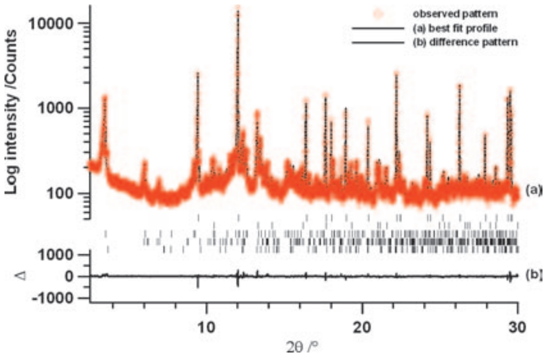


Fig. 10. Quantitative analysis Rietveld plot of cracked concrete.

simpler and more familiar technique. 20 kinds of 122 powder diffraction patterns for related substances of the F5 form and chlorartinite, whose crystal structure reported in this study, are registered in the PDF. However, among them, the crystal structures of only four compounds including the F5 form and chlorartinite have been reported. Many other compounds whose diffraction patterns are reported but their crystal structures have not yet been determined. Powder structure analysis is expected to speed up the determinations of their crystal structures. In addition, results obtained in this study demonstrate that powder crystal structure determinations of many compounds that have not been able to be determined are now possible. Crystal structure information of a powder sample is very useful for clarifying the mechanism of structure change and for advancing the research of solid state properties, and will become indispensable as an important technique for future structure determination soon.

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