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Development of technique for observing pores in hardened cement paste

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Abstract

Mercury intrusion porosimetry is a widely used technique to determine the pore size distribution in porous materials. However, this technique does not provide information about the shapes and locations of pores. A new technique is developed, in which gallium (Ga) is used as an alternative intrusion liquid because of its property of being solid at normal room temperature (melting point: 29.8 °C). This permits the examination of pores using image analysis. The technique is applied to hardened cement paste. The distribution of solid Ga is observed through an electron probe microanalyzer (EPMA), and the shapes and locations of pores in cement paste are discussed. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Microstructure; Image analysis; Cement paste; Gallium; Electron probe microanalyzer (EPMA)

1. Introduction

Physical properties of concrete, particularly strength and permeability, significantly depend on its pore structure. Information about pore structure is, therefore, essential for understanding such physical properties. Examination of pore structure of concrete includes elucidation of the shapes, volumes, locations, and distribution of pores resulting from cement hydration.

The significant dependence of the physical properties of concrete and mortar on their pore structures has attracted the attention of many researchers since early times, accumulating a vast body of studies including those by Powers [1]. Understanding of pores was substantially enhanced by the development of the mercury intrusion porosimetry method, which provides information on the distribution of pore sizes. This prompted the study of pore structure of mortar and concrete from various aspects, resulting in an abundance of useful data [2–7].

Meanwhile, computer simulation of growth of hydrates has been actively studied with regard to pore structure, particularly pore content, configuration, and distribution [8,9], permitting better understanding of pore structure from this aspect. As for observation techniques, measurement using an optical microscope and X-ray CT is possible and well documented [10] for pores of the order of 10 μm or greater, which are relatively easy to distinguish from hardened cement. However, no means are currently available for examining pores in the capillary range, which have a crucial impact on the physical properties of mortar and concrete, with few studies being reported in the literature.

Mercury intrusion porosimetry is widely used for investigating the pore structure of concrete, whereby mercury is pressed into the pores of concrete under high pressure, utilizing its properties of being nonwetting and liquid at normal temperatures. Each pore size is quantitatively determined from the relationship between the volume of intruded mercury and the applied pressure. However, this technique does not provide information on the shapes and locations of pores. Such information is essential for understanding the physical properties of concrete, such as air and water permeability, which strongly relate to its durability. This is because the size, continuity, and distribution of pores are critical factors governing the gas/liquid permeability of concrete.

To obtain information about the pore shapes and locations from mercury intrusion porosimetry, mercury needs to be retained inside the pores. However, being liquid at normal temperature, mercury intruded at high pressure is extracted when depressurized. To solve this problem, the authors attempted to use gallium (Ga) as an alternate

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intrusion liquid, which has a melting point around 30 °C and has the advantage of being solid at room temperature. By pressing liquid Ga into cement pastes at a temperature above 30 °C, and the cooling to room temperature, solid Ga inside the pores is examined to learn about the shapes and locations of pores. In this study, a device based on this principle was made as a first step, and the pores of hardened cement pastes were measured to investigate the feasibility of this technique.

2. Ga intrusion method

2.1. Choice of Ga as an alternative intrusion liquid

In the mercury intrusion method, liquid mercury is intruded in the pores under pressure. In order to transform the mercury from the liquid phase to the solid phase, it must be cooled to an extremely low temperature (<29.8 °C). However, the examination of pore structure of hardened cement paste under this temperature is practically impossible.

Ga was, therefore, investigated as a potential replacement to mercury because of its characteristic melting point of 29.8 °C, allowing the transformation of Ga from liquid to solid in the normal temperature range. In addition, Ga is a nonwetting liquid with a high contact angle and surface tension as given in Table 1.

The relationship between the estimated pore diameter and applied pressure is generally expressed by the following equation (Eq. (1)):

$$D = -4\gamma\cos\theta/P \quad (1)$$

where D = pore diameter (nm), γ = surface tension of liquid (dyn/cm), θ = contact angle, P = pressure (MPa).

Fig. 1 shows the relationship between the pressure and the calculated diameter of pores intruded with Ga and mercury under the pressure. Ga is also expected to be intruded in pores under pressure. Theoretically, Ga is intruded in smaller pores than mercury under the same pressure, presumably due to the smaller contact angle, i.e., the greater wetting property, of Ga.

2.2. Measuring method

The newly developed method is characterized by intruding molten Ga in pores of a sample under vacuum, solidifying it by cooling, and retrieving the sample containing solidified Ga. Since it is difficult to carry out these steps in a continuous operation using a single device, these are divided into two processes: one in which a sample is covered with liquid Ga under vacuum and the other in which Ga covering the sample is remelted to be intruded in the pores and then cooled to solidify in the pores.

Table 1
Comparison of the nature of mercury and Ga

	Melting point (°C)	Surface tension (dyn/cm)	Contact angle (°)	Specific gravity
Ga	29.8	484	130	6.1
Mercury	−38.9	358.2	140	13.5

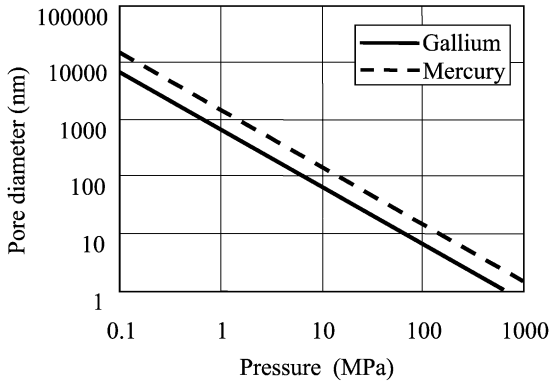

Fig. 1. Relationship between pressure and pore diameter.

2.2.1. Encasing sample in Ga

The sample is placed in a vacuum to completely evacuate the pores and should be maintained in a vacuum while being covered up by Ga. To this end, a device shown in Fig. 2 was fabricated. It is a steel container equipped with a heater at the bottom for heating the entire container. Fig. 3 shows a photo of the actual device.

The procedure is as follows: a cubic sample with a side length of around 5 mm is placed on a support 2 mm in diameter and 3 mm in length erected at the bottom of the container to maintain the sample in the center of molten Ga.

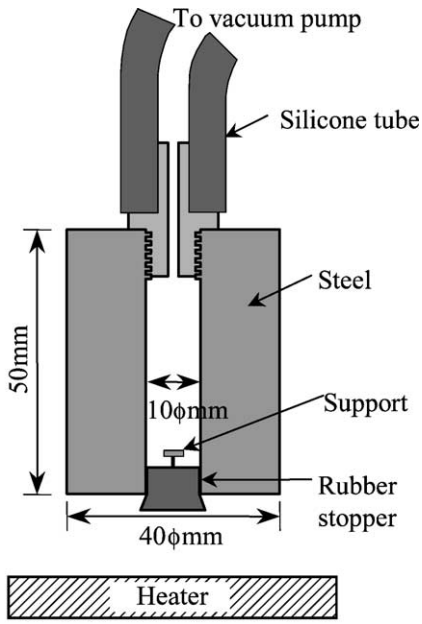

Fig. 2. Apparatus for covering specimen by Ga.

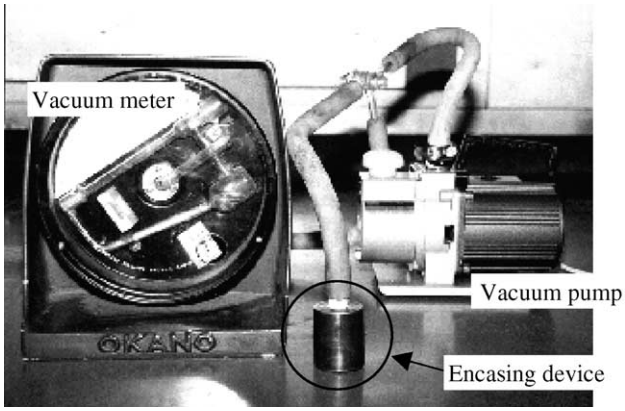

Fig. 3. The photo of the encasing device.

An adhesive is used to fix the sample on the support. A lump of Ga weighing approximately 7 g (approximately 1 cm^3) is placed in the container (Fig. 4(1)). The entire container is put under a vacuum of 13 Pa, which is slightly lower than that used for mercury intrusion (6.6 Pa). The container is then heated to around 50 °C to melt the Ga and allow it to encase the sample (Fig. 4(2)). Finally, the container is cooled to transform the Ga into solid (Fig. 4(3)). As the sample retrieved is hermetically sealed with Ga, the inside is maintained under vacuum.

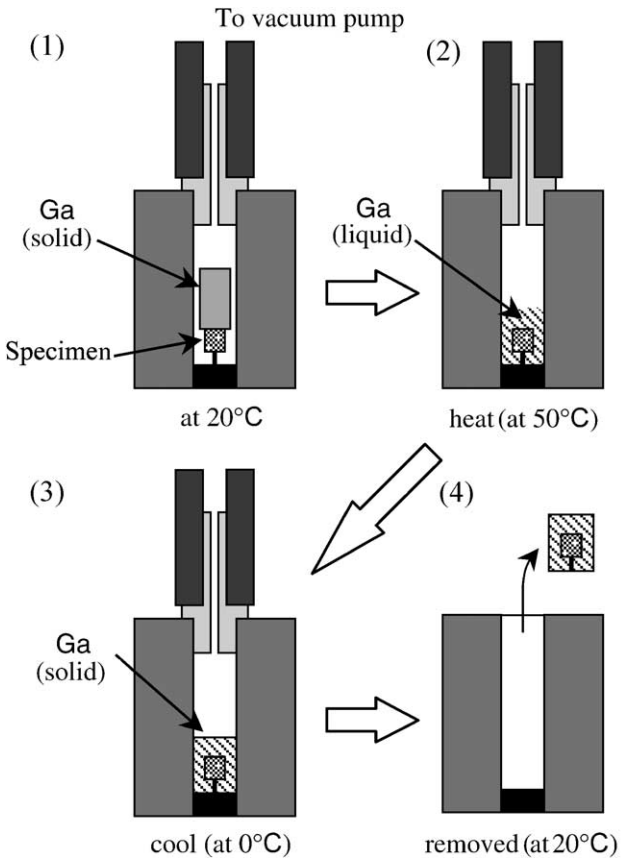

Fig. 4. Procedure of encasing specimen by Ga.

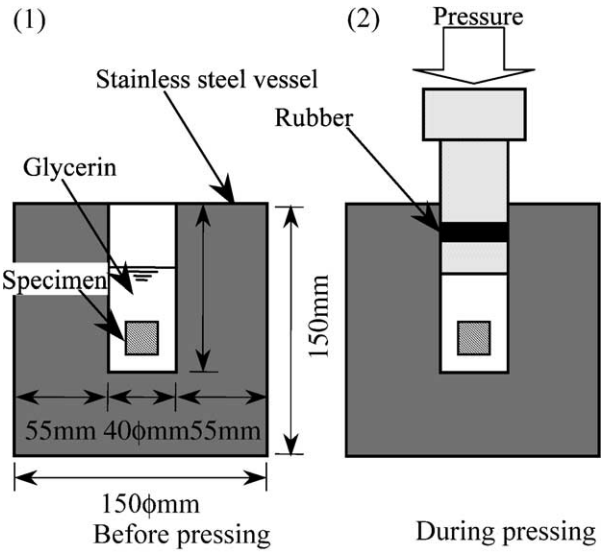

Fig. 5. Apparatus of intruding Ga into pore.

2.2.2. Intruding Ga into sample

In the second process, Ga covering the sample is intruded into the sample by the rubber press method. A device was fabricated for this purpose as shown in Fig. 5. This is a cylindrical stainless steel pressure vessel with a wall thickness of approximately 55 mm, which accepts a loading piston designed to be loadable up to 300 MPa. The state of the Ga intrusion process is shown in Fig. 6.

The procedure is as follows: the sample sealed with Ga is placed in a rubber bag and air is expelled. The rubber bag is placed in the pressure vessel containing glycerin (the pressure medium) (Fig. 5(1)) and the entire vessel is heated to remelt Ga covering the sample. Then, pressure is applied using the piston of the rubber press device (Fig. 5(2)) to intrude the liquid Ga into the pores of the sample. When the target pressure is reached, the entire vessel is cooled using liquid nitrogen to resolidify Ga in the vessel. The vessel is

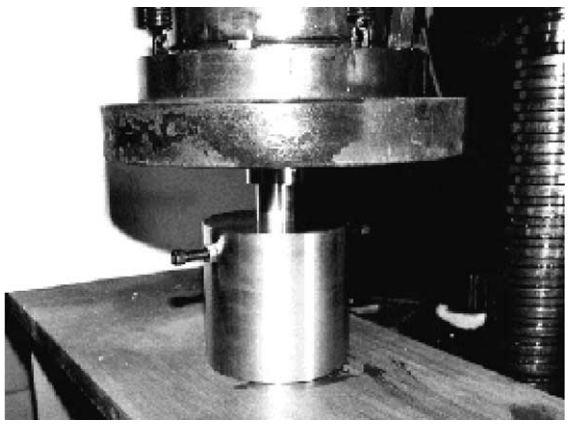

Fig. 6. The photo of the intruding device.

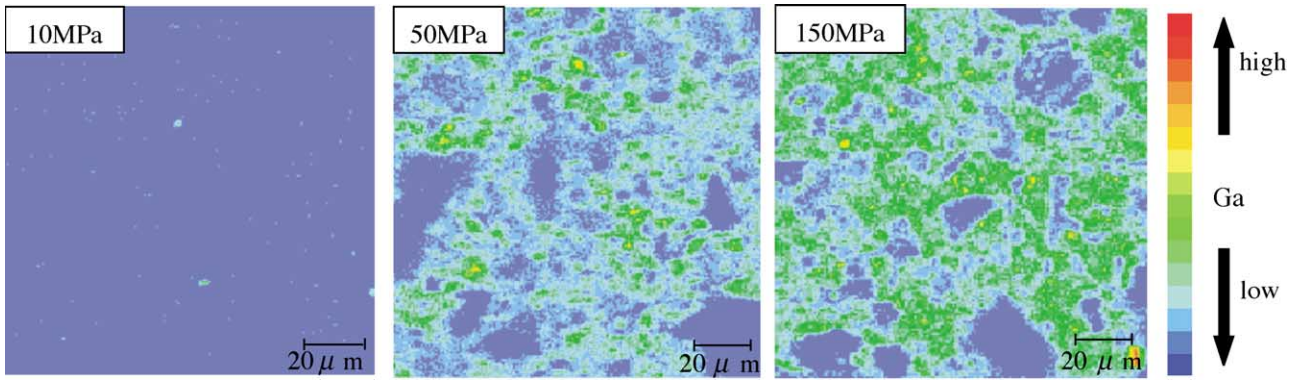

Fig. 7. Effect of intrusion pressure (W/C = 45%, 28 days).

then depressurized and the sample is retrieved. Ga intruded in the pores of the sample is fixed as a solid metal phase.

3. Experimental procedure

3.1. Mixing, casting, and curing

Cement pastes having different water–cement (W/C) ratios were used as hardened cement specimens. Normal cement was used as the cement and mixed in accordance with JIS R 5201-1997 (physical test methods for cement) with distilled water. The mold was a disk measuring 100 mm in diameter and 30 mm in depth. Cement was demolded 1 day after placing and water-cured for 28 days at 20 °C.

3.2. Sample preparation

3.2.1. Cutting of sample and preparation before intrusion

Cubic test pieces with a side length of approximately 5 mm were cut from near the centers of specimens using a diamond cutter and washed with acetone to terminate hydration. The test pieces were then dried by D-drying for 48 h to remove moisture in the pores.

3.2.2. Intrusion of Ga

Ga was intruded in each test piece and fixed. The maximum pressure was 150 MPa, which would theoretically intrude Ga into pores with a diameter of 5 nm.

3.2.3. Preparation of samples for electron probe microanalyzer (EPMA) measurement

After the intrusion process, Ga on the surface of the sample is thoroughly removed. The sample is placed in a mold 25 mm in diameter and 20 mm in depth, and the space around the sample is filled with epoxy resin. After the resin is cured, the contents of the mold are removed and the surface is polished progressively using polishing paper. Polishing is finished with 0.25 μm of diamond slurry, and is cleaned by ultrasonic cleaning. The sample is cooled during polishing to avoid melting of Ga. Finally, the surface is coated with platinum to impart conductivity.

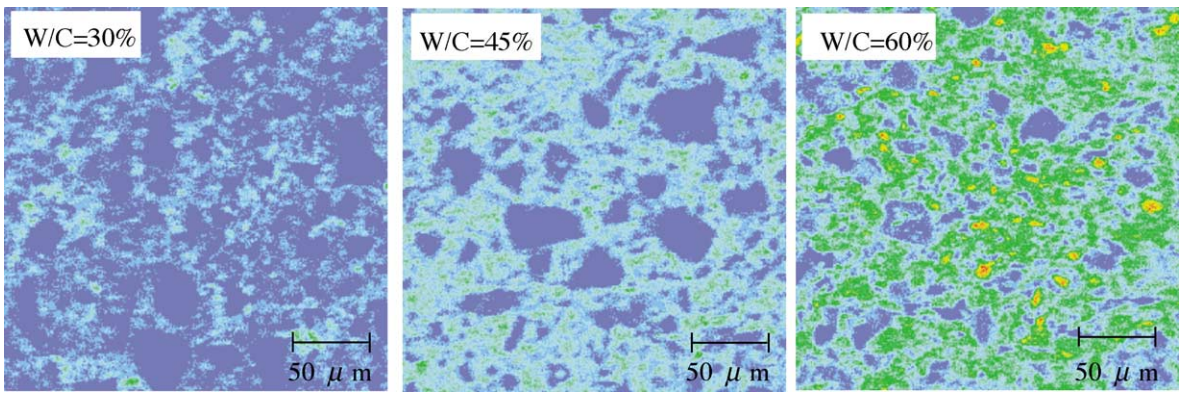

Fig. 8. Effect of W/C ratio on pore structure (at 150 MPa).

3.3. EPMA measurement

The observation of solid Ga in the pores is possible with the use of optical microscope, scanning electron microscope (SEM), or element mapping by an EPMA.[1] However, the visual distinction of cement hydrates from Ga in the visual field is extremely difficult with the use of optical microscope or SEM. For this reason, EPMA was used in this study.

An EPMA, EPMA-1400, with a measuring resolution of 1 μm, manufactured by Shimadzu (Japan), was used for the measurement. The measuring procedure is as follows: the measuring point is roughly determined using an optical microscope. The measuring point then is determined with more accuracy using the electron microscope function of the apparatus, and mapping is carried out. The measurement is conducted with an acceleration voltage of 15.0 kV and a beam size of 1 μm, representing the maximum capacity of the apparatus.

4. Results

The results of the measurement are all expressed by pixels on the screen, with each pixel conveying elemental information from a 1-μm square of the surface. The results are shown in regard to Ga: a color closer to red represents a higher weight percentage of Ga, while a more bluish color represents a lower weight percentage of Ga.

4.1. Effect of applied pressure

Fig. 7 shows the Ga distributions in the centers of samples under different pressures in cement pastes having the same W/C (45%) and the same age (28 days). Ga is scarcely found in the test piece under 10 MPa. In other words, little Ga is intruded in the pores in the center of the test piece. This suggests that Ga can be easily intruded into main branch pores but cannot be pressed through smaller inner pores without a high pressure. The same phenomenon is observed in mercury intrusion. With a pressure of 50 MPa, Ga distribution is observed, suggesting that Ga is intruded deeper inward. At 150 MPa, many large pieces of Ga indications are found, with Ga filling pores all over the range including finer pores. By changing the pressure, the state of Ga intrusion can be better understood, particularly the changes in the pore size that can be intruded.

4.2. Effect of W/C

Samples were prepared with different W/C ratios (30%, 45%, and 60%) to change the pore structure. Fig. 8 shows the measurement results at 150 MPa. At 30%, for which a dense microstructure is assumed, few Ga indications are found. On the other hand, Ga is widely distributed at 45% and 60%, indicating that qualitatively more Ga is intruded as the W/C increases.

5. Evaluation of measurement results

The previous results were limited to the qualitative aspects of Ga intrusion. In this section, a method of quantitative evaluation of pores is investigated. The purpose is the identification of pores in terms of pixels. Using EPMA with a resolution of 1 μm, any Ga present in the range is counted. It is, therefore, important to determine the threshold level of pixel colors to identify them as pores filled with Ga.

5.1. Verification of the validity of quantitative evaluation of Ga by image analysis

Any Ga present in a 1-μm square is indicated as a pixel with a certain density of Ga. Where the color density is blue, Ga may not be present all over the 1-μm square, but Ga present in one or more pores in the area is presumably sensed and observed. Accordingly, the percentage of Ga presence is estimated for each color of Ga pixels. A pixel exhibiting the highest value of Ga density is assumed to indicate the presence of Ga all over the 1-μm square of the pixel, and a pixel exhibiting half the highest value of Ga density is assumed to indicate the presence of Ga in half the area. Ga volume is calculated in this way by assuming the maximum value and minimum value to be 1 and 0, respectively, and relating halftones to areas between them. The Ga volume thus determined based on the image information is compared with the value obtained as the difference between the measured weights of Ga before and after intrusion, as given in Fig. 9. The analyzed and measured values were relatively close, suggesting that the Ga image reasonably represents the quantitative informa-

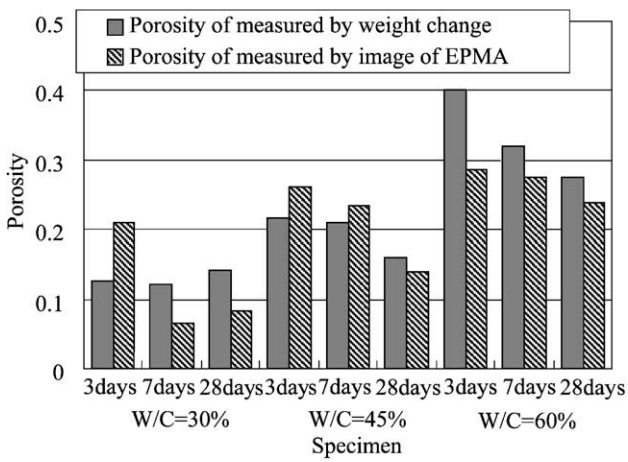

Fig. 9. Comparison of porosity measured in two methods.

[1] EPMA is an apparatus that irradiates electron beams onto a sample to observe the surface using the secondary and reflected electrons, while obtaining information on the elements in a microarea of the sample using simultaneously generated X-rays.

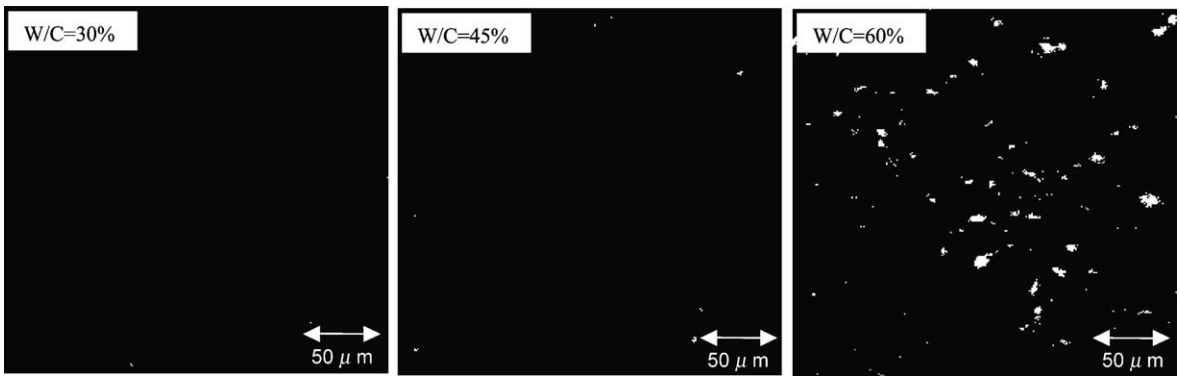

Fig. 10. Effect of W/C ratio on pore structure (pore size > 1 μm).

tion, though some exhibited wider differences, as the tested areas did not perfectly coincide with one another.

5.2. Investigation for pore size greater than 1 μm

Since a pixel is a 1-μm square, Ga intruded in pores greater than 1 μm can be surely recognized. Accordingly, the shape and locations of pores of this size can be directly identified from the image. Fig. 10 shows the distribution of pores 1 μm or greater obtained in this way. The white portions represent the pores. It should be noted that the EPMA image is treated so that a pixel would be identified as Ga only when the measurement on cement paste is identical to the value measured on pure Ga, in order to eliminate background noise.

The quantity of pores greater than 1 μm is not so large but strongly affected by W/C. Such pores scarcely exist when the W/C is 30%. At 45%, they are slightly more, but still few. With a W/C of 60%, pores greater than 1 μm are found to increase, and the shapes of some of the pores clearly indicate clusters of continuous pores.

5.3. Pores smaller than 1 μm

As stated above, it is impossible to identify the shapes of pores smaller than 1 μm by the EPMA analysis technique. Nevertheless, the quantity of Ga in each pixel is indicated, though the Ga density is lower, as shown in Fig. 8. Therefore, the information on the presence, quantity, and distribution of pores is roughly provided by this technique. As the W/C increases, the total area of pixels indicating the presence of Ga increases, suggesting the increase in pores less than 1 μm, and such pixels are found to distribute over the entire field of samples.

6. Conclusions

In this study, a method of examining the pore structures of hardened cement paste using Ga was investigated, and the following conclusions were reached.

(1) A method of intruding Ga into hardened cement was investigated, utilizing the fact that Ga is solid at room temperature. Ga was successfully intruded and fixed in the pores.

(2) By mapping of Ga fixed in the pores using an EPMA, it was possible to observe the shapes of pores. This had conventionally been unavailable by other methods, including mercury intrusion porosimetry. The Ga intrusion method was found capable of indicating the shapes and locations of pores 1 μm or greater. For pores smaller than 1 μm, the method can roughly provide their presence and distribution.

(3) In this study, the resolution of the EPMA limited the potential of this analysis method. A more precise analysis may be feasible when the technology in this field is developed in the future. At present, the instrumental limitations inhibit finer analysis.

The authors consider that this technique should be extended three-dimensionally in the future to express the three-dimensional existence of pores in hardened cement paste. They also intend to elucidate the pore structures of hardened cement paste more precisely under various conditions using this technique.

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References

[1] T.C. Powers, Structure and physical properties of hardened Portland cement paste, J. Am. Ceram. Soc. 41 (1) (1958) 1–6.
[2] W. Hansen, J. Almudaiheem, Pore structure of hydrated Portland cement measured by nitrogen sorption and mercury intrusion porosimetry, Microstruct. Dev. Hydration Cem., (1986) 105–114.

[3] P.W. Brown, D. Shi, Porosity/permeability relationships, Mater. Sci. Concr. II (1991) 83–109.
[4] R.A. Cook, K.C. Hover, Mercury porosimetry of hardened cement paste, Cem. Concr. Res. 29 (1999) 933–943.
[5] D. Winslow, D. Liu, The pore structure of paste in concrete, Cem. Concr. Res. 20 (2) (1990) 227–235.
[6] Y.W. Mai, B. Cotterell, Porosity and mechanical properties of cement mortar, Cem. Concr. Res. 15 (6) (1985) 995–1002.
[7] D.N. Winslow, C.W. Lovell, Measurements of pore size distributions in cements, aggregates and soils, Powder Technol. 29 (1981) 151–165.
[8] K. Van Breugel, Models for prediction of microstructure development in cement-based materials, Model. Microstruct. Potential Stud. Transp. Prop. Durability (1996) 91–105.
[9] D.P. Bentz, Modeling cement microstructure, pixels, particles, and property prediction, Mater. Struct. 32 (1999) 187–195.
[10] H. Uchikawa, S. Uchida, S. Hanehara, Measuring method of pore structure in hardened cement paste, mortar and concrete, Il Cem. 88 (1991) 67–90.