HYDRATION AND MICROSTRUCTURE
OF IRRADIATED CONCRETES

放射線を照射されたコンクリートの水和特性と微細構造

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This study aims to obtain basic knowledge of predicting the life of power reactors. To this end, biological shield concretes in Japan Power Demonstration Reactor (JPDR) exposed to radiations under long term operation was inspected in terms of hydration behavior and microstructure, and compared with model specimens cured under the same thermal conditions. Major findings are as follows,

- SEM observation showed that needle-like crystals in concrete exhibited greater development at the reactor core side than at the perimeter, and they had similar shapes to ettringite and C-S-H as observed in the model specimens.
- Bound water content of mortar was 5 % larger at the reactor core side than at the perimeter, whereas it was average 6.5 % larger in the model specimen. This tendency agrees well with the analysis of concrete in JPDR.
- Hydration products assigned by X-ray diffraction for the model specimens were monosulfate and calcium hydroxide, which were coincide with the analysis of concrete in JPDR.
- Pore size distribution of concrete showed larger amount of small pores at the reactor core side than at the perimeter. This tendency agrees well with the model specimens with a seal.
- Hydration and microstructure analysis of the model specimens supported the test results that the biological shield concrete undergoes no substantial changes.

Keywords : *Biological Shield Concrete, Neutron Fluence, Gamma-ray Dose, Hydration*

生体遮蔽コンクリート 中性子照射 ガンマ線照射量 水和特性

Pore Size Distribution, Microstructures

細孔径分布 微細構造

1. Introduction

Concrete structures is one of the key components which has a possibility to greatly affect the life of power reactors whereby it is necessary for life control to estimate, in a sufficient accuracy, changes of the concrete with time under operations. Studies of changes in properties of irradiated concretes, which is specific to power reactors, have been made with small specimens subjected to intensive radiations in a shot moment. The target reactor was the Japan Power Demonstration Reactor (JPDR), the first small light water reactor that generated power of thermal 45 MW (Modified for double 90 Mw : JPDR - II) in Japan, aged 26 years (18 years after operation was stopped) in 1986 [1]. Though the duration of actual operation was short, the irradiation dose of the biological shield concrete in the JPDR may correspond to that of 40 years operation of large power reactors now in use.

The irradiation dose of the biological shield concrete in the JPDR and the its effects on the mechanical properties were studied in our previous paper [3]. The maximum irradiation ($E > 0.11 \text{ MeV}$) was $1.1 \times 10^{18} \text{ n/cm}^2$ and the maximum gamma ray irradiation was $4.8 \times 10^8 \text{ Gy}$. The compressive strength and modulus of elasticity of the specimen subjected to fast neutron irradiation ($1 \times 10^{13} - 1.86 \times 10^{17} \text{ n/cm}^2$) were 29- 53 MPa and $2.1 - 4.7 \times 10^4 \text{ MPa}$ respectively.

This study aims to obtain basic knowledge of predicting the life of power reactors. To this end, biological shield concretes specimens in JPDR exposed to neutron and gamma ray heat generation were tested in terms of hydration behavior and microstructure and compared with model specimens under the same thermal conditions as JPDR [3].

本論文は、参考文献1, 3~7に加筆し、纏めたものである。

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2. Outline of the biological shield concretes

The biological shield concrete in JPDR was a reinforced concrete with a steel liner of 13 mm thick at reactor core side, a relay liner in the midpoint and epoxy coatings on the exterior surfaces. On the surface of the reactor core side, seven neutron monitor guide tubes and cooling pipes were settled to reduce temperature rise due to gamma ray radiation [1].

Design conditions for biological shield concretes are as follows [1, 2],

- Thickness of concrete : 150 to 300 cm ,
- Slump : 7.5 cm
- Mixture design : Designed strength : 35 MPa,
- Type of concrete : Normal weight concrete
- Mixture proportions : See Table 1

The other conditions such as reinforcement constructions, specifications for steel bars including tensile strength and strain, placement conditions for concrete, irradiation period (operation period) are shown in the chapter 2 of the reference No. 3.

3. Experiment

3.1 Items of tests

Methods and items of tests for hydration and microstructure of biological shield concretes (Experiment 1) [1] and model specimens (Experiment 2) are listed in Table 2.

3.2 Specimen preparations

(1) Biological shield concrete (Experiment 1)

The same core samples as used in the previous study [3] of irradiation dosage and mechanical properties of the biological shield concrete were subjected to analysis of hydration characteristics and microstructure. Thickness of the cores was all the same to have an equal effect of the degree of irradiation, but the distance from the reactor core was varied to see the difference in hydration characteristics and microstructure according to the degree of irradiation [3]. Sampling points (directions) and the height were the same as the previous study [3] and are shown in Fig. 1, and cutting points and names of sampled cores for analysis are shown in Fig. 2 and sampling procedures of specimens subjected to analysis are shown in Fig. 3. The concrete cores, sampled according to JIS A 1107, were prepared according to the need of the test described in 3.3 (1) and (2) [5, 6].

(2) Model specimen under thermal effects (Experiment 2)

Model specimens were prepared with a mixture proportion (Table 1) as close as possible to that of the biological shield concretes in JPDR and shaped in 150 mm in diameter and 300 mm in height according to JIS A 1132 [Method of preparing a specimen for strength tests]. Since the biological shield concrete has a steel liner of 13 mm thick in the interior surface, considerable moisture may have remained in concrete throughout the operation. To simulate this condition, concrete of the model specimens were placed into a thin copper tube with 0.3 mm in thickness, 150 mm in diameter and 300 mm in height, which was previously set in a steel mold. The concrete was placed in three evenly divided volumes, compacted by a vibrator, trowelled after bleeding and sealed with a copper plate. Unsealed specimens were prepared in the same fashion as the sealed specimen except for placing directly into a steel mold. Standard cured specimens were demolded after being kept in the steel mold for two days under a room temperature of 20°C and subjected to the standard curing, while steam cured specimens were demolded after a natural cooling from the preliminary curing of 10 hours after placing and subjected to the secondary curing.

3.3 Test method [5, 6]

(1) Biological shield concrete

Table 1 Mixture Proportions of Concrete

WATER CEMENT RATIO	SLUMP (cm)	UNIT WATER (kg/m ³)	UNIT AMOUNT (kg/m ³)			ADMIXTURES (Mass % of Cement)
			Cement	FA	CA	
0.47	7.5	139	290	853	1240	0.3

Notes : Cement : Normal Portland Cement

FA(Fine Aggregate) : Land sand

CA(Coarse Aggregate) : Nakagawa river

AWR : Air entraining and water reducing admixture

Table 2 Methods and Items of Test

METHODS	TEST ITEMS	SPECIMENS	
		JPDR*	MODEL**
MORPHOLOGY OF HYDRATION PRODUCTS	SEM OBSERVATION	○	○
X-RAY DIFFRACTION	IDENTIFICATION OF CRYSTALLINE HYDRATES	○	○
BOUND WATER CONTENT	STATE OF WATER IN CONCRETES	○	○
THERMAL ANALYSIS	DTA AND TG-DTA	○	○
PORE STRUCTURE	CHANGES IN PORE DISTRIBUTIONS	○	○

Notes * Hydration and microstructure of concrete for JPDR

** Hydration and microstructure of model concrete imagined influence of thermal

Fig. 1 Sampling Points (Directions) and the Height of Reactor Containment of JPDR

1) SEM observations

A mortar part (3- 5 cubic millimeter, dry condition) taken from a roughly ground concrete sample was dried in vacuum , subsequently split to have a fracture plane on which gold was deposited. Observation was made in a magnification of 500, 1000, 3000 and 10000 times at each two fields of view for a sample.

Fig. 2 Cutting Points and Names of Sampled Cores for Analysis

2) X-ray diffraction

About one grams of powder for gamma-ray diffraction analysis was taken from a mortar part (dry condition) finely ground less than 45 micrometers, placed on a glass plate and subjected to analysis. Diffraction angles (2θ) were measured and the spacings of lattice planes were calculated from the Bragg's equation and the crystalline phases were assigned with reference to the JCPDS card [5,6]. (indoor temperature : 20 - 25°C).

3) Bound water content and differential thermal analysis

A five grams of powder was taken from a mortar part finely ground less than 45 micrometers and dried at 40°C for 24 hours, and moisture content and bound water content were calculated using following formulas with weight loss data at temperatures of 105, 400, 650 and 950°C in an electric furnace . From the entire DTA curve , weight loss between 600°C to 700°C that corresponds to the decomposition of carbonates was negligible thereby 650°C was used as the upper limit temperature for the bound water estimation .

Moisture content = (weight before drying - weight after drying) × 100 / (weight before drying) (%),

Bound water content = (Moisture content at 650°C) - (Moisture content at 105°C).

A 10 milli- grams of powder was taken from a mortar part finely ground less than 45 micrometers and was heated at a heating rate of 10 deg / min up to 950°C by a differential thermal analyzer using an alpha (α) - alumina as a reference material. Calcium hydroxide content was calculated using the following formula.

Calcium hydroxide content = (moisture content at 440 - 500°C) / 0.246 (%),

where a coefficient of 0.246 is a water content of calcium hydroxide.

Area under the endothermic peak of Ca(OH)₂ dehydration was determined by block counting method in the grid paper where the chart output from the X-Y recorder was transferred .

4) Pore size distribution

A 30 grams of mortar part was taken from the concrete sample, subjected to ultrasonic cleaning in an ethanol solution and dried at 105°C for 30 minutes. Mercury porosimetry was operated at a pressure range of 0.09 to 200 MPa which

Fig. 3 Sampling Procedures of Specimens Subjected to Analysis

Fig. 4 Curing Conditions of the Model Specimens

side than at the perimeter and that of ettringite was much larger at the reactor core side.

(3) Amount of bound water and thermal analysis of hydration products

Heating weight loss and amount of bound water of mortar part of the specimens is shown in Table 3. Amount of evaporable water of specimens taken from the reactor core side was 12 % larger than that from the perimeter and

amount of the other type of water was less than 5 % in average and slightly larger than that of the perimeter.

Bound water content of specimens taken from the reactor core side was 6.89 % while that from the perimeter was 6.58 %.

An example of DTA chart is shown in Fig. 7. An endothermic peak due to a dehydration of calcium hydroxide can be seen at 0.75 to 1.3 times (Table 4) with respect to that from the perimeter. This implies that the amount of $\text{Ca}(\text{OH})_2$ in the reactor core side is less than that in the perimeter.

(4) Pore size distribution and pore volume

Pore size distribution and total pore volume of specimens taken from the reactor core side and from the perimeter are shown in Fig. 8 and Table 5. The differential pore volume exhibited a peak at a pore size range from 13 to 45 nm, which was common to all specimens, while a total picture of pore size distribution of samples taken from the reactor core side was shifted to the smaller side compared to that from the perimeter. Total pore volume of samples taken from the reactor core side, samples I and H for example, was $49.7 \text{ mm}^3/\text{g}$ which was 13 % smaller than that from the perimeter implying a slight densification of the matrix.

5.2 Hydration and microstructure of the model specimen

(1) SEM observations

Results of SEM observations according to curing conditions No.1, 2, 3 and 4 are listed in Table 6. In specimens cured in No. 2 condition presuming a location near the reactor core, monosulfate (a plate-shaped crystal about 1 micrometers in dimension), calcium hydroxide (a layered, plate-shaped crystal about few micrometers in dimension) and hydrogarnet (a small spherical crystal about 0.3 micrometers in dimension) were observed regardless of the presence of seal, while ettringite (a needle-like crystal about 1 micrometers in dimension) and C-S-H (a granulated or mesh-like particle less than 1 micrometers in dimension) were predominantly observed in samples without a seal than those with a seal. In specimens cured in No. 4 condition presuming a location far from the reactor core, ettringite, calcium hydroxide and C-S-H were observed while monosulfate and hydrogarnet were not observed, and amount and dimensions of calcium hydroxide and C-S-H increased with the lapse of time. Type of hydration products differed according to a temperature history at early ages (a curing condition of No.1 without a seal and No. 4), while as a whole, no significant difference was observed according to the long term temperature history or to the presence of a seal.

(2) X-ray diffraction of hydration products

Examples of X-ray diffraction pattern of specimens cured by No.2 method and changes in hydration products are

Table 3 Heating Weight Loss and Amount of Bound Water (BW) of Mortar

SAMPLING LOCATIONS	HEATING CONDITIONS	(Unit : wt%)			
		105°C	400°C	650°C	BW *
REACTOR CORE SIDE	1hr	1.86	4.27	2.82	8.32
	1hr	1.86	4.09	2.49	8.01
OUTSIDE		1.12	1.04	1.05	1.05

Notes, Reactor core side : Average of 1H-8A, 2H-3, 1I-3, 2I-4
Outside : Average of 1H-16A, 2H-20B, 1I-14, 2I-14

* Amount of bound water

Fig. 7 An Example of DTA Chart of Mortar

Table 4 Compared by Area under the Peak of Calcium Hydroxide

CORE NAMES	1H	2H	1I	2I	AVERAGE
SAMPLING LOCATIONS					
REACTOR CORE SIDE	(1H-8A)	(2H-3)	(1I-3)	(2I-4)	1.07
	1.30	0.75	0.85	1.14	
OUTSIDE	(1H-16A)	(2H-20B)	(1I-14)	(2I-14)	1
	1	1	1	1	

Notes, Reactor core side : Average of 1H-8A, 2H-3, 1I-3, 2I-4

Outside : Average of 1H-16A, 2H-20B, 1I-14, 2I-14

Fig. 8 Pore Size Distribution and Total Pore Volume of Mortar

Table 5 Compaction of Total Pore Volume

SAMPLING LOCATIONS	CORE NAMES	(Unit : mm^3/g)				
		G	1H	2H	2I	J
REACTOR CORE SIDE	(G-2)	68.30	39.90	42.90	49.80	56.6
OUTSIDE		-	(1H-16A)	(2H-20B)	(2I-14)	-
			65	56.5	51.7	

Notes, Reactor core side : Average of 1H-8A, 2H-3, 1I-3, 2I-4

Outside : Average of 1H-16A, 2H-20B, 1I-14, 2I-14

Table 6 Observations of Hydrates (SEM)

CURING CONDITIONS No.	EXISTENCE OF SEAL	AGES (Months)	HYDRATES *1				
			*4 ETT	*5 MONO	*6 CAL	C-S-H	*7 HYD
1	SC *2	AFTER PRIMARY CURING	○	⊙	○	⊙	⊙
		1 MONTH	○	⊙	⊙	⊙	⊙
		3 MONTHS	○	⊙	⊙	○	⊙
	AC *3	AFTER PRIMARY CURING	⊙	⊙	○	⊙	⊙
		1 MONTH	⊙	⊙	⊙	⊙	⊙
		3 MONTHS	⊙	⊙	○	⊙	⊙
2	SC	1 MONTH	○	⊙	⊙	○	⊙
		3 MONTHS	○	⊙	⊙	○	⊙
	AC	1 MONTH	○	⊙	⊙	⊙	⊙
		3 MONTHS	⊙	⊙	⊙	⊙	⊙
3	AC	1 MONTH	⊙	×	⊙	⊙	×
4	AC	1 MONTH	⊙	×	⊙	⊙	×
		3 MONTHS	⊙	×	⊙	○	×

Notes: *1 Mark : Amount of hydrates

⊙ : Significant, ○ : Present, × : Absent

*2 SC : Sealed Cured *5 MONO : MONOSULFATE

*3 AC : Air Cured *6 CAL : CALCIUM HYDROXIDE

*4 ETT : ETTRINGITE *7 HYD : HYDROGARNET

shown in Fig. 9 and 10 respectively. Crystalline phases of the hydrates assigned were unhydrated cement clinkers, calcium hydroxide, ettringite and monosulfate as well as quartz and feldspar originated from aggregates. A dehydrate gypsum was assigned in a specimen after the primary curing. Among the hydration reactions of cement at early stages, a C_3A reacts with a dehydrate gypsum to form an ettringite, however with a shortage of the gypsum, the ettringite may

Fig. 9 X-ray Diffraction Pattern

Fig. 10 Change in Hydration Products

transfer to a monosulfate in the presence of excessive C_3A . Subsequent reactions involve hydration of C_3S and C_2S , the main components in cement clinker, which results in a formation of C-S-H gels and calcium hydroxide. This reaction was traced by focussing on peaks at 32.1° , the most intensive peak for C_2S and C_3S , and 18° , the most intensive peak for calcium hydroxide, while C-S-H was not detected by X-ray diffraction due to its poor crystallinity.

In specimens cured by No.2 method presuming a location near the reactor core, intensive peaks associated with ettringite, monosulfate and calcium hydroxide were detected showing agreement with the results of the biological shield concrete in JPDR. Evolution of hydration was developed in specimens without a seal more rapidly than those with a seal and accelerated by the ambient temperatures. Specimens cured in a high temperature at early ages showed a slow or retarded hydration subsequently.

(3) Amount of bound water

Amount of bound water during the hydration is shown in Fig. 11 and 12. The bound water increased with an increase in age regardless of the curing method. Amount of bound water of mortar cured with No.2 method presuming a location near the reactor core was 3.5 – 10 % (average 6.5%) larger than that cured by No.4 method presuming a location in the perimeter at ages of 1 and 3 months as shown in Fig. 11. However as shown in Fig. 12, amount of bound water of mortar cured with No. 2 method was about 12% larger than that of No. 4 cured until the ages of 3 months. Bound water of specimens cured (at ages of 1 and 3 months) with No.2 method with a seal was 5 to 15 % larger than that without a seal. This tendency agrees well with the analysis of concrete in JPDR. Model specimens with a seal generally had larger amount of bound water, probably

Fig. 11 Amount of Bound Water during the Hydration Determined by the Heating Weight Loss

Fig. 12 Amount of Bound Water during the Hydration Determined by the Heating Weight Loss

Intensity of Endothermic Peak
S : Strong
M : Middle
W : Weak
B : Broad

Dehydration Temperature (DTA)
① Adhesion Water
② C-S-H (First)
③ Ettringite (First)
④ Gypsum
⑤ Ettringite (Second)
⑥ Monosulfate
⑦ Hydrogarnet

Fig. 13 Example of TG-DTA

because the dimension of the sample was small enough to be dried more quickly. Probably by the same reason, bound water content of air cured hardened concrete was 5.5 % larger than that cured in water (No. 3 method) but 10 % less than that of shaped mortar. Bound water content increased with ages when specimens were subjected to heating at early ages and no difference was observed among the specimens. Bound water content of specimens subjected to a long term high temperature also increased with ages and the evolution of hydration was accelerated.

Table 7 Differential Thermal-Gravimetric Analysis (Endothermic peaks)

ITEMS		ENDOTHERMIC PEAKS *1														
TEMPERATURE(°C)		45~55	70~80	95~105	110~120	130~135	145~155	360~390								
HYDRATES *2		AW	C-S-H	ETT	GY	ETT	MONO	HYO								
AGES (Month)	EXISTENCE OF SEAL CURING	SC	AC	SC	AC	SC	AC	SC	AC							
	CONDITION No.															
AFTER PRIMARY CURING		1	S	S	/	/	W	W	W	W	M	M	B	B		
1 MONTH	1	S	S	S	W	B	W	W	W	/	M	W	M	B	B	
	2	S	S	S	B	B	W	B	/	/	W	M	W	B	B	
	3	-	S	-	S	-	M	-	B	-	-	M	-	/	-	
	4	-	S	-	S	-	S	-	B	-	-	W	-	/	-	
3 MONTHS	1	S	S	S	W	W	B	B	B	/	W	W	W	M	B	B
	2	S	S	S	B	B	W	B	/	/	W	/	M	M	B	B
	3	-	S	-	S	-	S	-	B	-	-	W	-	/	-	
	4	-	S	-	S	-	S	-	W	-	-	W	-	/	-	

Notes: *1 Intensity of endothermic peaks

S: Strong, M: Middle, W: Weak, B: Broad, /: Absence

*2 AW: Adhension water, ET: Ettringite, MONO: Monosulfate

HYO: Hydrogarnet, GY: Gypsum

SC: Sealed cured, AC: Air cured

(4) Thermal analysis (TG-DTA)

An example of thermal analysis is shown in Fig. 13. Hydration products of cement were dehydrated at a range of high temperature, thereby amount of hydration products can be determined from endothermic peaks in the differential thermal - gravimetric analysis. Results are shown in Table 7. Amount of C-S-H in specimens cured with No. 3 and No. 4 method was larger than that cured with No. 1 or No. 2, while amount of ettringite was not so different with each other. Hydrogarnet was detected at a broad peak near 370 °C for all ages of specimens cured with No. 1 and No. 2 method, but not for specimens cured with No.3 and No. 4 method corresponding to the result of SEM observation. An endothermic peak of calcium hydroxide in specimens cured with No. 2 method, presuming a location near the reactor core, was 12 to 17 % larger than those cured with No. 4 method, presuming a location far from the reactor core, and an endothermic peak of calcium hydroxide in specimens with a seal was 17% smaller than those without a seal. Results of bound water content by thermal analysis is shown in Fig. 14, which exhibits a similar tendency to that determined by the heating weight loss (Fig. 11). Evolution of hydration of specimens without a seal became faster than that with a seal when a long term heating is applied.

(5) Pore size distribution and pore volume

A pore size distribution of specimen cured with No.2 method presuming a location near the reactor core is shown in Fig. 15. Differential pore volume of the mortar near the reactor core with a liner showed maximum at a pore size range from 7.5 to 45 nm, while that located far from the reactor core (No.4 curing method) distributed over 7.5 to 7500 nm. This tendency agrees well with the analysis of concrete in JPDR. Total pore volume, mean pore radius and age of specimens cured with No.1, 2, 3 and 4 are shown in Fig. 16. Total pore volume and mean pore radius of specimens cured with No.1 and No. 2 method and with a seal decreased slightly with ages implying the gradual densification of the matrix. When a heating applied at early ages, total pore volume of specimens without a seal exhibited no changes with time whereas the mean pore radius increased and specific surface area decreased. For specimens subjected to a long term high temperature, total pore volume increased and the pore size distribution shifted to a larger side with the lapse of time. Though this tendency was not confirmed by SEM observation, it may be attributed to a drying of hydration products due to a high temperature (50°C, 60%RH). The mean pore radius of specimens cured in air was much larger than that cured in water while the total pore volume was not different.

6. Discussions on the model specimens and conditions in JPDR

After 26 years of construction, the biological shield concrete in JPDR has been irradiated intermittently by gamma ray and neutron during the 1.3 years of full power operation. Although the dosage cannot be directly linked with the curing conditions of the model specimen, moisture conditions in concrete was assumed to be kept high since the high temperature side of the concrete was covered by a steel liner. Results of the model specimens thus could support the test

Fig. 14 Bound Water Content by Thermal Analysis

Fig. 16 (1) Relationships between Total Pore Volume and Ages

Fig. 15 Pore Size Distribution (20°C, 28day)

Fig. 16 (2) Relationships between Mean Pore Radius and Ages

results of hydration and microstructure of biological shield concrete in JPDR.

7. Conclusions

This study dealt with hydration behavior and microstructure of biological shield concrete used under a normal operation in JPDR and the model concrete specimens prepared in a variety of curing conditions that were equivalent to the environmental conditions in JPDR. Major findings are as follows.

(1) SEM observations

SEM observation showed that needle-like crystals in concrete exhibited greater development at the reactor core side than at the perimeter, and they had similar shapes to ettringite and C-S-H observed in the model specimens that were cured with No. 2 curing method presuming a location near the reactor core.

(2) X-ray diffraction of hydration products

X-ray diffraction peaks of ettringite were slightly intensive at the reactor core side rather than the perimeter. In model specimens cured by No.2 method presuming a location near the reactor core, intensive peaks associated with ettringite, monosulfate and calcium hydroxide were detected showing agreement with the results of the biological shield concrete in JPDR.

(3) Amount of bound water

Evaporable water content at the reactor core side was 12 % higher than that of the perimeter, and bound water content was 5 % larger at the reactor core side than at the perimeter. Bound water content of model specimens cured with No.2 method, which presumes a location near the reactor core, was average 6.5% higher than that cured with No.4 method, which presumes a location in the perimeter. This tendency agrees well with the analysis of concrete in JPDR.

(4) Amount of hydration products determined by thermal analysis

Hydration products determined by thermal analysis agreed with the SEM observations when the specimens were subjected to heating at early ages, and showed similar results to the X-ray diffraction analysis when the specimens were subjected to long term heating and with / without a seal.

(5) Pore size distribution and pore volume

Pore size distribution showed larger amount of small pores at the reactor core side than at the perimeter. This tendency agrees well with the model specimens cured with No.2 method with a seal. Total pore volume of specimens at the reactor core side were smaller than that at the perimeter implying a densification.

With above observations and discussions, we may conclude that the hydration and microstructure analysis of the model specimens under an equivalent thermal effects in JPDR, supports the test results that the biological shield concrete undergoes no substantial changes.

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和文要約

1. はじめに

今回、研究対象とした原子炉は、日本で初めて発電を行った動力試験炉（JPDR）で、長時間、低照射率で照射されたコンクリート構造物である。そこで、本研究は、放射線を照射された生体遮蔽コンクリートが中性子および γ 線の発熱によってコンクリートの水和特性と微細構造がどのような影響を受けているかを把握するためにJPDR³⁾と同様の温度条件下におけるモデルコンクリート試験体を新たに作製して、それらの挙動について比較検討することによって生体遮蔽コンクリートの物理・化学的变化から発電炉の寿命を予測する場合の有用な知見を得ることを目的として行ったものである。

2. 生体遮蔽コンクリートの概要

生体遮蔽コンクリートはRC造で、厚さ13mmの鋼製ライナーが炉心側内表面に内張りされ、内外表面の間には中継ぎライナーが配置され、外表面にはエポキシ系の塗装が施されている。

生体遮蔽コンクリートの概要、設計条件と調査を、本文 2章と Fig. 1, Table 1 に示す。

3. 試験概要

生体遮蔽コンクリート（実験 1）および放射線照射による温度の影響を想定したモデル試験体（実験 2）の水和特性と微細構造に関する試験項目と内容をTable 2 示す。生体遮蔽コンクリートの水和特性と微細構造の挙動は、放射線照射量の影響をみるために部材厚さ等の条件を同一として、炉心との位置関係による影響を確認するために平面对称で測定した。試料の採取位置は、Fig. 1 のように放射線照射量が最も多い炉心近房と照射量が少ない炉心から離れた位置、さらに放射線の照射を極力受けない位置のものとした。Fig. 3 に測定する試料の採取手順を示す。温度の影響を想定したモデル試験体は、JPDRの建設当時とできるだけ同一の材料と調査とした。モデル試験体は、原子炉からの放射線照射による熱エネルギーを長期に受けたコンクリートの挙動を再現するために、Fig. 4 に温度の影響を想定した養生条件で行った。モデル試験体は、遮蔽コンクリートが打込み厚さの大きいコンクリートであることから、炉心側ライナーに近いところおよびコンクリート中心部で水分の移動が制限されることを想定して、銅板筒型枠（厚さ0.3mm、外径15mm、内高30mm）による完全密閉を施すものをシール有りとし、熱が伝導されて室温に接する部分を想定してシール無しと設定した。想定した温度は、打込み時の水和反応に伴う発熱と運転時の放射線の照射に伴う発熱を考慮して、60℃とした。これらの計算方法は文献 3) の3.3 に、解析結果の要約は、本文の「4章」に示した。

4. 試験方法

(1) 生体遮蔽コンクリート

1) 走査型電子顕微鏡観察（SEM）

SEM の観察は、コンクリートの粗粉碎試料（乾燥状態）からモルタル部分（3 ～ 5 mm³）を採取して真空乾燥した後に、その試料を割裂した破断面に金を真空蒸着して行った。測定は微小部走査型電子顕微鏡によって1 試料につき 2 視野とし、倍率は、500, 1000, 3000, 19000 倍で行った。

2) X線回折

X線回折は45 μ m以下に微粉碎（乾燥状態）したモルタル部分（約 1 g）をガラス板に均一になるように詰めて、回折角（2 θ ）を測定し（室温：20～25℃）、Bragg's の条件式に代入して格子面間隔を求め、JCPDS カードにより同定した^{5) 6)}。

3) 結合水量及び示差熱分析

結合水量は45 μ m以下に微粉碎したモルタル部分を約 5 g 採取し、40℃で24時間乾燥させた後に電気炉により、105℃、400℃、650℃及び950℃で各 1時間、650℃の減少率より105℃減少率を減じて算出した^{5) 6)}。DTA の結果をみると、炭酸塩の分解に対応する600 ～ 700℃の減量はほとんど見られないので、試料の炭酸化はほとんどないものと考えて、結合水量算定上の上限温度を650℃とした。

結合水量の計算

$$\text{減少率 (\%)} = \frac{(\text{試験前の質量} - \text{試験後の質量})}{\text{試験前の質量}} \times 100$$

$$\text{結合水 (\%)} = 650^\circ\text{C 減少率} - 105^\circ\text{C 減少率}$$

示差熱分析（DTA）曲線は、45 μ m以下の微粉碎試料を約10mg採取して、示差熱分析装置を用いて昇温速度を10℃/min（室温：20～25℃）、温度 950℃まで α アルミナを標準試料として測定した。

示差熱分析の計算

$$\text{Ca(OH)}_2 \text{ (\%)} = 440 \sim 500^\circ\text{C の脱水による} \\ \text{減量率} / 0.243^{*1)}$$

$$*1): 0.243 = \text{H}_2\text{O} / \text{Ca(OH)}_2$$

吸熱ピーク面積比の算定は、3.3.3. (1), 3) に示した。

4) 細孔径分布（ポロシティ）

細孔量はコンクリートの粗粉碎試料からモルタル部分を約30 g 採取して、エタノールに入れ超音波洗浄をした後105℃で 30 分間乾燥し、水銀圧入式のポロシメータを用いて水銀圧力 0.9～20 00kg/cm²で細孔径を 6～9500nmの範囲で測定した。

(2) 温度の影響を想定したモデル試験体

水和特性と微細構造の試験は、Fig. 3 に準じて3.2(2)のコンクリートから骨材を取り除いた微粉碎試料（乳パチによる）を調製して、3.3. (1), 1)～4)と同様の方法で SEM観察、X線回折、結合水量、熱分析および細孔径分布などについて行った。

5. まとめ

試験結果およびその考察から、次のような知見を得た。

- SEM 観察の結果、針状結晶は炉心側試料の方が外側に比べて発達の数が多い。それは、モデル試験体のエトリンガイトとC-S-H の針状結晶と同じであった。
- 結合水量は、炉心側の方が外側に比べて約 5%大きい。モデル試験体では 6.5%程度大きくなり、JPDRの分析結果と同じ傾向を示した。
- X線回折による水和生成物は、モデル試験体のときモノサルフェート、Ca(OH)₂ のピークが強く検出されており、JPDRの分析結果と一致していた。
- 細孔径分布は、炉心側の方が外側より小さい細孔径が多く存在しており、この傾向はモデル試験体のシール有り（炉心側を想定）の場合とよく一致していた。
- モデル試験体の水和特性と微細構造は、生体遮蔽コンクリートの結果と特に変化を生じていないという試験結果を補足しているデータのの一つであると考えられる。

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