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## **Effect of Gamma Irradiation on Hardened Cement Paste**

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## ABSTRACT

Hypothesis about radiation carbonation of hydrated cement paste has been tested during our research. Radiation carbonation takes part in entire volume of gamma-irradiated samples contrary to "natural" carbonation, which takes part in surface layers only. The hypothesis is being verified by means of three sets of experiments: (a) changes of composition of hydrated cement paste (transformation of portlandite to calcite), (b) changes of porous space (changes of average pore diameter), (c) changes of mechanical properties (hardness). Experimental results support our hypothesis that besides of natural carbonation there is also carbonation due to irradiation.

### **INTRODUCTION**

Concrete is a composite material that consists mainly of mineral aggregates bound in the matrix of hardened cement paste (HCP). In this project the hardened mixture of Portland cement and water is studied. The HCP consists mainly of a complex of hydrates (so called tobermorite gel), crystals of Ca(OH)<sub>2</sub> in form of portlandite, particles of unhydrated cement and pore space more or less saturated by water. The long term performance of concrete buildings is primarily affected by the ability of concrete to withstand the potential influence of degradation. For so-called concrete nuclear safety structures (e.g. the containment buildings, the containers for radioactive waste etc.) is among others degradation factors such as irradiation due to fast neutrons and gamma rays [IAEA-TECDOC 1025 1998].

Interaction with gamma radiation has been studied only recently and mainly with emphasis to interaction of gamma radiation with aggregates. According to [Harbsmeier and Bolse (1998)] effect of irradiation on aggregates is manifested by phase transformation of crystalline form to amorphous form of quartz which is accompanied with an increase of volume of the aggregates. There has hardly been any research of effect of gamma irradiation on HCP. It is supposed, usually, that gamma radiation is a cause of radiolysis of water which can result into shrinkage of the HCP [Ichikawa, Koizumi, 2002]. [Vodák et al. 1989] presented, however, another hypotheses: inside of samples carbonation processes are accelerated above "natural" rate at which carbonation is governed by diffusion of  $CO_2$  from surface to depth of the samples. During the carbonation processes  $CO_2$  reacts with portlandite with calcite as a product. Crystals of calcite grow through pores decreasing their diameter and hardening the material (hardness of calcite on Mohs's scale is 3, while hardness of porlandite is 2) [Taylor 2004]. The aim of this paper is to verify following hypotheses.

Experimentally were determined following properties of HCP:

**1. Composition of HCP.** It is expected that with growing dose of gamma irradiation content of calcite is increasing while content of portlandite (and ettringite) is decreasing [Bouniol and Aspart, 1998].

**2. Porous structure of HCP.** It is expected that porous space is decreasing with dose of gamma irradiation

**3.** Hardness of HCP. It is awaited that hardness is growing with dose of gamma irradiation. Following sets of experiments were carried out: the first set of samples was ageing for six months after casting. No special curing was applied to the samples - they were exposed to air in laboratory during ageing. After six month of ageing all samples were relocated to exposure chamber for three month. Check samples were shielded immediately, other samples were shielded as soon as they received target dose (0.1 MGy, 0.2 MGy, 0.5 MGy, 1 MGy). Within the next 14 days after irradiation all samples were tested with aim to determine changes in composition, porous structure and hardness. During this experiment all samples were exposed to "natural" carbonation for at least 9 months and (simultaneously) to radiation carbonation for up to 3 month. Four samples from the previous set (two check samples and two samples exposed to 1 MGy) were put aside for another testing. They were stored in laboratory in same conditions as during ageing. Three month later these samples were cut into wafers 1 mm thick. Changes in composition, porous structure and hardness were determined on wafers cut from surface and depth of samples. Another set of samples was ageing wrapped in a foil in distilled water with aim to minimize "natural" carbonation. After six month of such curing the samples were relocated to exposure chamber for four month. Check samples were shielded, target dose of gamma irradiation of other samples was 1.6 MGy. Within the next 14 days after irradiation 1.3 mm thick wafers were cut from depth of all samples and tested with aim to determine changes in composition, porous structure and hardness.

## **ARRANGEMENT OF EXPERIMENTS**

#### Sample preparation

Samples were prepared as a blend of Portland cement (composition see table 1) and water with water cement ratio 0.4. Mixture was cast into moulds of size  $0.08 \times 0.16 \times 0.01$  m.

composition of cement		phase clinker composition			
clinker	95.0 %	C <sub>3</sub> S	68.5 %		
gypsum	3.5 %	$C_2S$	11.6 %		
fly ash	1.3 %	C <sub>3</sub> A	7.4 %		
slag	0.2 %	C <sub>4</sub> AF	11.5 %		
		C <sub>free</sub>	1 %		

#### Table 1: Composition of Cement 42,5R Mokrá (% by mass)

#### Irradiation

Samples were exposed to gamma irradiation in calibrated chamber with dose rate 512 Gy/h. In experiments EIa and EIb maximal dose reached 1 MGy, in experiment EII 1.6 MGy. For check samples as well as for samples with lower than maximal target dose lead bricks were used.

#### **Composition of HCP**

In our underlying hypothesis some changes in content of crystalline substances were expected, therefore we choose an x-ray powder diffraction analysis to investigate this changes. Instruments X'Pert APD and PRO MFD were used for this purpose. The last one was used in evaluation of the experiment EII with aim to perform a semi quantitative analysis of changes of content of crystalline materials.

#### Porosity

Mercury porozimetry (Micrometric Auto-Pore 9200) and adsorption of nitrogen (ASAP 2010) were used to investigate changes in porous space of HCP.

#### **Mechanical properties**

Due to limited volume of irradiation chamber and for the sake of homogenous irradiation samples of small sizes were used. The small size of samples did not allow using conventional non-destructive methods therefore a specific method of indentation was developed by Trtík (2006). The method involves pressing a "Cube Corn" indenter into material surface. Movement of the indenter is recorded with accuracy of 1  $\mu$  m. Typical record of the test see Figure 1. As the geometrical shape of the indenter is known, vertical stress can be calculated for each displacement of the indenter into the material surface. This stress is called hardness of the material.



Fig. 1: Example of an Indentation Test



Fig. 2: Ratio of Relative Intensities of Main Diffraction Peaks of Calcite (3.03 Å) and Portlandite (4.9 Å)

#### RESULTS

#### **Composition of the HCP**

A basic conception of changes in crystalline materials (such as portlandite and calcite) in HCP we can get using qualitative x-ray analysis. Within this analysis the most outstanding diffraction peaks of calcite (3.03 Å) and portlandite (4.9 Å) are compared.

#### EI

Original values of relative intensities of main diffraction peaks of calcite and portlandite are in table 2 and 3, while ratio of these peaks is displayed in figure 2. Each number in the tables and point in figure is an average from four (EIa) or three (EIb) measurements, with 50% probable error not exceeding 7.5 %. Ratio of relative intensities of main diffraction peaks of calcite and portlandite increases with dose of gamma irradiation.

#### EII

Semi quantitative analysis of x-ray experiments was performed for EII. In this analysis sum of mass of portlandite and calcite is considered to be 100 %, see table 4. It is obvious, that the proportion of calcite to portlandite increases due to irradiation.

Table	2:	Relative	Intensity	of	Diffraction	Peaks	of	Calcite	(3.03	Å)	and
Portla	ndit	e (4.9 Å) i	n Experim	lent	EIa (Entire	Sample	)				

	Relative intensity (%)				
Dose (MGy)	portlandite	calcite			
0	$100 \pm 0$	41 ± 5			
0.1	$100 \pm 0$	$46 \pm 4$			
0.2	$100 \pm 0$	$49 \pm 4$			
0.5	$100 \pm 0$	61 ± 6			
1	$100 \pm 0$	$70 \pm 5$			

# Table 3: Relative Intensity of Main Diffraction Peaks of Calcite (3.03 Å) and Portlandite (4.9 Å)

	Relative intensity (%)					
	Surface Depth					
Dose (MGy)	portlandite	calcite	portlandite	calcite		
0	$100 \pm 0$	$79 \pm 8$	$100 \pm 0$	$14.0 \pm 0.3$		
1	$68 \pm 5$	$100 \pm 0$	$100 \pm 0$	$20 \pm 0$		

 Table 4: Semi-quantitative Analysis of X-Ray Diffraction Records (EII, Depth of Samples)

Dose (MGy)	portlandite	calcite
0	$63.5\pm\ 6.9$	$36.5\pm\ 6.9$
1.6	$38.4 \pm 4.0$	$61.6 \pm 4.0$

#### Changes in porous space.

Changes in pore distribution were investigated. In all experiments maximum increase of pores has been observed in nanopore region (i.e. in range  $10^{-8} - 10^{-9}$  m). Typical results (EIb) are presented on figures 3 and 4.



Fig. 3: Pore-size Distribution Determined at Sample Surface (● Unirradiated Samples, □- Irradiated Samples (1 MGy))



Fig. 4: Pore-size Distribution Determined in Depth of Samples (◦ Unirradiated Samples, □- Irradiated Samples (1 MGy))

Changes of pore structure were expressed through the average pore diameter, which value is calculated automatically by software Auto-pore 9200 according to formula  $d = 4V_p/A_p$ , where  $V_p$  and  $A_p$  are experimentally determined volume and surface of the pore space, respectively. Results are presented in tables 5 and 6, relative changes in Figure 5.



Fig. 5: Decrease of the Average Pore Diameter (APD) Due to  $\gamma$ -Irradiation (Relative Changes)

Table 5: Average Pore Diameter (APD) as a Function of Irradiation dose (EIa)

Dose (MGy)	0	0.1	0.2
APD (nm)	$38.0 \pm 2.1$	$37.7 \pm 2.8$	$36.9 \pm 1.9$
Dose (MGy)	0.5	1	
APD (nm)	$31.1 \pm 0.9$	$27.5 \pm 2.0$	

Table 6: Average Pore Diameter (APD) as a Function of an Irradiation Dose Fe	or
The Surface and the Centre of the Samples (EIb)	

	Surface of sam	ples	Centre (depth) of samples		
	$d_s$	$d_{smax}$	$d_{c}$	$d_{cmax}$	
Dose (MGy)	0	1	0	1	
APD (nm)	$30.7 \pm 2.7$	$24.7 \pm 0.8$	$41.9 \pm 2.8$	$36.4 \pm 1.5$	

It may be assumed that natural carbonation acts from surface to the centre while carbonation due to irradiation takes its course within entire depth of the material. Comparably short time within which our experiments were performed (10 month) allows us to assume, that natural carbonation affects surface of the material only and the depth remains uncarbonized (in case of unirradiated check samples) or affected by radiation carbonation only (in case of irradiated samples). It may be assumed, therefore, that in the depth of an unirradiated sample the average pore diameter  $\P_c$  remains constant during the experiment, while the average pore diameter  $\P_s$  on the sample surface is affected by the natural carbonation. In case of irradiated samples a value of average pore diameter in the depth  $\P_c$  will be affected by irradiation only (reaching  $d_{cmax}$  at the maximal dose 1 MGy). This simplified model is illustrated on figures 6 and 7.



Fig. 6: Average-Pore-Cross-Section (Unirradiated Material), Schematically



#### Fig. 7: Average-Pore-Cross-Section (Irradiated Material), Schematically

The variation of an average pore diameter due to natural carbonation  $(d_n)$  and radiation carbonation  $(d_r)$  can be both, within this simplified model, determined using two independent experimental data sets (irradiated and unirradiated samples) from table 6 using arrays of equations 1 and 2.

$$\Delta d_n = d_s - d_c$$
  

$$\Delta d_r = d_{smax} - d_s \qquad (1)$$
  

$$\Delta d_n = d_{smax} - d_{cmax}$$
  

$$\Delta d_r = d_{cmax} - d_c \qquad (2)$$

Results presented in Table 7 indicate that beside decrease of average pore diameter due to "natural" carbonation there is also decrease due to radiation carbonation.

#### Hardness

Hardness was determined at thrust of indenter 0.4 mm, at which position hardness is close to the limit value. Results for all experiments are summarized in tables 8-10 and figure 8. Each point represents an average from 6 to 10 measurements, 50%-probable-error-bars are included. It is obviuous that hardness always growth with dose of irradiation, as expected.

Table	7:	Changes	Of	Average	Pore	Diameter	Due	То	Natural	Carbonation
$(\Delta d_n)$	An	d Radiati	on (	Carbonati	on ( $\Delta$	$d_r$ )				

Equation	1	2
$d_n$ (nm)	-11.25	-11.65
$d_r$ (nm)	-5.95	-5.55

## Table 8: Hardness as Determined in Experiment EIa

Dose (MGy)	0	0.1	0.2
Hardness (GPa)	$0.698 \pm 0.057$	$0.802 \pm 0.032$	$0.859 \pm 0.041$
Dose (MGy)	0.5	1	
Hardness (GPa)	$0.864 \pm 0.027$	$0.898 \pm 0.028$	

## Table 9: Hardness as Determined in Experiment EIb

Dose (MGy)	0	1
	sur	face
Hardness (GPa)	$0.825 \pm 0.046$	$0.888 \pm 0.040$
	de	pth
Hardness (GPa)	$0.552 \pm 0.023$	$0.710 \pm 0.022$

## Table 10: Hardness as Determined in Experiment EII

Dose (MGy)	0	1.6
Hardness (GPa)	$0.489 \pm 0.042$	$0.613 \pm 0.017$



Fig. 8: Relative Hardness of HCP as a Function of Irradiation

#### **Moisture content**

Substantial part of irradiation processes in HCP is hydrolysis and therefore drying of samples. Drying process was monitored by weighting of all samples during experiment EII. Mass of samples was determined at the beginning of irradiation, in time of shielding of samples subjected to the final dose of 0.5 MGy, and in time of withdraw of samples from the chamber. Relative changes of mass of the samples can be seen on figure 9.





#### CONCLUSIONS

Presented research confirms hypotheses about the radiation carbonation. There is an obvious increase of calcite content in HCP with growing dose of irradiation. The samples in all experiments were exposed to natural carbonation and simultaneously to radiation carbonation. It was proved by experiments that radiation at least augments natural carbonation. In experiments samples were sliced up with aim to research natural and radiation carbonation separately. It has been proved that radiation carbonation takes part both in depth and on surface of the samples which means, that it is independent on natural carbonation. The hypothesis of radiation carbonation is also supported by porosimetric experiments. Average pore diameter degreases with increasing dose of irradiation. It was shown that this decrease was caused by shift of pores to nanopore region. Contribution of two independent types of carbonation to the decrease of the average pore diameter was reliably distinguished. In some experiments content of calcite in depth of irradiated samples was doubled in comparison with uniradiated samples. On the contrary decrease of the average pore diameter with irradiation is less steep with higher irradiation. One may speculate that with growing dose (above 1 MGy) enhanced radiolytic dehydration of the samples and formation of microcraks may take part. Microcracks may be detected with porosimetric measurements as micropores, so the resulted picture is a superposition of the decrease of AVP due to carbonation and increase of the AVP due to radiolytic microcracking. Also extinction of ettringite may indicate radiolytic dehydration, as it contains substantial amount of water.

Validation of radiation carbonation hypothesis is, however, based on indirect proofs. As a direct proof may be considered monitoring of  $CO_2$  content in the samples during irradiation.

Further experiments should be heading for this beside with investigation of the role of dose rate.

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