Hardening Self-Compacting Mortar Exposed to Gamma Radiation

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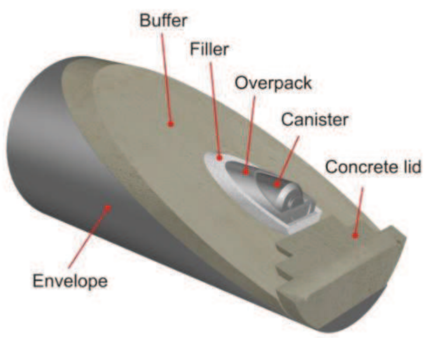
Abstract For the disposal of high level radioactive waste, cementitious barriers are considered worldwide and for various purposes. The Belgian supercontainer concept, for example, considers the use of cylindrical concrete containers: the radwaste is emplaced inside a hardened self-compacting concrete buffer, and for closure of the supercontainer the remaining gap is filled by casting a self-compacting mortar. As a consequence, this cementitious layer is exposed to the radioactive waste and gamma radiation during hardening.
In this research study, small self-compacting mortar samples are irradiated by gamma rays during hardening, and exposed to different doses (Gy) and different dose rates (Gy/h) at different hardening times at first exposure to investigate the cement-waste interactions that might occur during hardening of the cementitious barrier. The effect on the strength and the microstructure is investigated, by means of compressive strength tests, scanning electron microscopy, and nitrogen adsorption tests.
It was found that the observed strength loss due to gamma irradiation increases with an increasing total received dose. Furthermore, the age at which irradiation starts, plays a role in the effect of the gamma irradiation. A link between the strength of the mortar samples and its porosity is found by means of the nitrogen adsorption tests. A higher received dose increases the porosity which leads to a decrease in compressive strength. BET-analysis shows that the specific surface of the pores also increase due to gamma irradiation. Finally, SEM-analysis revealed that gamma irradiation during hardening of cementitious samples affects the microstructure.

Keywords: *Gamma radiation, Self-compacting mortar, Strength, Microstructure.*

Introduction

During fabrication of the supercontainer (Figure 1), the Belgian reference concept, applied for the disposal of vitrified high level waste (HLW) and spent fuel assemblies, the different cementitious layers are exposed to external gamma radiation. Once the buffer is cast and sufficiently hardened out of hot cell and in controlled environment, the radwaste is placed inside the opening of the buffer (construction step performed in radiation blocking hot cell) by means of a waste canister surrounded by a carbon steel overpack, and the remaining gap between this overpack and the concrete buffer is filled by casting a fresh mortar material (the filling: a self-compacting mortar). The self-compacting ability is desired to overcome the difficulty of vibrating the cementitious layer in hot cell, where radiation is present. The composition of the filling is based on the composition of the SCC (self-compacting concrete [1]) used for the buffer [2] and determined using the concrete equivalent mortar method [3]. As a consequence, the filling which is in direct contact with the carbon steel overpack containing the radwaste, will be exposed to gamma radiation during hardening (alpha and beta radiation are blocked by the overpack, the impact of the neutrons can be neglected [4]), with a dose rate inferior to 20 Gy/h [5]. In this paper, two main questions are investigated:

1) What is the effect of gamma radiation on the strength properties of the hardening self-compacting mortar?
2) What mechanisms are responsible for possible strength variations?



Therefore, a preliminary study is conducted by means of a literature review and a testing program including compressive strength tests, weight loss measurements, scanning electron microscopy, fluorescence microscopy analysis and nitrogen absorption.

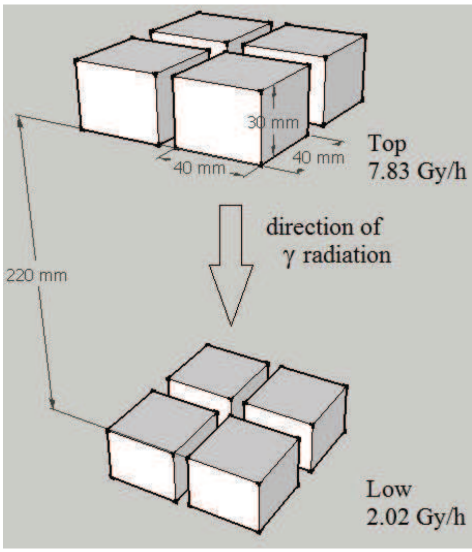


Figure 1 (right). 3D view of the supercontainer for vitrified HLW (C-level waste) [2]
Figure 2 (left). The irradiation test set-up for gamma radiation at the Physical and Nuclear Department of ISIB (dimensions in mm)

Effect of gamma radiation on cementitious materials

Gamma radiation of nuclear safety structures (such as containment buildings, radwaste disposal containers, etc.) can be an important degradation factor of the concrete layers used for these structures. The relevant and available research results concerning the effect of gamma radiation on cementitious materials is rather limited and a summary is given below:

- The most important effect of gamma radiation of concrete is the hydrolysis process (drying process), i.e. the radiolysis of the concrete pore water with a consequential gas production. The reaction product of the water radiolysis, i.e. hydrogen peroxide, can further react with portlandite present in the cement matrix, forming calcium peroxide. Furthermore, this can lead to a detrimental gas pressure build-up and simultaneous carbonation in the presence of CO_2 present in the air of the pore volume [6].

- Due to gamma irradiation a strength loss of 10 % is found due to changes of the pore structure of the matrix due to carbonation of the hydrated cement paste. Interaction of gamma irradiation with concrete leads to lowering not only its strength, but also its porosity (and other characteristics of pore space)[7].
- Gamma radiation can lead towards altered transport properties and increased carbonation depth [8]. With growing dose (> 1 MGy), enhanced radiolytic dehydration of the samples occurs and formation of microcracks takes place. However, no change of macroscopic properties of the irradiated material is found.
- The use of blast furnace slag cement can lead towards additional ettringite formation [9], and therefore the use of Ordinary Portland Cement is preferred.
- Irradiadition enhanced alkali-aggregate reactions (AAR) and an increase of volume of the aggregates was noticed in case high amounts of SiO_2 aggregates were used [10]. Therefore, the use of limestone is preferred to overcome AAR due to gamma rays [11].
- Gamma irradiation of hydrated cement paste leads to an accelaration of the ‘natural’ carbonation process driven by diffusion, only taking part in the surface layers of the samples. In addition, also independent radiation-induced carbonation due to gamma rays was found due to gas containing CO_2 which is produced due to gamma irradiation of the hydrated cement paste, and taking part in the entire sample [12]. Due to these two carbonation processes, CO_2 reacts with portlandite with calcite as a product. The arisen crystals of calcite grow through the pores of the hydrated cement paste, decreasing their diameter and hardening the material.

In most cases (except for [7, 11]), the effect of gamma radiation is negligible on behalf of alteration of mechanical properties or was not investigated. It must be mentionned that the total dose rates applied in these studies are rather high (> 200 Gy/h) compared to the estimated dose rate in the supercontainer concept (up to 20 Gy/h [4]). Moreover, these test results and conclusions are based on the radiation of hardened samples: the conrete or mortar samples have an age of 28 days or more at the first time of appliance of gamma irradiation.

Testing procedure

Composition of the self-compacting mortar (the filling)

The experiments are performed on self-compacting mortar samples, where radiation enhanced strength alteration is investigated, with limited size for the sake of homogenous irradiation throughout the whole sample. The mix design of three mortar compositions, with altered W/C-W/P-C/P-ratio, is listed in Table 1. The SCC1 mortar composition is derived from the composition of the self-compacting concrete for the buffer [2] by using the equivalent mortar method (MBE, [3]).

Table 1. Mortar composition of SCC0-SCC1-SCC2 (in kg/m³)

Component	SCC0	SCC1	SCC2
Cement CEM I 42.5N LH LA HSR	512	470	-
Cement CEM III/A 42.5N LA	-	-	470
Limestone filler	146	329	329
Crushed calcareous sand 0/4	1327	1410	1410
Superplasticizer (PCE)	14	4	5
Water	245	353	353
W/C	0.48	0.75	0.75
W/P	0.37	0.44	0.44
C/P	0.78	0.59	0.59

Sample preparation, fresh properties

First the dry components (calcareous sand, limestone filler and cement, in order of appearance) are added to the mixer (type: Hobart) and mixed with a rotational speed of 140 rpm for 30 seconds. Subsequently, the water is added to the blended dry components and the mixing continues for another 60 seconds at 140 rpm. Finally, superplasticizer (polycarboxylic ether PCE) is added, and an additional 60 seconds of mixing time (285 rpm) is supplied, totalizing a mixing time of 150 seconds. For each batch, 1 dm³ of mortar is mixed and the rheology of fresh mortar is characterized by means of the slumpflow value, by using the mini-cone.

Curing conditions and gamma rays exposure

Immediately after casting, the samples are irradiated. Two types of radiation sources are used in this test program:

- Irradiation by means of a ^{60}Co source (Jupiter C, Barzetti), with gamma energy level of 1.17 MeV and 1.33 MeV and an activity of 2 TBq. It generates gamma radiation with a dose rate up to 10 Gy/h. This type of radiation is applied to investigate the effect of cement-waste interactions in case of low dose rates (e.g. for the disposal of radioactive waste).
- Irradiation by means of a ^{137}Cs source, with an energy level of 0.662 MeV and an activity of 25 _ 8.5 TBq which generates gamma radiation with dose rates up to 2000 Gy/h. This type of radiation is applied to investigate the effect of cement-waste interactions in case of high dose rates.

For the low dose irradiation investigation, the samples are placed at two different levels (e.g. Figure 2). To quantify the total applied dose and the applied dose rate, dosimeters with radiochromic film (Gafchromic EBT, thickness of 234 mm) are placed at each level. For the samples at the level closest to the source a dose rate of 7.11-7.83 Gy/h is registered, whereas for the samples at the level underneath, the applied dose rate is 1.75-2.02 Gy/h.

For the high dose irradiation investigation, the samples are placed at one level, with a dose rate of 1360e2000 Gy/h, determined by means of Gammachrome YR dosimeters.

Note that for each batch, a number of samples remain unirradiated as a reference, but conserved at the same environmental conditions, thus with identical temperature and relative humidity as the irradiated samples. The samples have the same maturity and saturation degree, meaning: the gamma radiation dose and dose rate are the only influencing parameter.

Test methods

By means of these low and high dose rate investigation it is studied whether (i) gamma radiation has an effect on the mechanical properties of the mortar, (ii) gamma radiation affects the microstructure of the mortar, (iii) irradiation related parameters (received dose, applied dose rate, radiation time, and mortar age/maturity at first irradiation) alter the obtained results and (iv) mortar related properties (cement type, water-to-cement ratio) have an influence.

After 28 days of hardening, the compressive strength of the samples is determined to evaluate the effect of gamma irradiation on the strength of the hardening self-compacting mortar. Therefore, the samples are placed inside an Amsler compression testing machine. The relative strength loss is expressed in function of total dose of radiation received (expressed in Gy). The relative strength loss D_f of the irradiated samples. This can be found by using Equation (1):

$$D_f = (1-f_{irr}/f_{ref})\cdot 100\% \qquad (1)$$

where: f_{irr} is the compressive strength of the irradiated morta sample (MPa), f_{ref} is the compressive strength of the un-irradiated reference mortar samples (MPa).

Also the volumetric weight of the hardened samples is determined to estimate the weight loss and drying of the samples due to gamma ray exposure.

Thin section are made to investigate the effect of gamma radiation on the self-compacting mortar on a microscopic level, using fluorescence microscopy analysis according to the Nordtest Method (1991). Furhermore, scanning electron microscopy is performed by means of a JEOL JSM-5510 with microscope resolution of 3.5 nm and energy level between 0.5-30 kV for visualisation.

By means of nitrogen adsorption porosimetry, the pore size can be determined using the Barrete-Joynere-Halenda (BJH) method which allows the determination of the pore size distribution in mesopore range from the desorption part of the isotherm [13]. A Micromeritics Tristar 3000 equipment has been used in this work to perform the measurements.

Results and Discussion

The uniaxial compressive strength and the density were determined on small samples of both irradiated and un-irradiated samples. Overall, it is found that a strength loss is found, and the strength reduction D_f increases with increasing absorbed dose (Figure 3). The scatter on the results is, however, too wide to establish a reliable predictive model. Nevertheless, 75% of all tests resulted in a strength reduction higher than 5%. Gamma irradiation clearly has a negative effect on the strength of hardening self-compacting mortar. In all cases, except one, the strength reduction D_f is accompanied by a reduction in density between 0.2% and 2.9%, however no correlation was found between strength loss and density reduction.

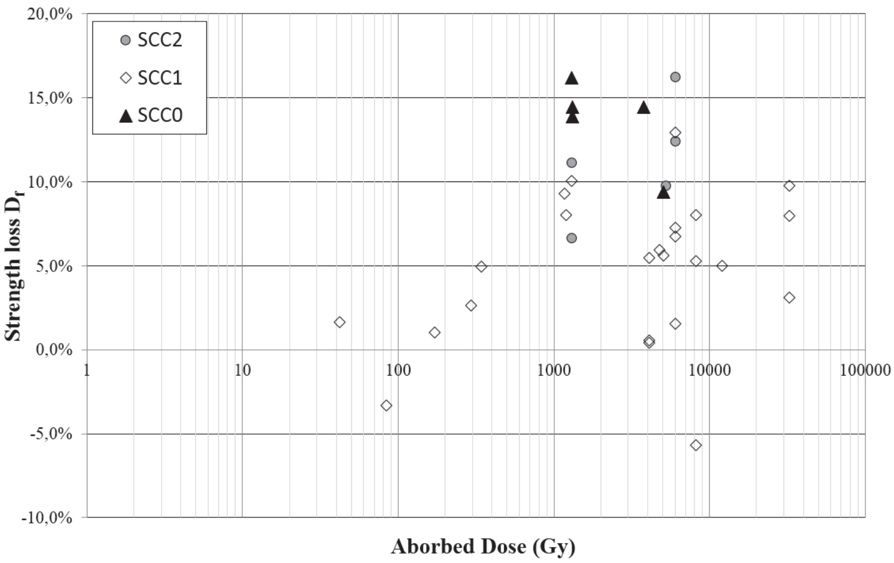


Figure 3. Strength loss vs. Absorbed dose of irradiated samples

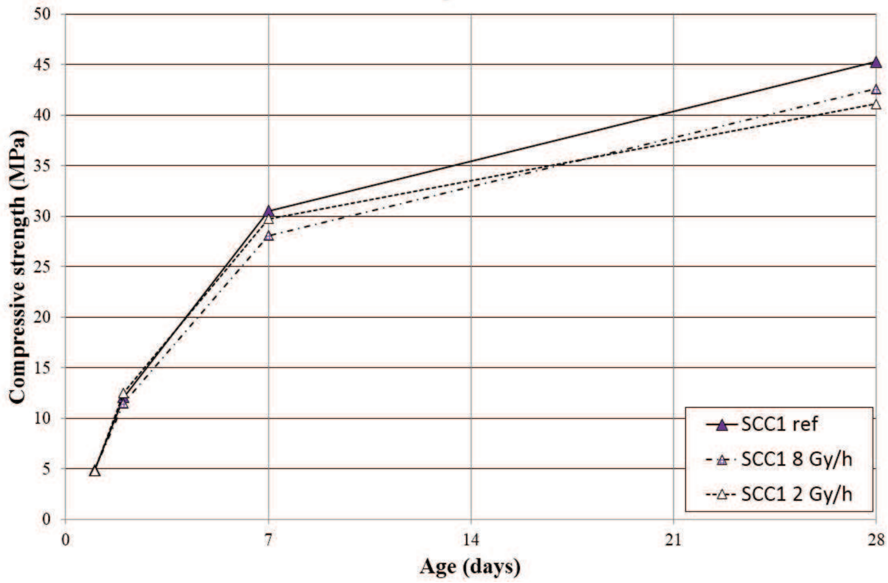


Figure 4. Evolution of compressive strength and effect of radiation

It is found that gamma radiation influences the strength development of the self-compacting mortars (Figure 4): the compressive strength evolves towards a lower 28-day value due to increased dose rates and absorbed doses.

By means of nitrogen absorption tests and fluorescence microscopy analysis the microstructure of irradiated an unirradiated samples is compared. Mainly the desorption pore volume of irradiated samples is higher compared to the reference samples, linked with the applied dose rate (Figure 5). This explained the previously found compressive strength loss and reduction in density.

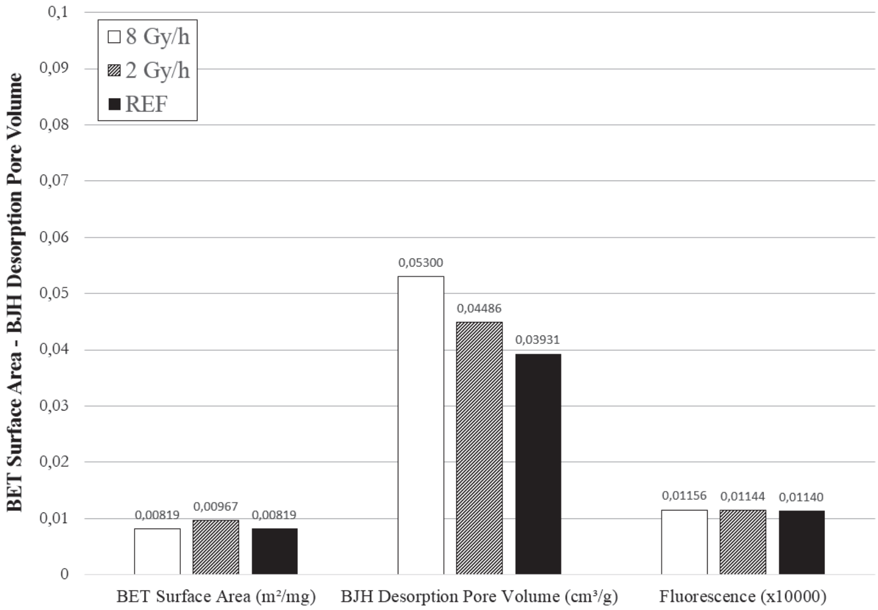


Figure 5. Quantification of the mortar's microstructure (low dose rates)

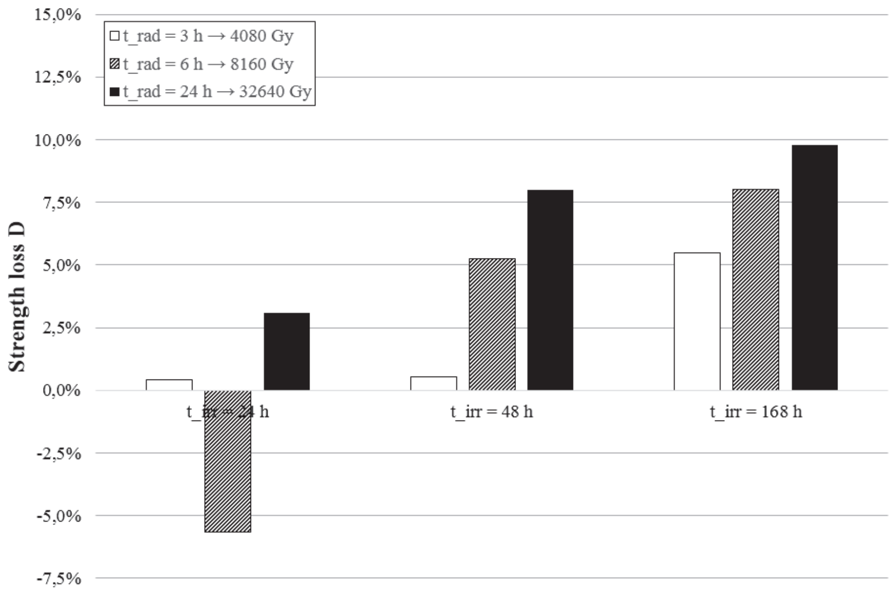


Figure 6. Effect of radiation duration and age ate first radiation (high dose rates)

It was already mentioned that the strength loss due to gamma irradiation increases with increasing the absorbed radiation dose. In case low irradiation dose rates (<10 Gy/h) are applied, the age of the concrete at which irradiation starts does not have a significant effect on D_f. However, in case high dose rates are applied (>1000 Gy/h) a certain trend is found: the older the concrete at which irradiation starts (i.e. higher t_{irr}), the higher the observed strength loss (Figure 6).

Compared to SCC1, the type of cement is changed for SCC2: blast furnace slag cement is used instead of Portland cement. The use of blast furnace slag cement has a significant effect on the strength reduction D_f, especially for medium to high irradiation dose rates. By means of SEM-analysis it was found that due to gamma irradiation, needle formation occurred in the mixes containing blast furnace slag (CEM III/A, Figure 7). These needles are most likely ettringite ones ($C_3A._{3CaSO4}.32H_2O$), in accordance with the findings of [9]. The decrease in strength can be related to the formation of expansive ettringite, which causes internal microcracking within the mortar microstructure.

In case a lower water-to-cement ratio is applied, a higher strength reduction is also found. Fluorescence microscopy analysis indicates that the capillary porosity is not significantly affected. As mentioned by [6] gamma radiation of cementitious materials is linked with radiolysis of the pore water, meaning part of the free water will evaporate and can no longer take place in the hydration process. As a consequence, not enough free water is available to react with all cement, leaving unhydrated cement particles into the matrix, which can lead to an increase in strength loss.

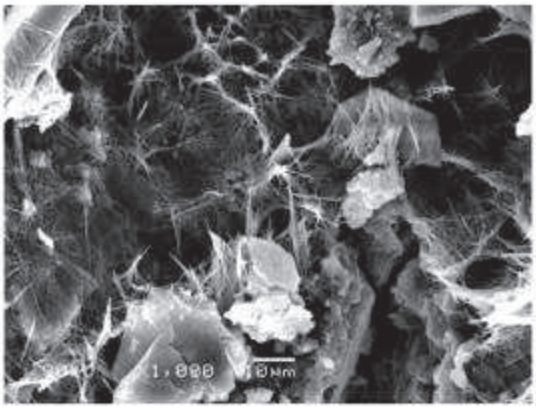


Figure 7. Needle formation after irradiation of samples containing blast furnace slag

Conclusions

Based on an experimental programme, the following conclusions have been obtained:

(1) Gamma radiation during hardening of cementitious materials negatively affects the strength development. The higher the absorbed dose of radiation, the higher the strength decrease will be.

(2) Due to gamma radiation, the porosity (nano, micro and capillary) and pore volume increases. Lowering the water-to-cement ratio and using blast furnace slag cement instead of Portland cement, worsened the above mentioned phenomena.

(4) The total absorbed dose and the age of the concrete at which irradiation starts also influences the strength development.

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