Effects of Gamma Radiation on Cementitious Materials in Repository Environment – 16300

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ABSTRACT

Cementitious materials are widely used in the management of radioactive waste and have to perform as required for the period of service life of the installation. In order to assess the long term durability of cement paste in a deep borehole for radioactive wastes, specimens were casted in laboratory and exposed to a gamma radiation field. The effects of the radiation in the specimens were evaluated by X-Ray Diffraction, as changes observed in the mineralogy and microstructure of the material after irradiation doses varying between 0 (without radiation) and 10 MGy. It was observed that the specimens exposed to higher doses of gamma radiation (up to 3MGy) presented differences between surface and core, when compared with the samples with no radiation or exposed to low doses. These results are important to model the behavior of cementitious materials under the conditions expected in a borehole repository and to provide data for the safety assessment of the installation.

INTRODUCTION

Cementitious materials are widely used in the management of radioactive wastes, as waste immobilization matrix, engineering barriers or structural material in repositories. In each case, the cement has to perform as required for the period of service life of the installation. This period can range from hundreds to thousands of years, depending on the characteristics of the wastes to be disposed [1, 2].

The Radioactive Waste Management Laboratory at the Nuclear and Energy Research Institute in São Paulo, Brazil (IPEN-CNEN/SP) collaborates in Brazilian projects to dispose of low and intermediate level wastes and disused sealed radioactive sources. Moreover, studies on the disposal of spent fuel and high level wastes will be conducted in the future. In all concepts, cementitious materials are intended to be used and their behavior and durability are key points regarding the safety of the facilities [3].

In the last four decades, the behaviour of cement under several repository conditions has been assessed by many groups of researchers. The intrinsic variability and complexity of hydrated cement, however, makes this assessment a difficult and laborious work [3, 4, 5, 6]. To overcome the lack of knowledge about the durability of the structures based on cement, and considering that this material can be severely damaged under certain conditions, no credit are usually given to them in the safety assessment in the long-term.

The project developed at IPEN-CNEN/SP investigates the behaviour of cement paste under several deleterious conditions in order to establish a relationship between its behaviour and durability. The conditions that are expected under repository conditions are:

- Water penetration from the environment causing infiltration of deleterious ions into the cement paste, and leaching of cement compounds [7, 8, 9, 10, 12, 13];
- Elevation of the temperature caused by the radiation field and geothermal gradient (for high depths) [14, 15, 16, 17];
- Pressure gradients during the cure and service life of the installation;
- Radiation doses that cement will accumulate under the service life of the installation [18, 19, 20, 21, 22];
- Natural evolution of cement in thousands of years (for long-lived waste, including disused sealed sources).

Under irradiation, pore water present in cement paste undergoes radiolysis and some products can be highly reactive, as electrons, hydroxyl radicals and hydrogen peroxide. These radiolysis products will interact with cement paste components and its hydration products, forming a wide range of compounds [18, 19, 20].

Bouniol & Bjergbakke (2008) [19] showed that the calcium hydroxide equilibrium can be affected by the radiolysis products, releasing ions calcium to react. In the presence of hydrogen peroxide, calcium peroxide octahydrate can be formed.

However, the released calcium ions can react with a wide range of chemical species in the repository environment, for instance sulfate and carbonate ions, or they can be leached from the cement matrix by the groundwater.

The objectives of the present work are to assess the influence of a gamma radiation field in cement microstructure and mineralogy and establish a relationship between irradiation and durability. For this purpose, cast cement paste specimens were exposed to a gamma radiation field and then examined to show any changes.

METHODS

Cubic cement paste specimens (cubes of 2 cm edge length) were prepared with type V cement [23] that is similar to High Early Strength Portland cement [24], with a water/cement ratio of 0.35 following the procedure of Brazilian standards [23]. Specimens were allowed to set and cure during seven days inside a high humidity chamber. After cure, specimens were irradiated in a Co-60 multipurpose irradiator with doses varying between 1 and 10 MGy.

After the irradiation, the specimens were drilled in order to take samples for the evaluation of the effects of irradiation in the surface and in the core of the specimens. Surface samples were taken drilling the specimen up to 0.5cm depth, and core samples were taken drilling from 0.5 to 1.5cm depth.

The powder samples from surface and core of the specimens were then evaluated by X-Ray Diffraction in the X-ray powder diffraction beamline (XPD) at Brazilian Synchrotron Light Laboratory (LNLS). The powdered samples were put in 0.7mm borosilicate capillary tubes (Figure 1) and analysed in a Huber diffractometer. The data acquisition was performed with 24 Mythen detectors, with a X-Ray energy of 12 keV (Figure 2).

A quantitative Rietveld Analysis was made with the XRD patterns obtained in the XPD beamline. The Software TOPAS was used to perform the quantification of six different minerals commonly found in cementitious materials: Portlandite [$Ca(OH)_2$], Calcite ($CaCO_3$), Periclase (MgO), Ettringite [$Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$], C_3S (also called Alite or tricalcium silicate (Ca_3SiO_5)), and C2S (also named Belite or dicalcium silicate (Ca2SiO4)). The TOPAS Software was used to perform a Rietveld analysis of the XRD results.

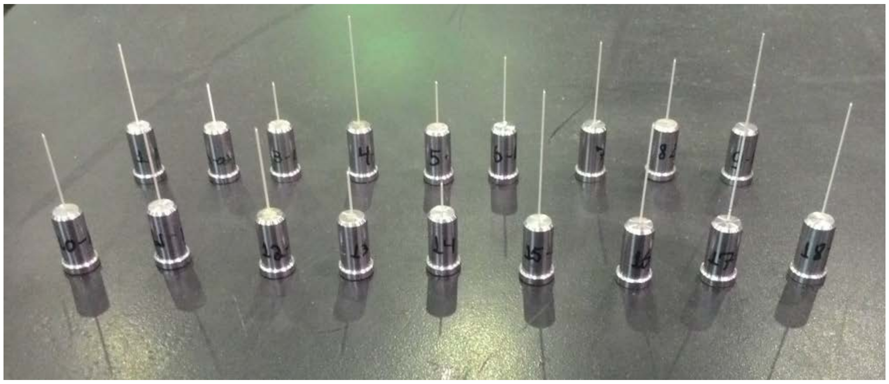

Fig. 1 – Samples in 0.7mm borosilicate capillary.

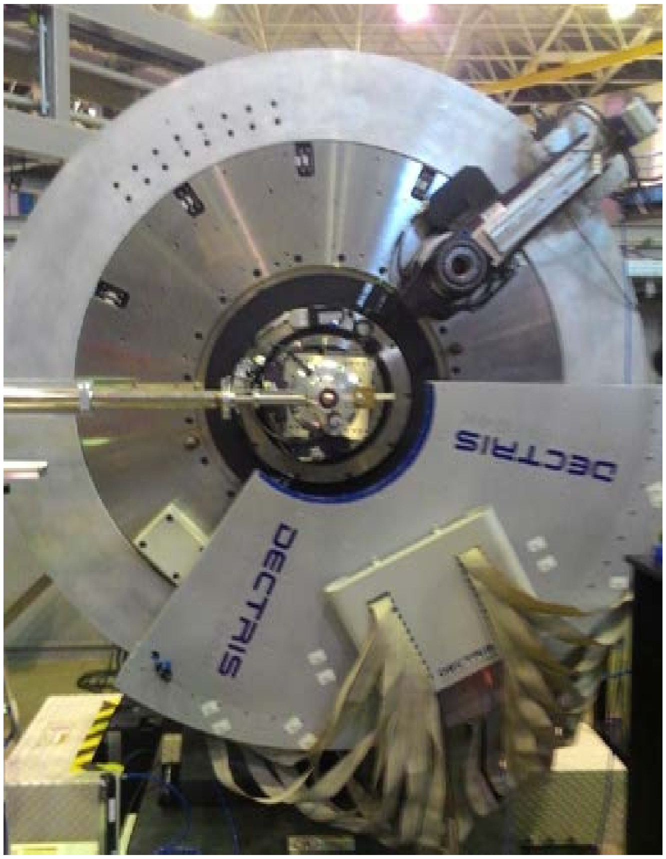

Fig. 2 – Huber Diffractometer and Mythen detectors.

RESULTS AND DISCUSSION

The results of irradiated specimens are divided in two steps. At first, samples from specimens exposed to a gamma radiation dose of 1, 2 and 3 MGy were analysed in the XPD beamline at LNLS. After six months, samples from specimens with doses of 4, 8 and 10 MGy were analysed. Furthermore, samples without radiation were analysed in each step and are named 0 MGy. These specimens were the reference baseline samples and were kept in dry storage until the day of the analysis.

The results of Rietveld analysis of the specimens exposed to doses of 0, 1, 2 and 3 MGy are presented in Figures 3 and 4. The results of the specimens exposed to doses of 0, 4, 8 and 10 MGy are presented in the Figures 5 and 6. In the first figures of each step (Figures 3 and 5), all six minerals are showed. In the second figures (Figures 4 and 6), just the Portlandite, Calcite and Ettringite are showed, since these three minerals had the more important differences.

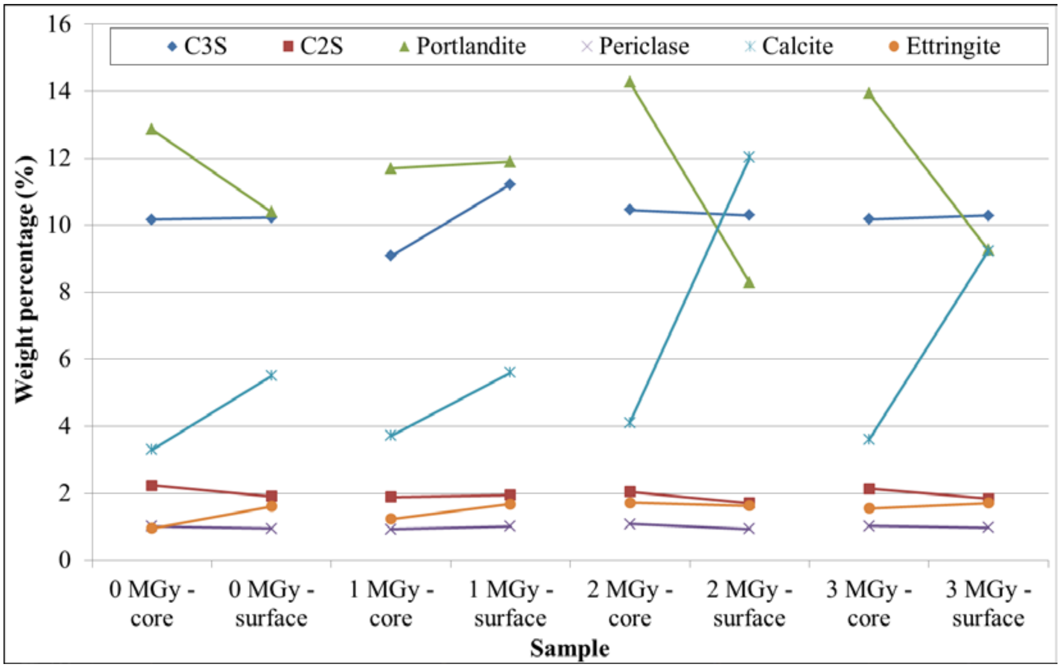

Fig. 3 – Quantities of each phase in the Rietveld Refinement of specimens exposed to radiation doses of 0, 1, 2 and 3 MGy.

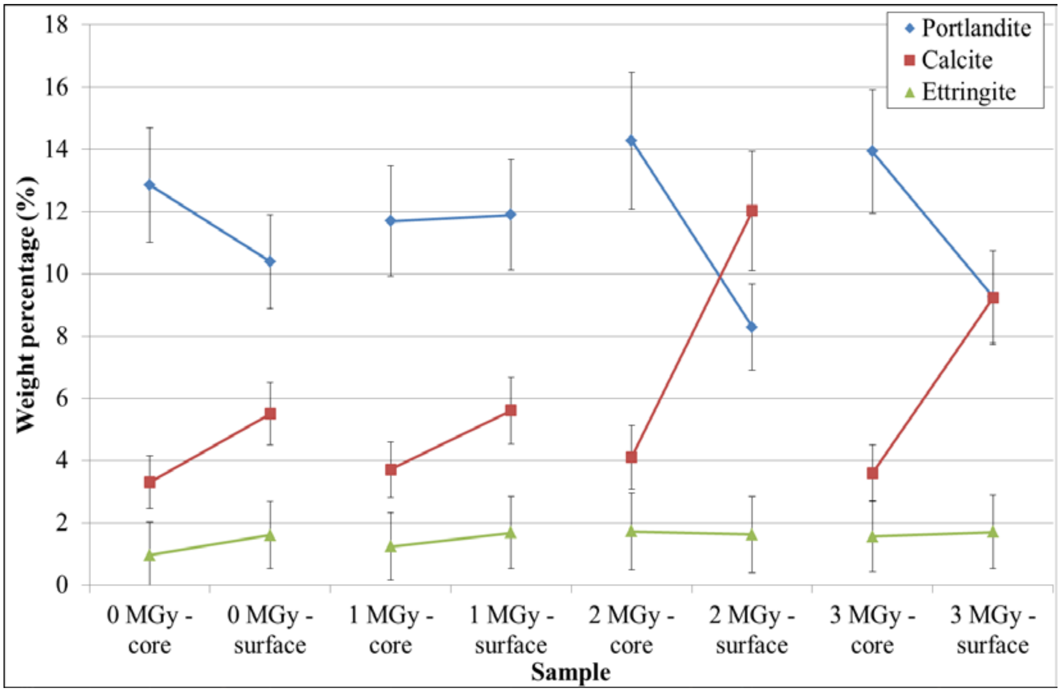

Fig. 4 – Quantities of Portlandite, Calcite and Ettringite in the Rietveld Refinement of specimens exposed to radiation doses of 0, 1, 2 and 3 MGy.

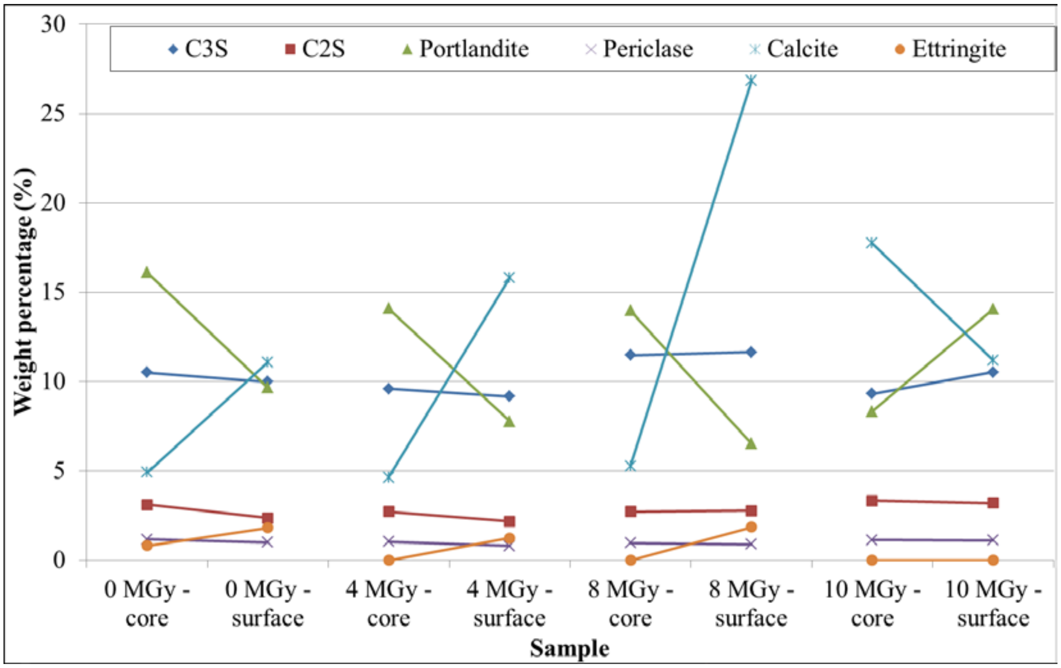

Fig. 5 – Quantities of each phase in the Rietveld Refinement of specimens exposed to radiation doses of 0, 4, 8 and 10 MGy.

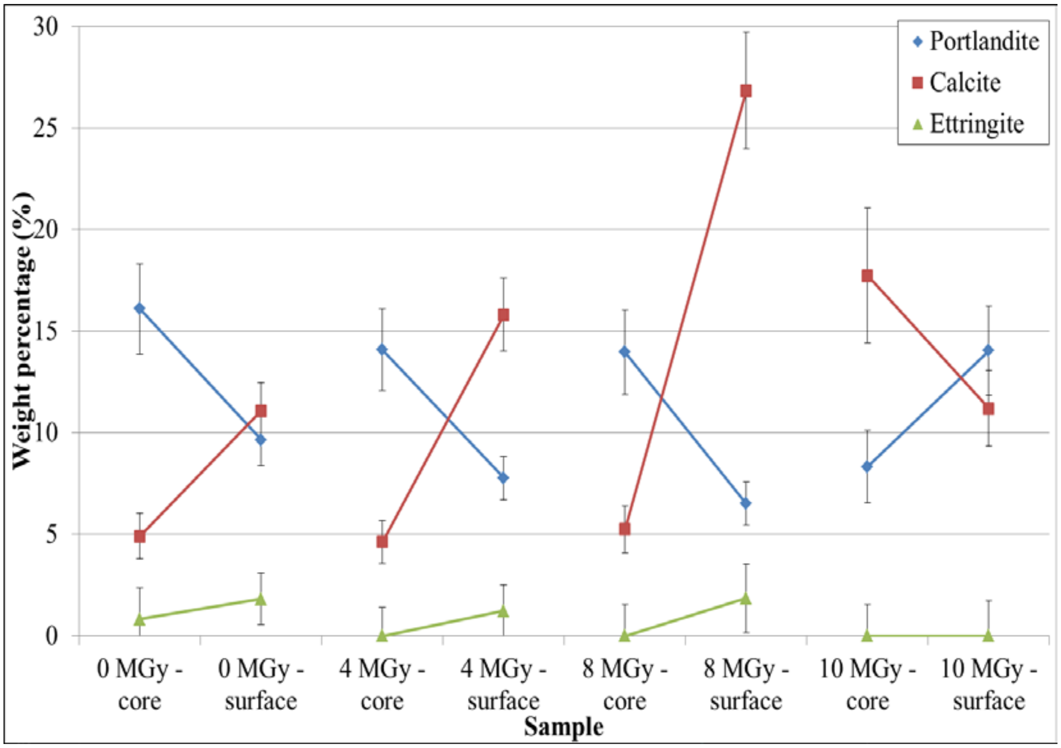

Fig. 6 – Quantities of Portlandite, Calcite and Ettringite in the Rietveld Refinement of specimens exposed to radiation doses of 0, 4, 8 and 10 MGy.

It is possible to detect some mineralogical differences in the Rietveld analysis between the reference and the irradiated specimens. In both groups, it was possible to notice that the quantities of C3S, C2S and Periclase did not change with the increase of the radiation dose, neither in the surface nor in the core. However the quantities of Calcite, Portlandite and Ettringite had changed significantly between the surface and core and with increasing radiation doses.

In all samples, it was possible to observe a depletion of Portlandite and an increase of Calcite quantity in the surface of the specimens. This process, called carbonation, can be explained by the reaction of Portlandite with the carbon dioxide present in the atmosphere, as showed in the equation below:

$$Ca(OH)_2 + CO_2 \leftrightarrows + CaCO_3 + H_2O \qquad \text{(Eq. 01)}$$

This calcite formation was less pronounced in the specimens' core. It occurs probably due to the fact that the calcite can block the cement pores and prevent the carbon dioxide penetration to the inner part of the specimen.

Although it was possible to observe the carbonation in all specimens, those which were exposed to a radiation doses between 2 and 8 MGy presented a more pronounced reaction rate in comparison with the reference sample.

The specimens exposed to 10 MGy dose present high quantities of calcite and portlandite, both in the core and on the surface. This can indicate that this dose is high enough to saturate the specimen and that other reactions can occur in this situation.

The specimens exposed to 4 and 8 MGy doses presented no ettringite in its core, while the specimen with 10 MGy dose has no ettringite in its composition, neither in the core nor in the surface.

These results indicate that the portlandite depletion can be increased by irradiation, releasing calcium ions in the pore water of the cementitious materials. In this case, the calcium release increases the carbonation in the specimens. In a repository environment, many other reactions can occur when calcium ions are released from the cement matrix.

CONCLUSIONS

The results show that the gamma radiation field can affect the cement paste mineralogy and microstructure. It was observed that the equilibrium between portlandite ($Ca(OH)_2$) and calcite ($CaCO_3$) is directly affected by the irradiation. In the environment of a repository for radioactive waste, this reaction can occur by the presence of bicarbonate ions in the groundwater, or due to the presence of others factors (as presence of sulfate and chloride, temperature difference, pressure, etc.).

More studies are been carried out in order to evaluate how the chemistry and mineralogy of the cementitious materials can vary in the repository environment. Furthermore, more analysis on the specimens exposed to the irradiation will be done, for instance, thermogravimetric analysis and imaging analysis.

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