XRD Analysis of Cement Paste Samples Exposed to the Simulated Environment of a Deep Repository – 12239

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ABSTRACT

Portland cement materials are widely used as engineered barriers in repositories for radioactive waste. The capacity of such barriers to avoid the disposed of radionuclides to entering the biosphere in the long-term depends on the service life of those materials. Thus, the performance assessment of structural materials under a series of environmental conditions prevailing at the environs of repositories is a matter of interest. The durability of cement paste foreseen as backfill in a deep borehole for disposal of disused sealed radioactive sources is investigated in the development of the repository concept. Results are intended to be part of the body of evidence in the safety case of the proposed disposal technology. This paper presents the results of X-Ray Diffraction (XRD) Analysis of cement paste exposed to varying temperatures and simulated groundwater after samples received the radiation dose that the cement paste will accumulate until complete decay of the radioactive sources.

INTRODUCTION

Cement paste is one structural material of the engineered barriers foreseen in the concept of a deep borehole repository for disposal of disused sealed sources under development in the Nuclear and Energy Research Institute (IPEN), in São Paulo, Brazil [1,2].

There are about ten thousand sources already collected as radioactive waste, safely stored in centralized facilities, under the responsibility of the Brazilian National Commission on Nuclear Energy. Many tens of thousands more sources are presently under the possession of licensees, all of which will eventually become radioactive waste. They contain Co-60, Ni-63, Sr-90, Cs-137, Ra-226, Pu-238, Am-241 [2], and many more radiologically significant radioisotopes. The individual activities of many sources are in excess of 1 TBq and the total estimated present activity is in the order of 10 PBq. If Am-241 and Ra-226 sources being extracted from the rods of radioactive lightning arresters recovered from commercial and industrial buildings or households are accounted for, the total inventory of sealed sources in the country amounts to about three hundred thousand sources.

Safety analyses indicate that the isolation time required for this inventory is thousands of years [1, 2]. Therefore, these sources cannot be disposed of safely in a shallow ground disposal sites; instead, they require a deep geological repository, for which a borehole concept is the more practical choice. However, to demonstrate that such a facility is acceptable from the point of view of long-term safety, it is necessary to provide evidence that the repository system will perform as required during the isolation period negotiated with the licensing authorities. The behavior of cement paste under the conditions prevailing at the depths of the disposal system is a key point in this task [3].

In the borehole, cement paste will function as a structural material, as a barrier against the flow of water between different strata of the geological medium, and as an additional barrier against the migration of the radioisotopes toward the biosphere. During the working life of the facility, the cement paste will be exposed to the radiations emitted by the sources, under the temperature, pressure, and geo-chemical environment of the deep repository neighborhood [4, 5]. These external factors coupled to the natural evolution of hydrated cement compounds, an internal factor, can lead to detrimental effects on the material performance [6]. Notwithstanding this, to be acceptable, the material must perform adequately, without any maintenance, during the thousands of years of exposure to these deleterious effects.

Portland cement materials are widely used in engineering works but their durability, i.e. their working life can be observed directly only for less than two hundred years based on the accumulated practical experience since Portland cement started to be used. For longer periods, the service life can only be estimated based either on theoretical models and evidence from more ancient man-made cement-like analogues, or on the results of accelerated tests in laboratory.

The published literature approaching this issue is relatively scarce but provided the basis for the research program that is under way in the Laboratory of Radioactive Waste at IPEN. This research aims at studying the use of accelerated tests in laboratory to assess the cement paste durability and the applicability of results to estimate the service life of the material under the above mentioned exposure conditions.

One way of measuring the deleterious effects on cement paste is analyzing the chemical and mineralogical changes underwent by their constituents, after exposure of samples to the environmental conditions deemed to prevail in the repository and correlating these changes with the evolution of the mechanical and hydraulic properties of the material [7, 8].

Radiation induced cleavage of chemical bonding of water molecules, for instance, produces hydrogen radicals and hydroxide radicals that further react with other molecules and can destroy structures that are responsible for the mechanical strength of the cement paste [9]. The presence of aggressive chemicals from pore water of granitoid rocks and the high temperature and pressure at the depth of disposal, may also intensify the degradation effect [3, 6, 10-13].

In this paper, the results of X-ray diffraction analysis obtained with samples exposed to varying radiation doses, temperatures and concentrations of aggressive chemicals are presented as a progress report of the ongoing research.

METHODS

Cement paste specimens were prepared with type V cement [14] that is similar to High Early Strength Portland cement [15], with a water/cement ratio of 0.35 following the procedure of Brazilian standards [14]. Cylindrical plastic moulds with 5.0 cm high and a 1:2 diameter to height ratio were used to cast 144 specimens in one single batch operation. Specimens were allowed to set and cure during seven days under sealed conditions, at room temperature. After cure, specimens were randomly grouped in twenty four sets of six specimens.

Accelerated tests in laboratory included: (a) exposure of cement paste specimens to a fraction of the dose that the actual material is expected to accumulate on the repository backfill, until all radioactive sources have decayed; followed by (b) storage of specimens immersed in distilled water or salt solutions (representative of groundwater of a granitic geological medium), by 30 or 60 days, (c) at room temperature or at the higher temperatures expected at the depth of the repository. Results were compared with those from unexposed specimens, kept at room temperature and 60% relative humidity. The tests were conducted as a complete multifactorial design experiment, each factor at two levels, with six specimens for each treatment level. Results were always the average of the six measurements.

Evaluation of the effects includes: (a) analysis of chemicals leached from specimens into immersion baths; (b) measurements of dimensional variation and mechanical strength of exposed and unexposed specimens; (c) Scanning Electron Microscopy of specimen surface; (d) Thermo Gravimetric Analysis and (e) X-Ray Diffraction Analysis (XRD) of ground samples taken from exposed and unexposed specimens. Results of these experiments, except XRD Analysis, were reported elsewhere [16].

For XRD analysis, ground samples of about 0.5 g each, taken from specimen shards left by the compression mechanical strength tests, were analyzed by one of the authors in the Technological Characterization Laboratory of the Mining Engineering Department at the Polytechnic School of the University of São Paulo. Crystalline phases were identified and the diffractogram of 12 representative samples is presented in figure 1. A classification of the according to their mineralogical composition and grouped in a dendrogram graph showing the taxonomic grouping of sample mineralogical compositions.

RESULTS AND DISCUSSION

Twenty four selected samples taken from specimens that underwent the treatments indicated in Table 1 were analyzed by XRD. The samples were selected in order to compare each treatment in multifactorial tests. Although the specimens were rather small, care was taken to select samples from points near the center and from points near the surface of the specimens as to detect any differences in the depth of the effects.

Table I - Identification of samples for XRD analysis.

Sample No.	Sampling Points	Irradiation	Storage conditions[a]	Temperature	Immersion time
1 2	Center Surface	No	SS	60°C	30 days
3 4	Center Surface	No	SS	60°C	60 days
5 6	Center Surface	No	DS	20°C	-
7 8	Center Surface	No	DS	20°C	-
9 10	Center Surface	No	DS	60°C	30 days
11 12	Center Surface	No	DS	60°C	60 days
13 14	Center Surface	No	DW	20°C	30 days
15 16	Center Surface	No	DW	20°C	60 days
17 18	Center Surface	No	SS	20°C	30 days
19 20	Center Surface	No	SS	20°C	60 days
21 22	Center Surface	No	DW	60°C	30 days
23 24	Center Surface	No	DW	60°C	60 days
25 26	Center Surface	Yes	DW	20°C	30 days
27 28	Center Surface	Yes	DW	20°C	60 days
29 30	Center Surface	Yes	SS	20°C	30 days
31 32 33	Center Surface Center	Yes	SS	20°C	60 days
34 35	Center Surface	Yes	DW	60°C	30 days
36	Center	Yes	DS	20°C	-
37 38	Center Surface	Yes	DW	60°C	60 days
39 40	Center Surface	Yes	SS	60°C	30 days
41 42	Center Surface	Yes	SS	60°C	60 days
43 44	Center Surface	Yes	DS	20°C	-
45 46	Center Surface	Yes	DS	20°C	-
47 48	Center Surface	Yes	DS	60°C	30 days
49	Center	Yes	DS	60°C	60 days

a - Storage conditions: DW = Distilled Water; SS = Salt Solution; DS = Dry Storage

A cluster analysis of the results is presented in Figure 1 as a dendrogram showing the classification of cement paste samples. It is a measure of the degree of change induced by the treatments, considering that the composition of all samples before treatment was the same.

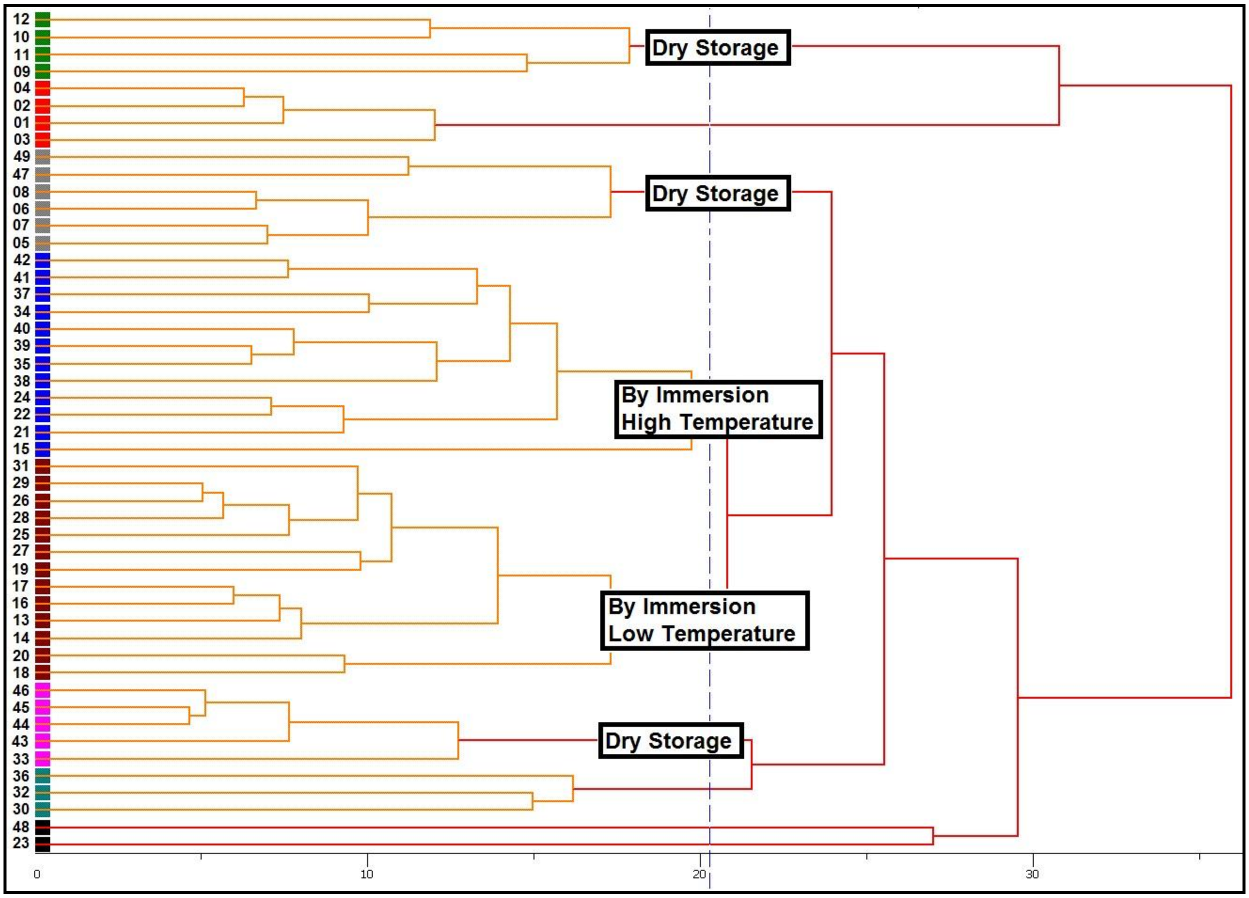

Fig. 1 - Dendrogram of samples obtained by cluster analysis

A diffractogram of twelve samples are presented in Figure 2, to show how to differentiate the samples and compare exposed and unexposed cement paste specimens. Relative peak heights indicate the concentration of species in each sample. The most important peaks are shown and each peak represents a mineral compound, as follows:

1. Main peak of ettringite
2. Peak of ettringite
3. Main peak of portlandite
4. Peak of ettringite and calcite
5. Main peak of calcite
6. Main peak of alite

Figure 3 shows a close-up of the 7° to 26° range of the diffraction angles obtained with the twelve samples to exemplify how different mineralogical components show up in the analysis results.

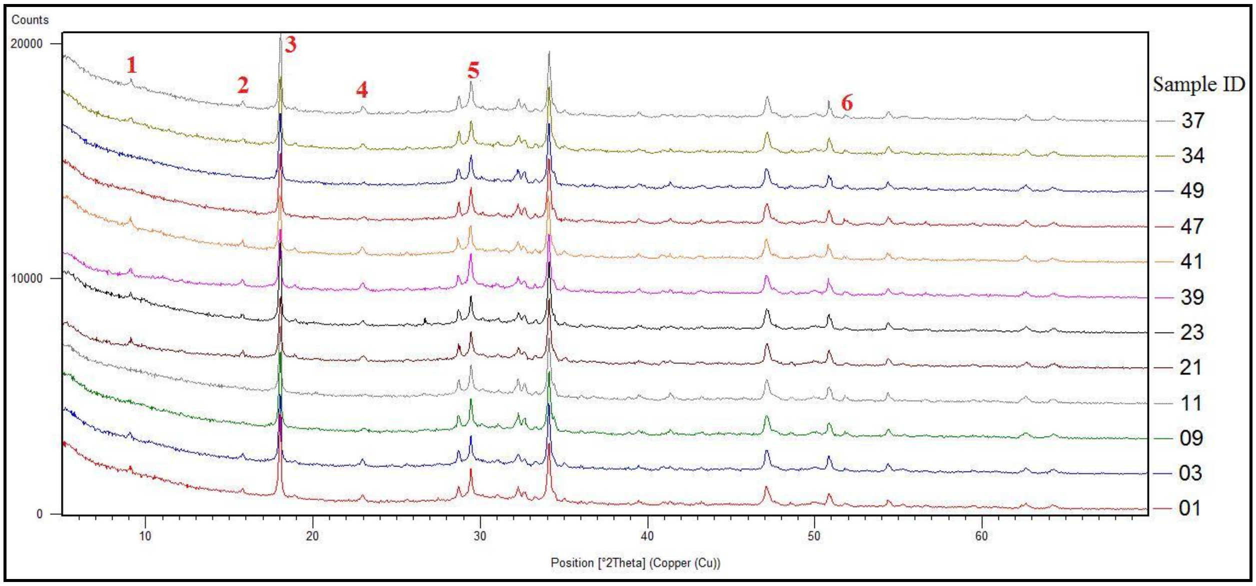

Fig. 2 - Diffractograms of 12 cement paste samples.

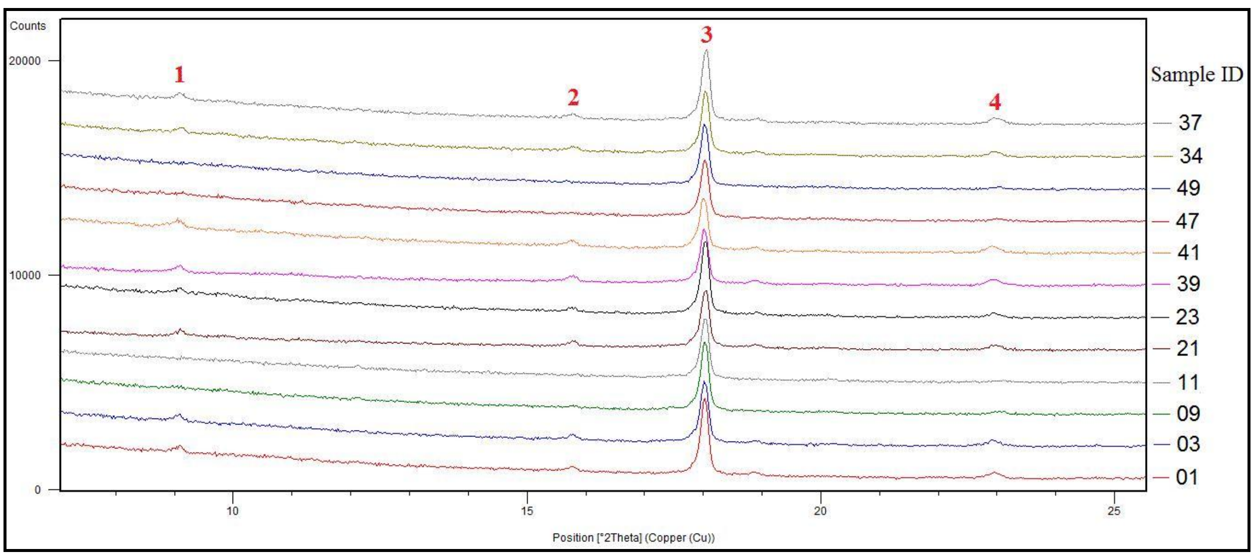

Fig. 3 – Close-up of the 7° to 26° range of the diffractograms of the 12 cement paste samples

The cluster analysis which resulted in the dendogram in Figure 1 shows that XRD can group or separate the results consistently with the treatments that samples underwent during multifactorial tests. However, the XRD patterns in Figures 2 and 3 show differences in the mineralogy of samples too small to be perceived by visual inspection, except by the ettringite lines (1, 2 and 4) that are missing in both irradiated and not irradiated specimens kept in dry storage at the highest temperature level.

Under the conditions of the laboratory tests, the treatments had little, if any, influence in the mineralogical composition of specimens.

CONCLUSION

The XRD analysis of cement paste samples realized in this work allowed observing some differences in the results of cement paste specimens that were submitted to different treatments. The cluster analysis of results was able to group tested samples according to the applied treatments. Mineralogical differences, however, are tenuous and, apart from ettringite, are hardly observed.

The absence of ettringite in all the seven specimens that were kept in dry storage at high temperature had hardly occurred by natural variations in the composition of hydrated cement paste because ettringite is observed in all tested except the seven specimens. Therefore this absence is certainly the result of the treatments and could be explained by the decomposition of ettringite. Although the temperature of decomposition is about 110-120°C [17, 18], it may be initially decomposed to meta-ettringite, an amorphous compound, above 50°C in the absence of water [17-19].

Influence of irradiation on the mineralogical composition was not observed when the treatment was analyzed individually or when analyzed under the possible synergic effect with other treatments. However, the radiation dose to which specimens were exposed is only a fraction of the accumulated dose in cement paste until complete decay of some sources.

Therefore, in the short term, the conditions deemed to prevail in the repository environment may not influence the properties of cement paste at detectable levels. Under the conditions presented in this work, it is not possible to predict the long term evolution of these properties.

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