

MINERALOGY AND CHEMISTRY OF CEMENT PASTE IN BOREHOLE RADIOACTIVE WASTE REPOSITORY

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ABSTRACT

Results of chemical characterization of cement paste samples after irradiation and immersion in salt solutions are presented. This is part of a research on cement paste behavior aiming at investigating the durability of cementitious materials in the environment of repositories for radioactive waste. Portland cement paste is intended to be used as a backfill in a deep borehole for disposal of sealed radiation sources which concept is under development. The service life of the engineered barrier materials plays an important role in the long term safety of such facilities. Accelerated tests in laboratory are being used to evaluate the performance of cement paste under the temperature expected at some hundred meters below grade, under exposure to the radiation emitted by the sources, and under the attack of aggressive chemicals dissolved in the groundwater, during the millennia necessary for the decay of the most active and long-lived radionuclides present in the waste. ICP-OES, Ion chromatography, X-ray diffraction, SEM and TGA are some techniques being employed in this research project.

1. INTRODUCTION

The Radioactive Waste Management Laboratory (RWML) at the Institute of Energy and Nuclear Research is developing the concept of a repository for disused sealed radiation sources in a deep borehole. It is intended as a disposal facility where all sealed sources of the Brazilian inventory can be disposed of.

According to this concept, the borehole is drilled to a depth of about four hundred meters in a granite batholite and the annular space between the steel casing and the geological formation is backfilled with cement paste. Cement water slurry is pumped and left to harden in place. The hardened cement paste is intended to function as an additional barrier against the migration of radionuclides toward the biosphere and as a blockage to hinder the flow of water between different layers of the geological setting crossed by the borehole [1].

As the service life of cementitious materials under various environmental conditions is as yet unknown more research is needed to improve the confidence that the engineered barriers in the repository will perform as required in the long term [1,2,3].

In the repository the cement paste will be exposed to high temperatures and pressures, aggressive chemicals dissolved in the groundwater, and the radiation field of the sources, factors that are deemed to affect negatively its durability.

The durability of cementitious materials can be investigated by different methods – comparison of the long term behavior of cement with natural and anthropogenic analogues, modeling, and accelerated tests in laboratory [1,4]. In the present paper, we report the results of accelerated laboratory tests in which cement paste samples were subjected to the stress conditions deemed to prevail in a deep borehole repository.

A series of multi-factorial treatments was designed to provide evidence of the effects of single factors as well their interactions. Exposure factors included radiation dose, temperature, and time of immersion in distilled water or salt solution with concentration typical of granite groundwater.

The objective of the work reported in this paper is to evaluate the effects of some environmental factors on cement paste as observed by changes in chemistry, microstructure, mineralogy, and morphology of samples and by changes in the concentration of selected ions in solution after sample immersion tests.

The research is in progress and results obtained as far show that adopted methodologies perform as expected to produce useful data to estimate service life of cement paste under repository conditions.

2. MATERIALS AND METHODS

Cement paste samples were exposed to extreme values of the environmental conditions and analyzed in respect to changes in their chemistry, mineralogy, and morphology.

Changes in cement paste mineralogy and morphology, after exposure to degrading factors, were investigated by X-ray diffraction, scanning electron microscopy, and thermogravimetric analysis of paste samples.

Changes in the chemistry of samples were observed by analysis of the composition of leaching solutions. The concentration of leached cations was analyzed by inductively coupled plasma optical emission spectroscopy and anions by ion chromatography.

Twenty four sets of Type V [5] (ASTM HES [6]) cement paste samples, with six specimens each, were cast, left to set inside plastic sealed moulds for seven days, and then stored under the aggressive environmental conditions used to accelerate stress effects. Samples had half scale size that is 50 mm high and 25 mm in diameter. This size was necessary because of the small space for irradiation and because radiation doses as uniform as possible over the sample volume was required.

The test conditions were established on the basis of the environmental conditions, which are deemed to prevail in the repository at the depth of waste emplacement. Exposure conditions included:

- a) Immersion in salt solution (SS) or in distilled water (DW), or kept in dry storage (DS);
- b) Room temperature (20°C) or high temperature (60°C);
- c) Immersion time of 30 days (30D) or 60 days (60D);
- d) Irradiation in a gamma irradiator (400 kGy) or kept at background radiation (0 kGy).

Tests were designed as a complete multi-factorial design, at two levels, with storage conditions at three levels. Table 1 shows the assignment of each sample set to the exposure conditions.

Sets identified by U and V were kept in dry storage, at room temperature, without irradiation, and so functioned as zero level, or reference base line, to which the other samples were to be compared.

Table 1. Sample set ID and test conditions assignment.

Sample ID	Immersion/dry storage			Temperature		Immersion time		Irradiation	
	DW	SS	DS	20°C	60°C	30D	60D	0 kGy	400 kGy
A	X			X		X		X	
B	X			X			X	X	
C		X		X		X		X	
D		X		X			X	X	
E	X				X	X		X	
F	X				X		X	X	
G		X			X	X		X	
H		X			X		X	X	
I	X			X		X			X
J	X			X			X		X
K		X		X		X			X
L		X		X			X		X
M	X				X	X			X
N	X				X		X		X
O		X			X	X			X
P		X			X		X		X
Q			X	X			X	X	
R			X	X			X	X	
S			X		X	X		X	
T			X		X		X	X	
U			X	X			X		X
V			X	X			X		X
W			X		X	X			X
X			X		X		X		X

DW - distilled water; SS - Salt solution; DS - kept in dry storage

Characterization analyses included:

- a) Concentration of selected ions in immersion solutions, before and after exposure to stress factors, to detect chemical species leaching from samples and precipitating by reaction with cement paste compounds.
- b) X-ray diffraction of hardened cement paste samples, before and after exposure, to detect changes in structure and mineralogy;
- c) Scanning electron microscopy to detect changes in structure and elemental composition of micrograins at the sample surface;
- d) Thermogravimetric analysis to detect chemical changes.

Changes in mechanical resistance, as measured by axial compression of the cylindrical samples, and changes in sample masses and volumes were also observed

3. RESULTS AND DISCUSSION

3.1. Ion Concentration Analyses

Analyses of bath solutions detected changes in concentration of selected ions after immersion test of cement samples. This assay was intended to observe the behavior of cement paste under attack by aggressive chemical species dissolved in ground water. Selected cations were Ca^{2+} , Na^+ , K^+ , Mg^{2+} , Al^{3+} , Fe^{3+} e Si^{4+} , measured by ICP-OES, and results were expressed in g.L^{-1} . Concentration of anions F^- , Cl^- , NO_2^- , Br^- , NO_3^- , PO_4^{-3} , and SO_4^{-2} were measured by ion chromatography and results also expressed in g.L^{-1} . Both analytical methods were employed by the Center of Environmental Chemistry of IPEN in two samples of each immersion bath and results express the mean of the two determinations. NO_2^- , Br^- and PO_4^{-3} were below the detection limits

Figure 1 shows the results of each ion concentration in bath samples that initially were distilled water, after immersion tests at 20°C and 60°C.

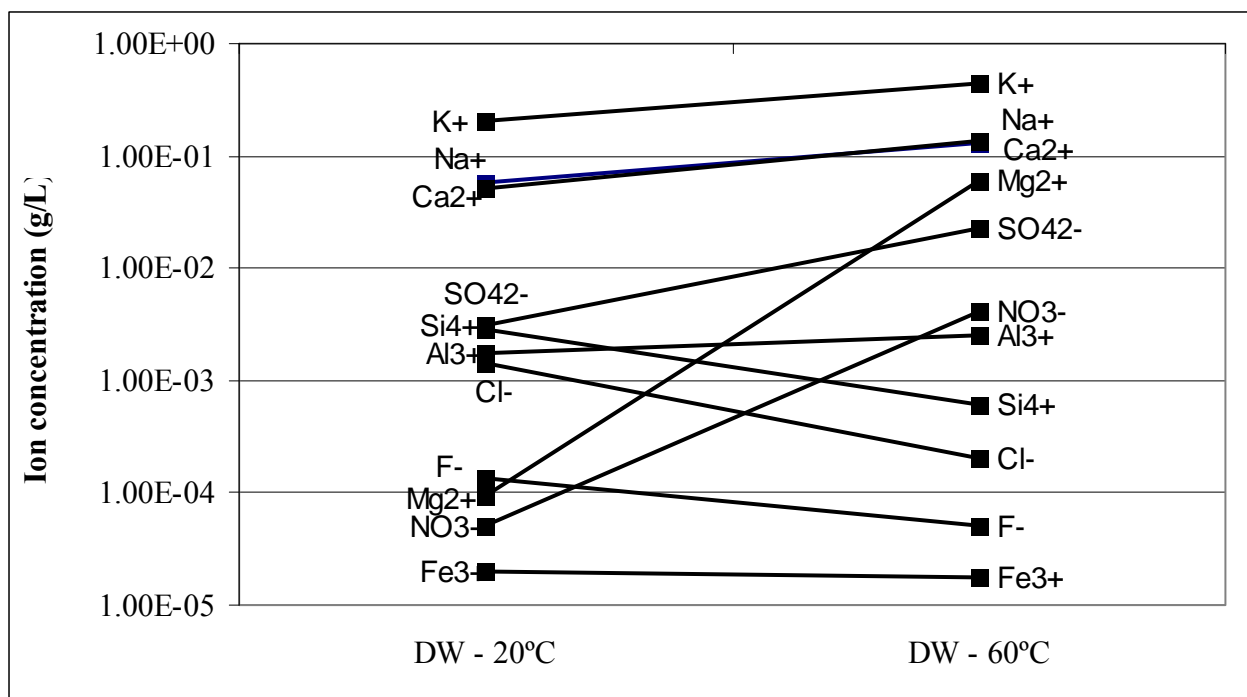


Figure 1. Ion concentrations after immersion tests at 20°C and 60°C.

Concentrations of ions, after immersion tests, in baths that initially were salt solutions are presented in Figure 2, as the ratio of the initial concentration.

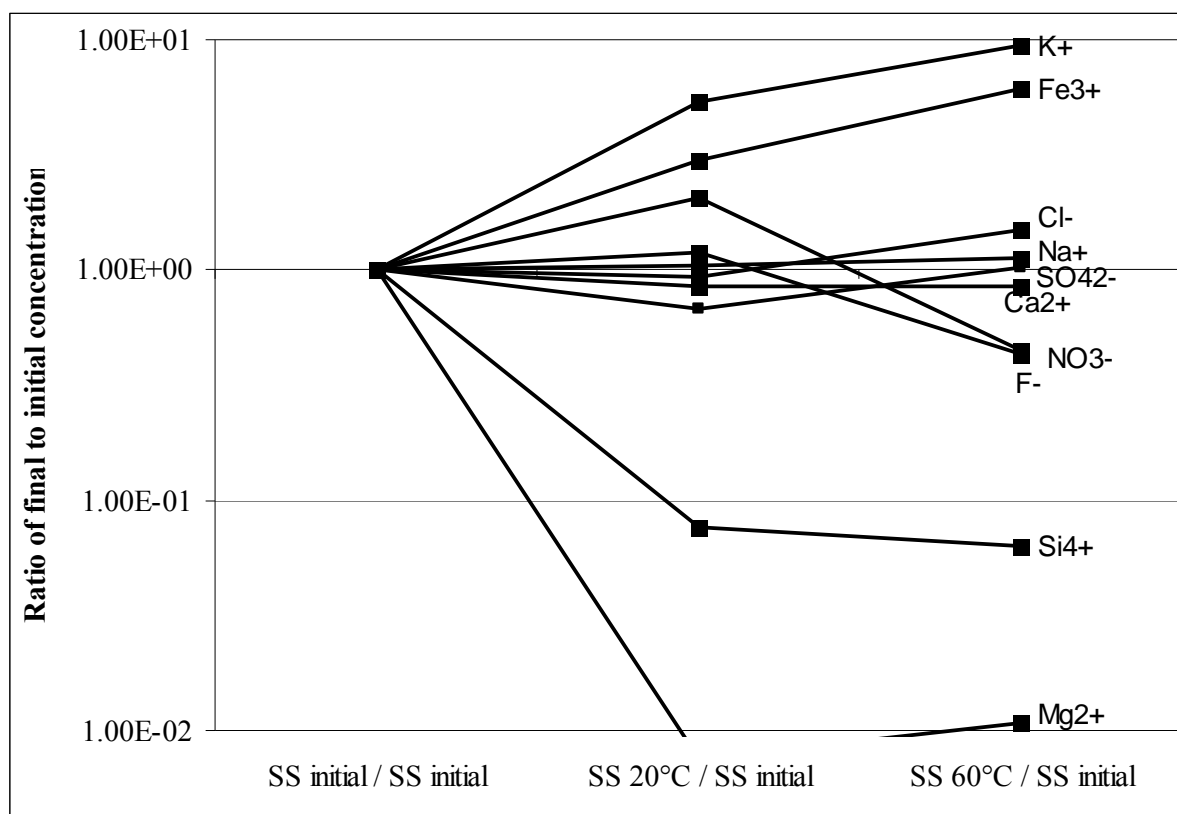


Figure 2. Ratio of final to initial concentration of selected ions in bath solutions.

The observed changes in concentrations are being investigated and possible explanations for these behaviors will be reported in a future communication.

3.2. X-ray Diffraction

Ten samples of cement paste, randomly selected from the complete set, but representing most treatments, were grinded to a fine powder in agate mortar and pestle, and analyzed by the Laboratory of Technological Characterization of the Department of Engineering of Mines, Polytechnic School of the University of São Paulo. Figure 3 shows the superimposed diffractograms of the ten samples.

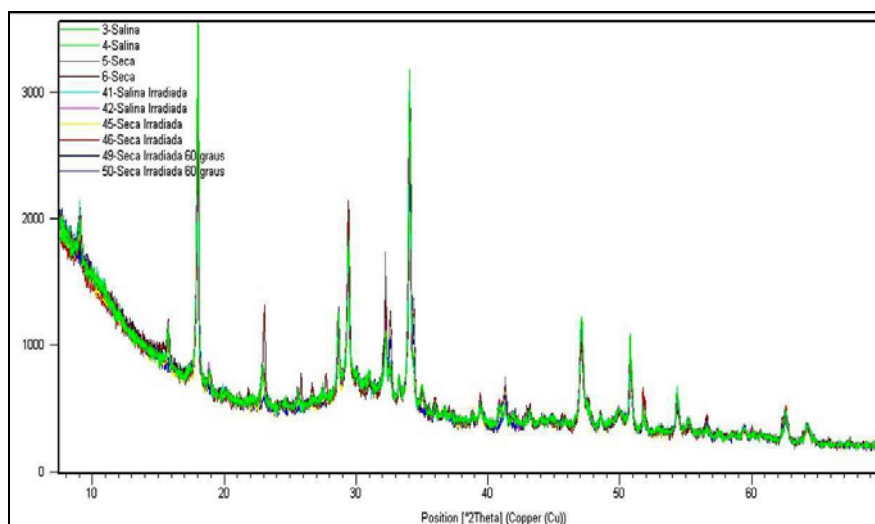


Figure 3. Diffractograms of the 10 cement paste samples.

These spectra were compared and used as input in an algorithm for cluster analysis. A dendrogram was constructed (Fig. 4), pairing and grouping samples and sample sets by similar mineralogical content in three levels. Samples were numbered but not identified to the analyst. The method was able to pinpoint powder samples extracted from the same test sample, as indicated by the left-most pairing and was able to group sample sets that were exposed to similar treatments.

This result indicates that this method of analysis will be useful in further characterizing the materials and will also allow to recognize and to quantify the changes induced by the treatments.

3.3. Scanning Electron Microscopy

Precipitates on the surface of immersed samples were analyzed by SEM. Figure 5 shows an electron micrograph with clearly visible needlelike crystals and grains. Needles are identified as ettringite crystals. The elemental composition of both types of crystals is shown in Figure 6. The sulfur and aluminum peaks that are present in the left diagram and that are absent in the right diagram identify the ettringite mineral, the result of the reaction of calcium aluminate found in hydrated Portland cement system with calcium sulfate present in the bath solution [3].

3.4. Thermogravimetric Analysis

TGA analysis of cement paste samples was done in the Laboratory of Materials Characterization of the Navy Technological Center in São Paulo. Six samples were analysed after they were submitted to irradiation and immersion. Only one result of the analyses is shown here, that of sample number 6, a not irradiated, immersed in distilled water at 20°C sample. Figure 7 shows the TGA spectrogram. The other results will be presented in a later detailed report. Important here is to report that this method of analysis will help in identifying

and quantifying chemical and mineralogical changes in the cement paste as consequence of the exposure of the material to the aggressive environmental factors [7].

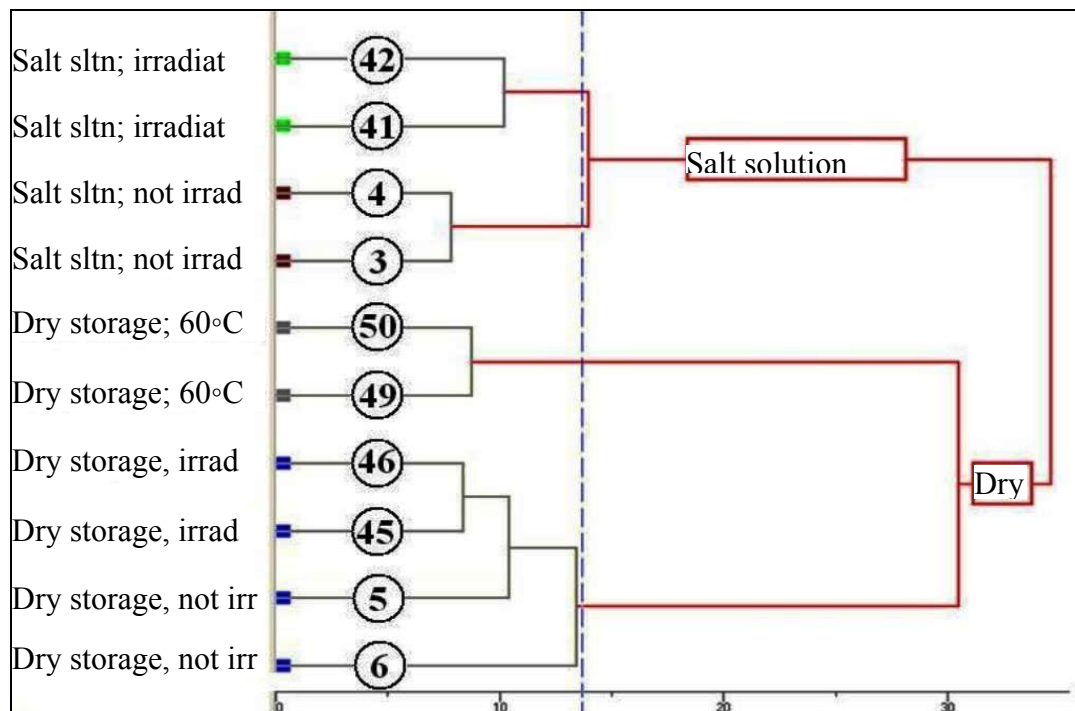


Figure 4. Dendrogram of samples obtained by cluster analysis.

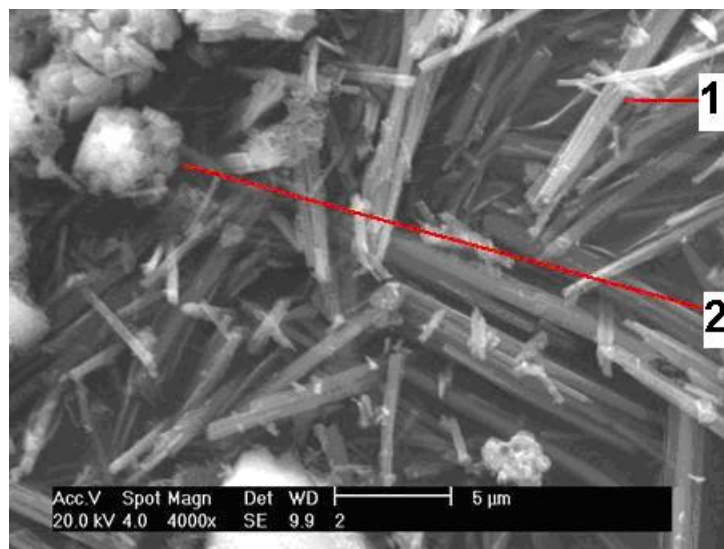


Figure 5. Scanning electron micrograph of precipitates on the sample surface showing crystal needles (1) and grains (2).

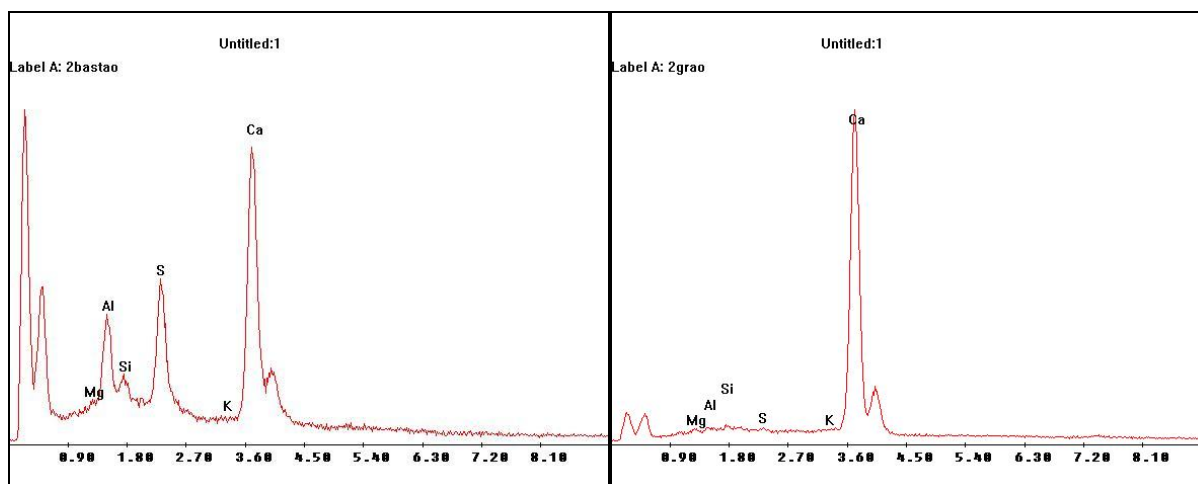


Figure 6. Elemental composition of needle crystals (left) and grains (right).

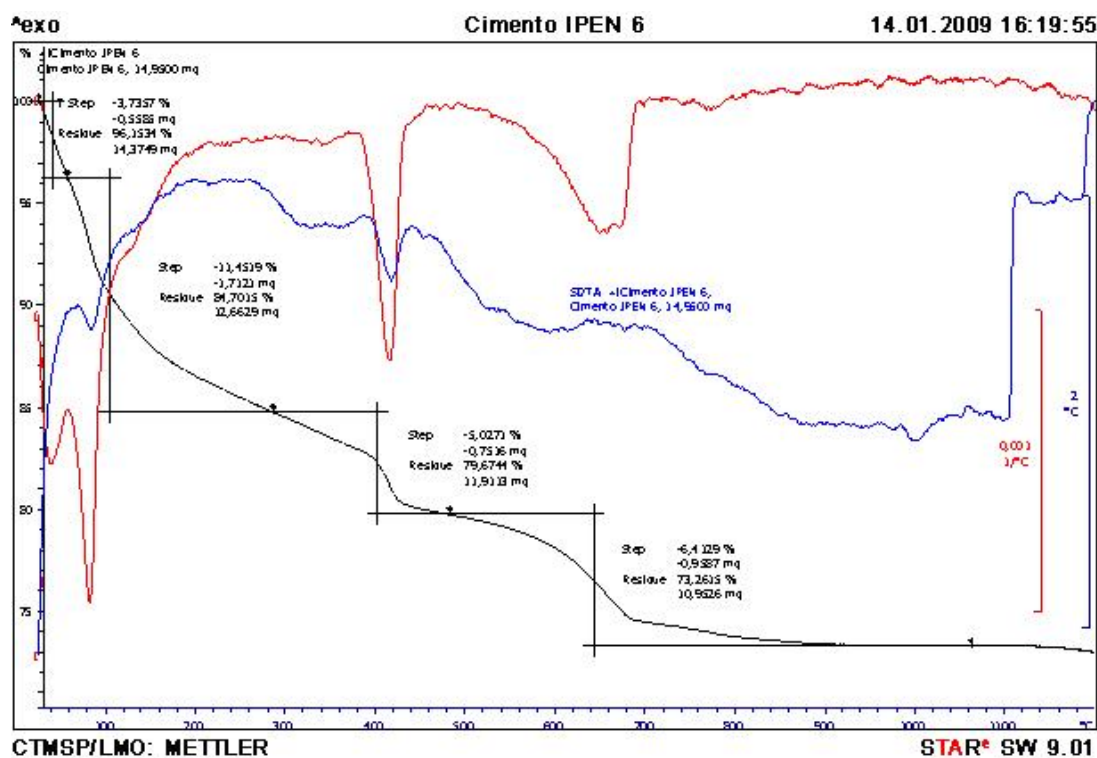


Figure 7. TGA of sample number 6.

Table 2 shows the percent loss of weight of each sample at the indicated temperatures.

- The weight loss between 30 and 105°C is due to the evaporation of free water present in pores. This water is totally eliminated below 120°C.
- 110–170°C: decomposition of gypsum, ettringite and loss of part of the water from hydrated carboaluminate compounds.
- 180–300°C: loss of water from CSH and hydrated carboaluminate compounds.
- 450–550°C: dishydroxilation of portlandite.

- 700–900°C: decarbonation of calcium carbonate.

Table 2. Percent loss of weight of each sample at the indicated temperatures.

Sample ID	Weight loss (%)				Residues at
	25-60°C	60-290°C	290-485°C	485-1000°C	1000°C
1	4,5	10,8	5,0	4,9	74,5
2	4,4	11,0	4,8	5,1	74,6
3	3,2	8,6	5,1	4,1	79,0
4	3,1	9,0	5,5	7,5	74,9
5	4,4	11,9	4,9	6,2	72,7
6	3,7	11,5	5,0	6,4	73,3

4. CONCLUSIONS

Chemical changes in cement pastes induced by radiation, temperature, and attack of aggressive chemical species in bath solutions were observed by many techniques. ICP-OES and Ion-chromatography showed changes in chemical concentration of cations and anions in bath solutions at different experimental conditions. X-ray diffraction could identify differences in the mineralogy caused by exposure of the samples to the aggressive environments represented by irradiation and immersion in salt solutions. Scanning electron micrographs allowed the observation of crystalline compounds in the hydrated Portland cement paste and the products of reaction with dissolved ions in bath solutions. TGA results indicate the main composition of samples and how it is affected by experimental conditions.

These are very preliminary results that show the analytical potential of the available infra-structure of RWML and other associate laboratories to proceed with the ongoing research program aiming at studying the long term behavior of cementitious materials and the expected service life of this important engineered barrier in radioactive waste repositories.

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