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Research Article

Assessment of Cement Durability in Repository Environment

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Abstract

Portland cement paste is proposed as the material to filling in the annulus between the casing of a borehole and the geological formation in a deep repository for spent sealed radiation sources in Brazil. The cement paste is intended to function as structural material, an additional barrier against the migration of radionuclides outside the repository, and as a blockage against the transport of water between the different strata of the geological setting. The objective of this research is to investigate the behavior of the cement paste and to estimate its service life. In this paper we present the results of mechanical strength measurements and chemical and mineralogical analysis of samples to detect the changes caused by radiation, temperature and aggressive chemicals of groundwater to which the material will be exposed. Methods of analysis included Inductively Coupled Plasma Atomic Emission Spectroscopy, Ion Chromatography, XRay Diffraction, and Thermo-Gravimetric Analysis.

Introduction

The Nuclear and Energy Research Institute (IPEN-CNEN/SP), in São Paulo-Brazil, stores disused sealed radioactive sources (DSRS), formerly used in radiotherapy, industrial gauges and irradiators, as radioactive waste. Many sources have long-lived radionuclides and high activity. The inventory amounts to tens of thousands sources and the total activity reaches hundreds of terabecquerels [1].

Final disposal of this kind of radioactive waste is an unresolved issue in Brazil and a difficult problem in most countries. Shallow boreholes and shallow-ground disposal sites for low- and intermediate-level wastes cannot accept disused sealed sources for disposal and intermediate depth boreholes may be unacceptable for large inventories in humid climates [2].

In order to find an alternative option for disposal of the large inventory of high activity and long-lived sealed sources in Brazil, the Radioactive Waste Management Laboratory (RWL) at IPEN-CNEN/SP is developing a concept of disposal in deep boreholes, where DSRS could be isolated from the human environment by the millennia that are needed by

those sources to reach an acceptably low radiation risk [1].

In this concept, a borehole is drilled to a depth of a few hundred meters in a granite batholite, encased with a steel pipe and cemented by pumping down Portland cementwater slurry, which is left to harden in place, backfilling the annular space between the steel casing and the geological formation. 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 [3].

The long-term safety of this concept relies on multiple engineered and natural barriers. The overall performance of the whole system depends on the behavior of all barriers, their interactions with the disposed wastes and the components of the environment, and their evolution over time. Of all components of the system, the cement paste is the material with the least known behavior in the long term [4-9]. Although studies on the performance of cementitious materials as structural material in bridges and buildings date back to several decades, the issue of the long term behavior of cementitious materials under repository conditions seems far from being resolved. The complex chemistry of Portland cement and the variability of wastes and repository conditions is a possible explanation for the persisting question on whether cementitious materials will endure long enough in repository.

In the repository for sealed sources, the cement paste will be exposed to some factors that are deemed to affect negatively its durability. Attempts to investigate the degradation of cement paste under several conditions have been undertaken by various authors, exposing the cement paste or mortar to some factors, as higher temperatures and pressures [10-14], aggressive chemicals dissolved in the groundwater [15-24] , and the radiation field of the sources [25-29]. However, there is a lack in the study of synergetic effects and the simulation in long term.

The present research aimed to investigate the durability of cement paste under repository conditions using accelerated tests. Specimens of cement paste were exposed to the high levels of the stressing factors foreseeable at the depth of the repository in order to evaluate the exposure effects on the cement paste. Specimens' mechanical strength and mass variation allowed to observe changes in physical characteristics of cement paste, while, ion penetration/leaching analysis, X-ray diffraction (XRD) and thermo-gravimetric analysis (TGA) allowed to observe changes in their chemical, structural and mineralogical characteristics.

Materials and Methods

Materials

All experiments were conducted with cement paste specimens (cps) composed of Portland Cement Type V, according to NBR 5733 Brazilian Technical Standards Association [30] equivalent to the HES cement of ASTM specifications [31] with water to cement (w/c) ratio of 0.35.

Cubic (20 x 20 x 20 mm) cps were tested. Twenty four sets, with five specimens in each one, were cast and left to set inside plastic molds, for one day. Then, they were demolded, cured

in saturated limewater for more six days and stored under the aggressive environmental conditions used to accelerate the stress effects [32].

Tests were planned as a complete multi-factorial experiment. Table 1 shows the assignment of each sample set to the exposure conditions. Sets U and V functioned as reference base line to which the other samples were compared.

The following exposure conditions were selected:

- Immersion in salt solution (SS) or distilled water (DW), or kept in dry storage (DS);

- Room temperature (20°C) or high temperature (60°C);

- Immersion time of 30 days (30D) or 60 days (60D);

- Irradiation to a dose of (400 kGy) or background radiation (0 kGy)

The salt solution was a simulation of groundwater with the average composition of water found in granitic geological media. The concentrations of ions are presented in Table 2.

Table 1. Sample set ID and test conditions assignment.

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

Table 2. Composition of the Salt Solution used in the tests.

Initial Salt Solution Composition (mg/L)											
Ca	Cl⁻	F⁻	Fe	HCO₃⁻	K⁺	Mg	Na⁺	NO3⁻	Si	SO4⁻²	pH
1790	4900	---	0.131	60	33	55.9	1300	1.72	0.1	505	6.0

A multipurpose compact irradiator with 3.4 TBq of ^{60}Co, was employed to irradiate the samples to accumulate a radiation dose of 400 kGy what required about 100 hours of exposure. The limited space for samples in the irradiator and, more important, the objective of keeping the exposures as uniform as possible led to use the small cps instead of the standard sizes foreseen in the cement standards [32].

Experimental characterization techniques

After exposure to the combination of factors, the effects on the cement paste specimens (cps) were observed by changes in their chemical, structural, and mineralogical characteristics. Compressive strength tests were performed in all cps and some of them were investigated in terms of changes in mineralogy by X-ray diffraction (XRD), and thermo-gravimetric analysis (TGA).

To the XRD and TGA analysis, samples of cement paste, randomly selected from the complete set, but representing all treatments, were separately, grinded to a fine powder in agate mortar. XRD analysis of cement paste samples was conducted in 24 samples and TGA analysis in six samples, which were analyzed after they were submitted to irradiation and immersion.

Mass variation was also evaluated to investigate water loss/gain and chemical species leaching/penetration.

After the assays, the solutions were analyzed by ICP-OES (Ca, Fe, Mg, and Si), Flame Atomic Absorption Spectrometry (Na and K), Volumetry (HCO₃), Potenciometry (Cl and F) and Ultraviolet–visible spectroscopy (NO₃ and SO₄) to detect leaching / penetration of chemical species from/into cement paste.

Results

The cement hydrates are unstable in the long-term because the microstructure and the mineralogy of the paste change with time as a consequence of re-crystallization of the cement gel and as a result of chemical reaction with aggregates and substances of the environment. One way of measuring the deleterious effects on cement paste is analyzing and correlating these changes with the evolution of the properties of the material [33-35].

In this work, mechanical properties were evaluated by compressive test and chemical properties by changes in mineralogy and microstructure.

Compressive Strength

Student's t-test GraphPad's online QuickCalcs statistical calculators [36], at the 0.05 level of significance, was used assessing the significance of differences between the mechanical strength of cps submitted to each treatment. The cut-offs adopted to indicate the strength of the evidence of p-values were: p-value < 0.0001 - extremely statistically significant; 0.0001 > p -value > 0.0100 - very statistically significant;

0.0100 > p -value > 0.0500 statistically significant; 0.0500 > p -value - not statistically significant . All cps submitted to the same treatment were grouped and analyzed as just one, in order to evaluate each treatment individually. The results of t-test are presented in Table 3.

Table 3. Mechanical strength and results of t test for each treatment.

Treatment		Mechanical Strength (MPa)	Statistically significance
Immersion	SS or DW DS	117 ± 17	Extremely significant
		89 ± 11	
Immersion solution	DW	123 ± 13	Very significant
	SS	111 ± 17	
Temperature	20°C	104 ± 18	significant
	60°C	112 ± 22	
Immersion time (days)	30 days	106 ± 21	not significant
	60 days	110 ± 20	
Irradiation dose (kGy)	0 400	107 ± 20	not significant
		109 ± 21	

It is possible to notice that the immersion in both SS and DW, as well as the higher temperature increased the mechanical strength of samples. Immersion in saline solution lowered the mechanical resistance. This behavior could be explained by the hydration degree of samples that was incomplete in early ages and completed after immersion.

Variation of Sample Mass

The influence of each treatment on cps mass is shown in Figure 1. Each column in the graphs represents gain or loss of mass in relation to the initial mass of the samples, measured one day after being removed from the curing process.

One day after being removed from the immersion or dry storage (before irradiation) and one day before compressive test (after irradiation), all cubic cps were weighted. Mass samples measured before irradiation were named as "M2" and before compressive test as "M3". Initial masses (M1) were obtained after the curing time. Grey columns represent the weight variation after treatment, while the black ones after irradiation.

The cps kept in dry storage at room temperature had no variation during the storage, while samples kept at elevated temperatures showed weight loss. This was expected since, after hydration, the cps kept water absorbed in the cement pores, which evaporated.

Cps immersed both in DW and SS had gain of mass after treat-

ment, except those kept under immersion in DW, 60 d, 60 °C, that presented loss of mass. This behavior can be explained because, with time and high temperature, some compounds of hydrated cement, as Portlandite and C-S-H gel can be dissolved in the bath water, resulting in loss of mass.

In all other cps immersed in DW, M2 was higher than M1, what is caused by absorption of water into cement pores. However, M3 was lower than M1 (for both irradiated or not irradiated cps), probably due to loss of absorbed water and leaching of other Portlandite or C-S-H from the paste [37,38].

Chemical species present in SS may react with the compounds of hydrated cement paste causing cracking and spalling (e.g. sulphate reaction with Portlandite, forming ettringite). Penetration of high quantities of chloride and sulfate can produce these phenomena. On the other hand, reaction of bicarbonate and calcium can produce calcite, which is capable to block pores and reduce permeability [39-42]. It was possible to observe that all cps immersed in SS gained mass, probably caused by penetration and reaction of chemical species.

After irradiation, all cps show mass loss (M3 was lower than M2 in all cases), mainly due to loss of water adsorbed in cement pores. The radiation field caused radiolysis of water, causing crack of water molecules and the formation of a large number of radicals. In cps immersed in SS, M3 was higher than M1, but lower than M2, which shows that the absorbed water reacted in the cement matrix, and was not free to be cracked when cps were irradiated.
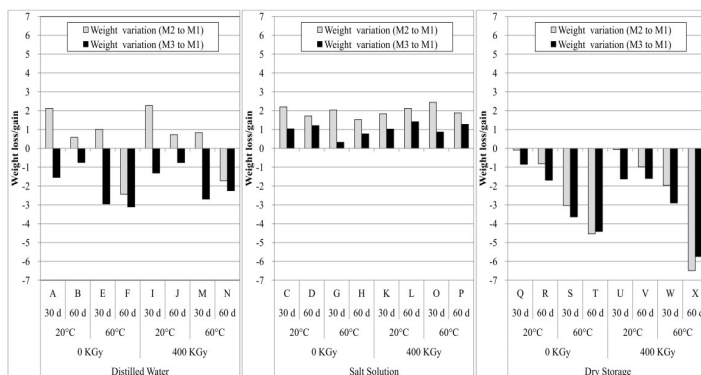
Figure 1. Mass variation of cps that were submitted to each treatment.

Analyses of the immersion solutions

Chemical species dissolved in immersion solutions were analyzed in order to evaluate the behavior of cement paste in aggressive environment. Results of analyses showed some changes in concentration of selected ions, as shown in Figure 2. Significant variations in the concentrations of Fe, NO_3^-, Cl^- and F^- were not observed.
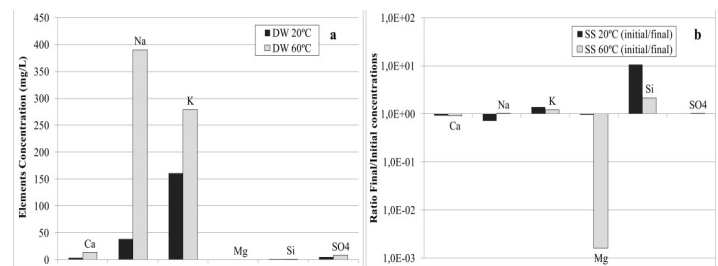
Figure 2. Concentration of chemical species after cps immersion in a) DW; and b) SS (initial/final ratio).

Ca is present in almost all compounds of the hydrated cement paste and, as expected, Ca leached from cement paste under immersion in DW. On the other hand, the calcium concentrations decreased in SS, indicating Ca penetration in the samples. Ca may be absorbed by the C-S-H or react with bicarbonate to produce calcite, a compound that can block cement pores and reduces the permeability of cement paste.

Concerning silicon, it was observed that its concentration did not change in samples that were kept under immersion in distilled water, while those kept in salt solution showed some variation. Despite this, Si added to the initial solution was too small and its variability was considered not significant, since the concentration of Si compounds in cement matrix is much higher than the concentration in immersion solution.

Leaching of alkalis (Na and K) was observed in samples kept in DW, mainly those kept at the highest temperature. This can be explained by the solubility of compounds, which increases with the temperature. The leaching of these species can induce the penetration of Ca and Mg, once alkalis are released from C-S-H sites which are filled by Ca and Mg species. In fact, a decrease of Mg species in solution was observed indicating penetration into the cement paste.

The sulfate species are responsible for one of the most important process that can degrade the cement paste: the delayed ettringite formation causing cracking and spalling of hardened cement paste. It was observed that this process hardly occurred in this case since the sulfate penetration was too low and the temperature used in this work was below 70ºC.

X-ray Diffraction (XRD)

The spectra of X-ray diffraction taken from 49 samples were compared and used as input in an algorithm for cluster analysis. A dendrogram was constructed (Figure 3), pairing and grouping samples according to similar mineralogical content in three levels. Samples were numbered but not identified to the analyst. The method was able to correctly group sample sets that were exposed to similar treatments.

The diffractograms of twelve samples that underwent higher temperature (60°C) and the various treatments indicated in Table 4, are presented in Figure 4. In general, the XRD patterns in Figure 4 show no differences in the mineralogy, except by the ettringite peaks (1, 2 and 4) that are missing in both irradiated and not irradiated specimens kept in dry storage (samples 47, 49, 9 and 11).

A semi quantitative analysis (Relative Intensity Ratio analysis – RIR) was made by the relative peak intensity of each mineral compound of some samples. Table 5 shows the identification of samples kept in dry storage and those that underwent different treatments. Figures 5 and 6 show the diffractograms of these samples and the RIR analysis results, respectively.

These analyses confirmed the absence of ettringite in samples that were kept in dry storage at the highest temperature. Furthermore, samples kept in immersion showed higher hydration degree since belite and alite quantities were lower than in those that were kept in dry storage (with high amount of belite and alite). No significant changes caused by radiation or time of immersion were observed in the cement mineralogy.
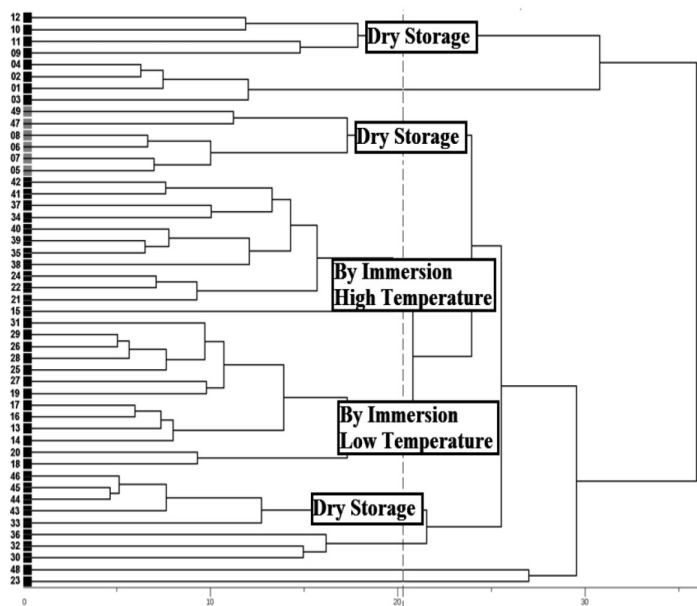
Figure 3. Dendrogram of samples obtained by cluster analysis of diffractograms of cement samples.

Table 4. Identification of samples for XRD analysis.

| Irradiated Samples				Non-irradiated Samples			
Sample ID	Sample Set ID	Storage Condition	Exposure Time	Sample ID	Sample Set ID	Storage Condition	Exposure Time
37	N	DW	60 Days	23	F	DW	60 Days
34	M	DW	30 Days	21	E	DW	30 Days
49	X	DS	60 Days	11	T	DS	60 Days
47	W	DS	30 Days	09	S	DS	30 Days
41	P	SS	60 Days	03	H	SS	60 Days
39	O	SS	30 Days	01	G	SS	30 Days
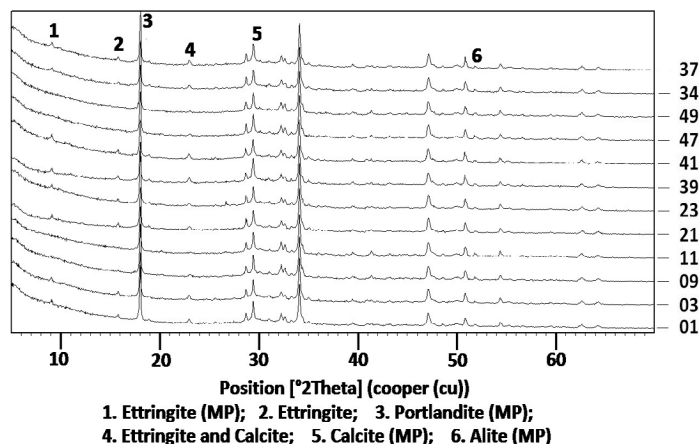
Figure 4. XRD diffractograms of the 12 selected cement paste samples.

Table 5. Identification of samples kept at DS for XRD RIR analysis.

Irradiated Samples				Non-irradiated Samples			
Sample ID	Sample Set ID	Temperature	Exposure Time	Sample ID	Sample Set ID	Temperature	Exposure Time
43	U	20ºC	30 Days	47	W	60ºC	30 Days
45	V	20ºC	60 Days	49	X	60ºC	60 Days
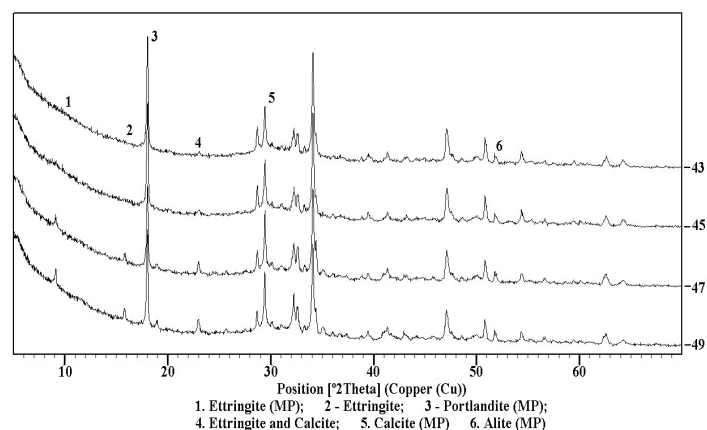
**Figure 5.** XRD diffractograms of samples kept in dry storage.
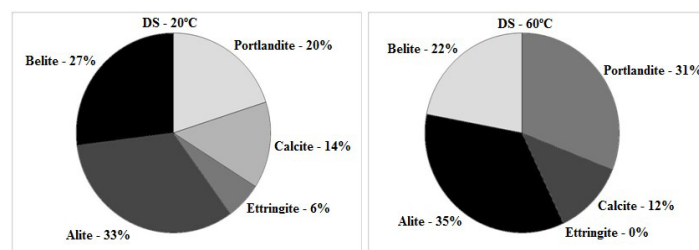
Figure 6. XRD RIR analysis of two samples kept in dry storage at 20°C and 60°C.

Thermogravimetric Analysis

Six samples were analyzed after they were submitted to irradiation and immersion. Table 6 shows the percent loss of weight of each sample at the indicated temperatures ranges. The temperature range was indicated by TG curves when cement specimens showed loss of weight. Figure 7 shows one of the TGA curves.

Table 6. Weight loss percentage of each sample at the indicated temperatures ranges

TGA Samples ID	1	2	3	4	5	6
Sample Set ID	Q	U	S	W	C	A
Storage condition	DS	DS	DS	DS	SS	DW
Exposure time	60 days	60 days	30 days	30 days	30 days	30 days
Temperature	20°C	20°C	60°C	60°C	20°C	20°C
Irradiated	No	Yes	No	Yes	No	No
Weight Loss (%) 25 to 60°C	4.5	4.4	3.2	3.1	4.4	3.7
60 to 290°C	10.8	11.0	8.6	9.0	11.9	11.5
290 to 485°C	5.0	4.8	5.1	5.5	4.9	5.0
485 to 1000°C	4.9	5.1	4.1	7.5	6.2	6.4
Residues at 1000°C	74.5	74.6	79.0	74.9	72.7	73.3
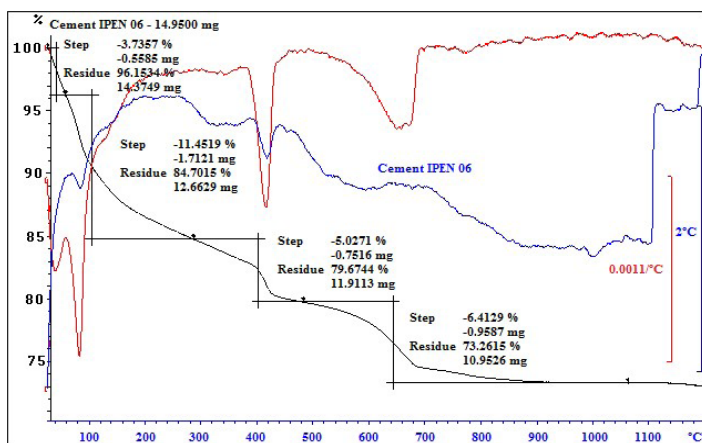
Figure 7. TGA of cement sample submitted to immersion in DW, in 20ºC for 30 days.

The weight loss at each temperature zone shows the decomposition of some mineral compounds or loss of pore water. In Table 5 it is possible to see that samples kept in DS at 60°C showed the lowest weight loss between 25°C and 290°C, indicating low quantities of ettringite and pore water [43].

Discussion

The results obtained in this work allow some interpretations about the behavior of cement paste when submitted to each treatment. Some considerations about the influence of treatments in cps hydration and changes in mineralogical and chemical properties are shown below.

Immersion and dry storage effects

According to the literature, the mechanical strength of cps submitted to aggressive chemical compounds, like sulfate and chloride, could be lower than that presented by cps kept in dry storage. However, it was observed that resistance of cubic cps immersed (both in SS or DW) was higher than those presented by cps kept in dry storage. This behavior can be explained by the time that cps were kept under immersion. Lee et al [44] observed that mechanical strength of cps increased after 28 days under immersion, but decreased after 90 days [44].This phenomenon was attributed to ettringite formation that in early ages fills the cement paste pores increasing the resistance. On the other hand, in later ages, ettringite formation causes cracks and spalling of cement paste [45,46]. Cps immersed in SS presented lower resistance than cps immersed in DW, probably caused by magnesium penetration into cement paste. According to Bénard [47], the presence of some chemical species in solution could affect the hydration process by poisoning, adsorption or precipitation.

The cement hydration starts immediately after water addition. In this work, the used cement hydrates quickly and consequently its setting time is short (usual,HES cement is above 90% hydrated with 7 days, instead of 28 days of Ordinary Portland Cement). Although these characteristics are desired in the borehole, its quickly hardening can difficult the complete hydration of the anhydrous grains. After cure, the hydration was not complete in cps and this process was restarted when cps were immersed, leading to an increase of mechanical strength. It was also observed by Aziz [48] who investigated the relationship between hydration process and durability of sulfate-resistant and slag cement blends, concluded that the mechanical strength is higher in samples kept for a longer hydration time.

Chemical changes in cement pastes induced by attack of aggressive chemical species in immersion solutions were evaluated by some analytical techniques. ICP-OES and ionchromatography showed changes in chemical concentration of cations and anions in immersion solutions at different experimental conditions. It was observed the leaching of Na^+ and K^+ from cement paste to solution and the penetration of Ca^{2+} and Mg^{2+} into cement paste. Decalcification and delayed ettringite formation, which are important processes that lead to cement degradation, were not detected once Ca^{2+} was not leached neither SO_4^{2-} penetrated into cement paste. Immersion factors (concentration, time of exposure, temperature, etc.) were not able to induce Ca^{2+} or SO_4^{2-} exchanges between cement paste and solution. Marumo [49] investigated the sulfate penetration into cement specimens immersed in solutions with concentrations of 0.005M (equivalent to the concentration adopted in this work) and 0.5M and did not observe penetration of significant quantities of this ion in specimens immersed in low concentrations, in contrast with specimens immersed in higher concentrations.

The XRD cluster analysis could identify differences in the mineralogy caused by exposure of the samples to the aggressive environments. However, except by ettringite mineralogical differences were tenuous and hardly observed.

The absence of ettringite in cps that were kept in dry storage at high temperature had hardly occurred by natural variations in the composition of hydrated cement paste. Therefore, this absence is certainly the result of the treatments and could be explained by the decomposition of ettringite. Although its temperature of decomposition is about 110-120°C [50,51], it may initially decompose to meta-ettringite, an amorphous compound, above 50°C in the absence of water [50-52].

Cps kept in dry storage showed significant weight loss after exposure, mainly those kept at higher temperature. This behavior is expected once the loss of water is a natural process in DS while cps immersed absorbed water and gained mass. In fact, lower quantities of pore water in cps kept in dry storage were confirmed by TGA.

Temperature effects

Although temperature rise increases damages in cement paste, this rise is profitable to cement resistance during curing time [53,54]. In this work, temperature proved to be significant and capable of altering the mechanical strength, as expected. Once the hydration process results from chemical interactions, higher temperature may accelerate the reaction kinetics of the specimens, resulting in higher mechanical strengths.

Since cps immersed were considered as in hydration process (see section 4.1), temperature rise increased mechanical strength from 113 MPa (for cps kept at 20°C) to 121 MPa (for cps kept at 60°C).

Mineralogical changes associated to temperature were just observed in cps kept in dry storage at 60°C, which contained less or no ettringite, as showed in XRD and TGA analysis (See discussion in section 4.1).

Radiation effects

The presence of a radiation fields at the repository environment can lead to the radiolysis of pore water of cement paste, and the intensity of the effect is a function of the radiation type and dose and the chemical composition of pore water. The formation of radicals can affect negatively the repository barrier durability.

However, no influence of irradiation on the mineralogical composition was observed when it was analyzed individually or under the possible synergic effect with other treatments. The radiation dose used in this work was not capable to induce alterations in cement paste. However, in the repository, the accumulated doses can achieve ten times more than the value used in this work. More studies is, then, necessary to assess if the radiation at the expected levels, will negatively affect the cement mineralogy and microstructure and, therefore reduce its durability.

Time of exposure effects

Only mass variation was observed in cps exposed to 30 days or 60 days test. The main difference was in cps kept under dry storage, which showed a higher loss of weight after 60 days due to higher water evaporation. Loss of weight of cps immersed in DW at 60°C for 60 days can be assigned to decalcification process that can be induced by high temperatures at later ages.

Time of exposure was not able to alter the mechanical strength of cps, as well its mineralogy. It has been proposed that the times of exposure used in this work were too short to show any influence.

Conclusions

Durability of cement paste was investigated using accelerated tests in order to establish its service life under repository conditions. Short-term results obtained under laboratory conditions were analyzed and correlated with the intrinsic properties of the material. It was possible to conclude that:

- Immersion of cps in water promoted a better hydration and higher mechanical resistance. Chemical aggressive species present in SS degraded cement paste and reduced mechanical strength. However, ion concentrations was too low to seriously damage the cement paste and the immersion had more important role increasing resistance due to a better hydration.

- Dry storage hinders a complete hydration as a consequence of pore water evaporation. High temperatures intensified this process and led to the ettringite decomposition to meta-ettringite;

- High temperatures accelerated hydration kinetics and promoted better hydration and higher mechanical resistance.

- The irradiation doses applied were not able to change the mineralogy of cps;

- The time of exposure in the assay did not influence the mechanical strength or the mineralogy of the cement paste.

Despite the parameters evaluated in this work induced changes in mineralogy of cement paste, they were not able to damage specimens and alter drastically its mechanical resistance. The complete hydration of specimens during the curing process is an important factor to evaluate immersion and dry storage effects. Furthermore, a longer period of immersion/storage and higher irradiation doses must be applied to induce mineralogy changes in cement paste. Further work is expected to extrapolate the shortterm results obtained under laboratory conditions to the actual conditions in the repository over the long-term as an attempt to determine de service life of the cement paste.

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