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BEHAVIOR OF CEMENT PASTE AS BACKFILL IN WASTE DISPOSAL BOREHOLES

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ABSTRACT

The Radioactive Waste Management Laboratory (GRR) at the Nuclear and Energy Research Institute (IPEN) in São Paulo, Brazil, is developing the concept a repository for disposition of disused sealed radioactive sources in a deep borehole, aiming at providing a feasible and inexpensive alternative for final disposal. A relevant fraction of the Brazilian inventory of sources has long half-life which prevents them to be disposed of in shallow ground disposal facilities. In the concept of repository under study, Portland cement paste is intended to be used as a backfill between the steel casing and the geological formation around the borehole. Cement paste will 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 durability of cementitious materials under the conditions prevailing at the depth of disposal is as yet unknown. 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 present in ground water. Techniques of analysis included Inductively Coupled Plasma Atomic Emission Spectroscopy, Ion Chromatography, X-Ray Diffraction, and Thermo-Gravimetric Analysis.

1. INTRODUCTION

The Nuclear and Energy Research Institute (IPEN), in São Paulo-Brazil stores, as radioactive waste, disused sealed radioactive sources (SRS), formerly used in radiotherapy, industrial gauges and irradiators. Many sources have long-lived radionuclides and high activity. The main radionuclides present are ^{60}Co, ^{63}Ni, ^{90}Sr, ^{137}Cs, ^{226}Ra, ^{238}Pu and ^{231}Am. The inventory amounts to tens of thousands sources. The individual activities of many sources are in excess of 1 TBq and the total estimated activity is in the order of 10 PBq.

Final disposal of this kind of waste is an unresolved issue in Brazil and a difficult problem in most countries because a geological repository is required, which is as yet unavailable. Many shallow ground disposal sites for low- and intermediate-level wastes cannot accept disused sealed sources for disposal because of regulatory restrictions based on long-term radiological safety concerns. The practice of disposing SRS in shallow boreholes, which has been adopted by some countries since fifty year ago, should probably be revised at least for sources with long half-life. The proposal of disposing SRS in intermediate depth boreholes (BOSS Concept) [1] may be unacceptable for large inventories and in humid climates.

In order to find an alternative for disposal of the large inventory of high activity and long-lived sealed sources in Brazil, the Radioactive Waste Management Laboratory (GRR) at IPEN is developing the concept of disposition in deep boreholes, where the SRS could be isolated from the human environment by the millennia that are needed for those sources to reach an acceptably low radiation risk [2].

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 a cement-water slurry, which is left to harden in place, backfilling the annular space between the steel casing and the geological formation. In the operational phase of the repository, SRS are packaged in lead containers that are lowered down the steel casing and stacked to about one hundred meters from the bottom.

In the closure phase, fresh concrete is poured down the pipe sealing the borehole. The ground surface at the site is then reworked in order to remove all signs of the facility to a depth of a few tens of meters, thus allowing the surface facilities to be decommissioned immediately thereafter. This last action of the concept is recommended because the extent of time during which post-closure surveillance could be assured is deemed irrelevant before the decay and isolation times that is needed [3, 4] until all sources decay to safe levels.

The long-term safety of this concept relies on multi-engineered barriers and on the natural barrier provided by the emplacement of the waste within a deep and stable crystalline granitic medium. The overall performance of the whole system depends on the behavior of all barriers interacting with each other and interacting with the disposed wastes, and on the evolution of this behavior over time. Of all components, the cement paste is the material whose long term behavior is the lesser understood [5].

The function of the hardened cement paste is threefold: structural material, a blockage to prevent the flow of water between different layers of the geological setting crossed by the borehole, and as an additional barrier against the migration of radionuclides toward the biosphere. The performance of cement paste to accomplish these functions is the object of the present research [3].

Although studies on the performance of cementitious materials as structural material in bridges and buildings date back to many decades, the issue of the long term behavior of cementitious materials under repository conditions seems to be far from resolved. Recently, the International Atomic Energy Agency organized and sponsored a Coordinated Research Program (CRP) [6] on the behavior of cementitious materials. The complex chemistry of Portland cement and the variability of wastes and repository environments is a possible explanation for the persisting question on whether cementitious materials will endure long enough the service in repository.

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

The present research aims at investigating the durability of cement paste under repository conditions, attempting to establish the service life of this engineered barrier.

Service life of a material is defined as the period during which all functions established in the design are fulfilled within a given environment. In other words, service life is the period of time after the start up of the installation, during which all properties of the material exceed the minimum acceptable value [8].

The long term durability of cementitious materials can be approached by different methods: empirical analysis of old concrete structures, comparison with natural and anthropogenic analogues, modeling the reactions and interactions of the components of the material over time, and accelerated tests in laboratory [4, 5, 9].

In the present paper, the results of accelerated laboratory tests that are expected to provide some evidence of the service life under the expected conditions prevailing in the repository are reported. In such tests, cement paste samples are exposed to extreme values in the range of values of each environmental condition. The select values are deemed to produce the most severe deleterious effect on the capacity of the material to withstand further stress. It is assumed that the observation of the rate of change in the properties of the material during consecutive trial runs can allow extrapolation of results. It is expected that this assumption can be accepted or rejected by short term and long term test results.

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

The objectives of the present work are:

a) To accelerate the deterioration of cement paste properties by exposing specimens of cement paste (CPS) to the high levels of the stressing factors foreseeable at the depth of the repository in a granitic geological medium;
b) To evaluate the effects of that exposure on the CPS by observing changes in their chemical, structural, and mineralogical characteristics.
c) To extrapolate the short-term 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.

The research is in progress and results obtained so far show that the adopted methodology can produce useful data to estimating service life of cement paste under repository conditions.

2. MATERIALS AND METHODS

Cement paste specimens were prepared with fresh ARI (Brazilian Association of Technical Standards Type V cement), equivalent to the High Early Strength Portland cement (HES cement of ASTM specifications) with a water/cement ratio of 0.35 following the procedure of Brazilian standards [10,11].

Twenty four sets, with five cubic specimens each one, were cast, demoulded after 24 h, cured for 6 days in a humid chamber at 20 °C, and then stored under the environmental conditions that accelerate the stressing effects [11,12,13]. Specimen size was 20 mm x 20 mm x 20 mm. Small specimens were used because of the limited space for sample irradiation and because radiation doses as uniform as possible over the sample volume was required. Furthermore, results of mechanical strength measurements are not to be compared with results from other laboratories, thus making unnecessary the use of standard size specimens.

The test conditions were established on the basis of the environmental conditions that are deemed to prevail in the repository at the depth of waste emplacement. After exposure, the CPS were analyzed in respect to changes in their chemistry, mineralogy, and morphology.

Changes in the chemistry of specimens were observed by analysis of the composition of leaching solutions. The concentration of leached cations was measured by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and anions by Ion Chromatography. Changes in structure and mechanical stability were measure by mechanical strength tests.

Exposure conditions of specimens were:

a) Immersion in salt solution (SS), distilled water (DW), or keeping them 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 to a dose of (400 kGy), or background radiation (0 kGy).

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

Sets identified by U and V were kept in dry storage, at room temperature, without irradiation, and so functioned as 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	*			*		*		*	
B	*			*			*	*	
C		*		*		*		*	
D		*		*			*	*	
E	*				*	*		*	
F	*				*		*	*	
G		*			*	*		*	
H		*			*		*	*	

Table 1. Sample set ID and test conditions assignment (continued)

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

DW - distilled water; SS - salt solution; DS - dry storage

3. RESULTS

3.1. Compressive Strength

Figure 1 shows maximum, median and minimum values of the mechanical strength of cement paste specimens of all sets. Statistical analysis shows the extent to which each exposure conditions could affect the mechanical strength of specimens. Each treatment was analyzed separately. All CPS that were exposed to levels A or B of a treatment (for example, irradiated or not irradiated) were separated in two groups. Then, within these two large groups, we analyze how each of the other treatments affected the values of rupture pressure of the CPS´s. The statistical analysis shows how different is a set of data from another. Thus, a large difference between sets means they can be considered different and that the conditions affecting their strength and, consequently, their durability. The differences in results of each group can be classified in five different levels of statistical significance:

1. No statistical significance.
2. Little statistical significance.
3. Statistical significance.
4. Large statistical significance.
5. Very large statistical significance.

Results are shown in Tables 2 to 6.

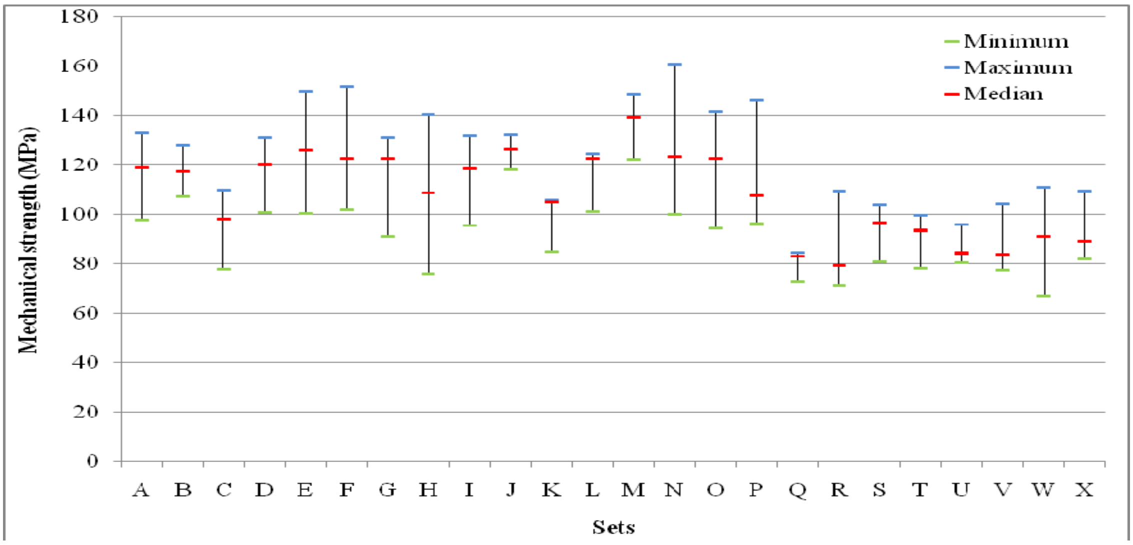

Figure 1. Maximum, minimum and median of mechanical strength of each set.

Table 2. Difference between CPS that were kept in immersion or dry storage.

	Immersion or dry storage			
Treatment	Immersion		Dry storage	
Significance level	**5**			
Treatment	20° C	60°C	20° C	60°C
Significance level	**3**		**1**	
Treatment	30 days	60 days	30 days	60 days
Significance level	**1**		**1**	
Treatment	0 kGy	400 kGy	0 kGy	400 kGy
Significance level	**1**		**1**	

Table 3. Difference between CPS that were immersion in distilled water or salt solution.

	Immersion Solution			
Treatment	Distilled water		Salt solution	
Significance level	**4**			
Treatment	20° C	60°C	20° C	60°C
Significance level	**2**		**1**	
Treatment	30 days	60 days	30 days	60 days
Significance level	**1**		**1**	
Treatment	0 kGy	400 kGy	0 kGy	400 kGy
Significance level	**1**		**1**	

Table 4. Difference between CPS at room temperature (20°C) or 60°C

	Temperature			
Treatment	20° C		60° C	
Significance level	3			
Treatment	Immersed	Not Immersed	Immersed	Not immersed
Significance level	5		5	
Treatment	Distilled Water	Salt solution	Distilled water	Salt solution
Significance level	3		3	
Treatment	30 days	60 days	30 days	60 days
Significance level	3		1	
Treatment	0 kGy	400 kGy	0 kGy	400 kGy
Significance level	1		1	

Table 5. Difference between CPS that were exposed by 30 days or 60 days.

	Time of exposure			
Treatment	30 days		60 days	
Significance level	1			
Treatment	Immersed	Not Immersed	Immersed	Not immersed
Significance level	5		5	
Treatment	Distilled water	Salt solution	Distilled water	Salt solution
Significance level	4		2	
Treatment	20° C	60°C	20° C	60°C
Significance level	4		1	
Treatment	0 kGy	400 kGy	0 kGy	400 kGy
Significance level	1		1	

Table 6. Difference between CPS irradiated (400 kGy) or not irradiated (0 kGy)

	Irradiation			
Treatment	0 kGy		400 kGy	
Significance level	1			
Treatment	Immersed	Not Immersed	Immersed	Not immersed
Significance level	5		5	
Treatment	Distilled water	Salt solution	Distilled water	Salt solution
Significance level	2		4	
Treatment	20° C	60°C	20° C	60°C
Significance level	1		1	
Treatment	30 days	60 days	30 days	60 days
Significance level	1		1	

3.2. Analyses of Ion Concentration

Analyses of bath solutions were performed to detect changes in concentration of selected ions after the immersion test. This assay was intended to observe the behavior of cement paste under attack by the dissolved aggressive chemical species in ground water. Selected cations were Ca^{2+}, Na^{+}, K^{+}, Mg^{2+}, Al^{3+}, Fe^{3+} e Si^{4+}, measured by ICP-OES, and concentration of anions F^{-}, Cl^{-}, NO_2^{-}, Br^{-}, NO_3^{-}, PO_4^{-3}, and SO_4^{-2} were measured by ion chromatography; results are expressed in $g.L^{-1}$. All samples were analyzed in duplicate by the Poços de Caldas Laboratory (LAPOC-CNEN) and results express the mean of the two determinations. NO_2^{-}, Br^{-} and PO_4^{-3} were below the detection limits.

Figure 2 shows the results of each ion concentration in bath samples that initially were distilled water, after the immersion tests at 20◦C and 60◦C. Concentration of ions, after immersion tests, in baths that initially were salt solutions are presented in Figure 3, as initial to final concentrations ratio. Both graphs show the change from initial to final conditions resulting from leaching of some species from the cement paste or resulting from the precipitation onto, or reaction with compounds at specimen surfaces.

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

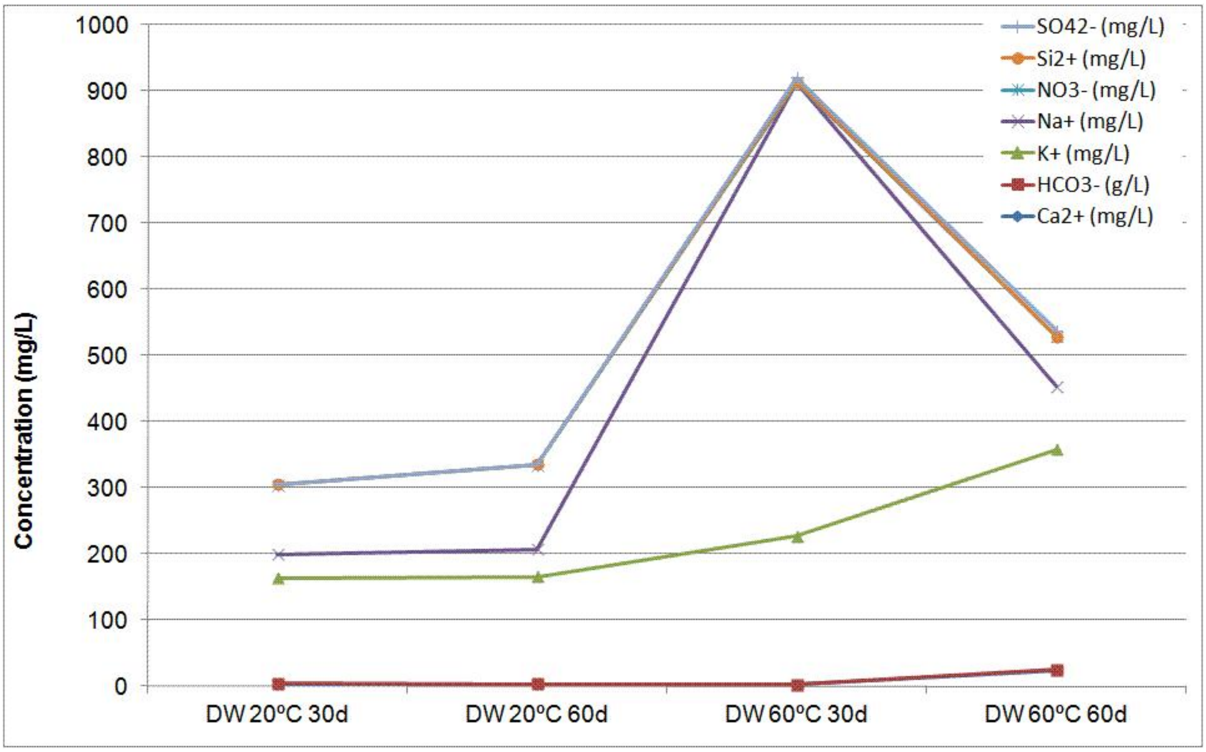

Figure 2. Ion concentrations after immersion tests at 20◦C and 60◦C.

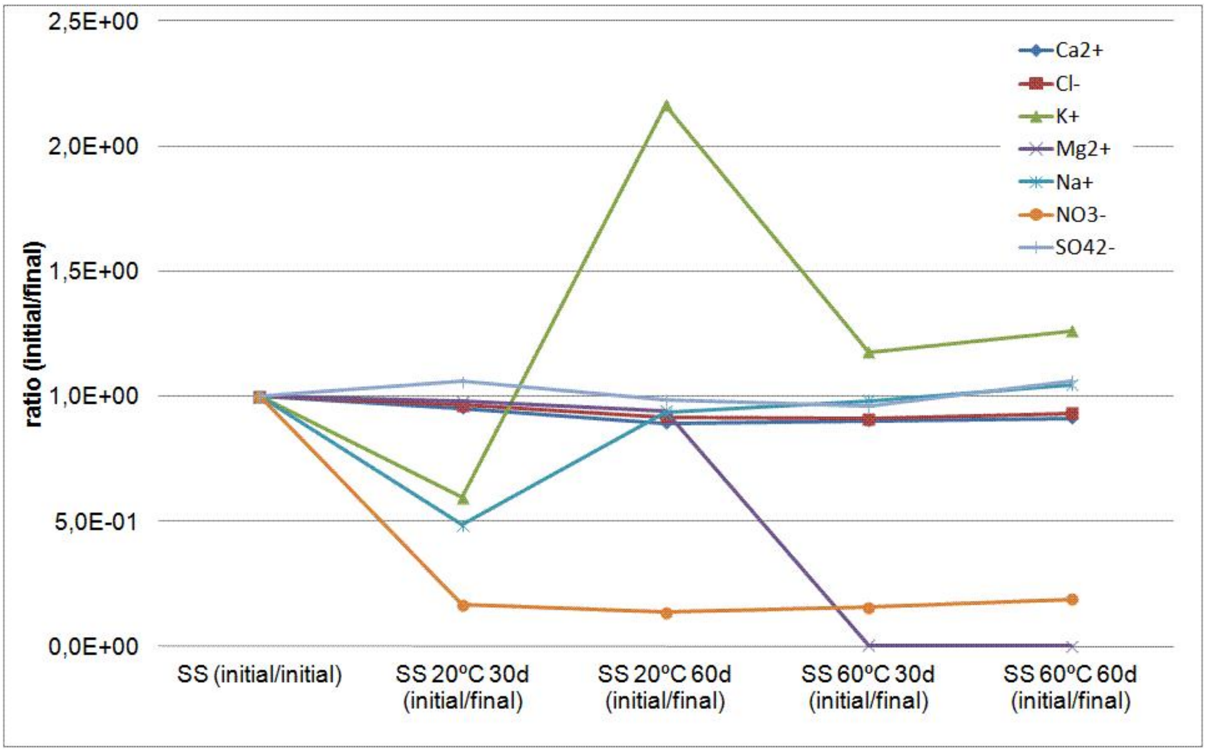

Figure 3. Ratio of final to initial concentration of selected ions in bath solutions.

4. CONCLUSIONS

Results obtained thus far show that the observed variations of mechanical strength are small as compared with 'natural' variation of cement samples, measured by axial compression. 'Natural' variation means the observed variability in the strength of cement paste samples, which is discussed in a previous report [6].

Results show that immersion of specimens is capable to change the properties of cement paste. However, while literature says immersion causes a decrease in mechanical strength, an increase was observed instead, that could be interpreted as an enhancement of the durability of the material. Perhaps the curing process of specimens may have been insufficient to ensure that all species contained in cement have completely reacted and this process continued during the immersion test. Although formed on small quantities, some hydration products like ettringite could be further increasing the mechanical strength of the paste.

The chemical changes induced by radiation, temperature, and attack of aggressive chemical species in specimens kept in immersion bath solutions were observed by means of changes in the chemical concentration of cations and anions in the bath solutions at different experimental conditions. Concentrations were measured by ICP-OES and Ion-chromatography techniques.

These are very preliminary results that show the analytical potential of the available infra-structure of GRR 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.

Further work is expected to elucidate how the investigated factors act to aging cement paste, as to affect its service life under the repository conditions.

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