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DURABILITY OF CEMENT PASTE AS ENGINEERED BARRIER IN BOREHOLE WASTE REPOSITORY

Vera L. Keiko Isiki, Eduardo Gurzoni A. Ferreira, Hissae Miyamoto, Julio Takehiro Marumo, and Roberto Vicente

Instituto de Pesquisas Energéticas e Nucleares, IPEN - CNEN/SP
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
rvicente@ipen.br

ABSTRACT

The Radioactive Waste Management Laboratory of the Nuclear and Energy Research Institute, in São Paulo, Brazil, is developing the concept of a repository for disposal of sealed radioactive sources. The concept is a deep borehole drilled a few hundred meters below surface in a granite batholith. Portland cement paste is the material intended to backfill the annular space between the steel casing and the geological formation around the borehole. The hardened cement paste is intended to function as barrier against water flow between the different strata of the geological setting crossed by the borehole and also as an additional barrier against inflow of water and migration of the radionuclides present in the sealed sources. A service life of thousands of years is a necessary characteristic of the engineered barriers in this repository because many sealed sources are long-lived. The durability of cementitious materials is known only for short periods and must be evaluated for long periods. This research aims at evaluating the durability of Portland cement paste under the repository conditions foreseen in that disposal facility, by accelerated tests in laboratory. In this paper we present results of mechanical strength, mass, and volume variations of cement samples under irradiation, high temperature and immersion in saline solutions, as a function of time.

1. INTRODUCTION

The Radioactive Waste Management Laboratory (RWML) at the Nuclear and Energy Research Institute (NERI), in São Paulo, Brazil, stores disused sealed radioactive sources formerly used in radiotherapy, industrial gauges, and irradiators. Many sources have long-lived radionuclides with high activity, the main radionuclides being ^{60}Co, ^{63}Ni, ^{90}Sr, ^{137}Cs, ^{226}Ra, and ^{231}Am. The Brazilian inventory amounts to tens of thousands sources and total activity reaches hundreds terabecquerels.

Final disposal of this kind of radioactive waste requires a geological repository that is as yet unavailable anywhere. Actually, shallow ground disposal sites for low- and intermediate-level wastes cannot accept most of the disused sealed sources for disposal, because of safety reasons in the long-term.

One option for final disposal of sealed sources, particularly for developing countries, is keeping them in deep, dedicated borehole repositories, where the waste could be isolated from the human environment for the millennia required to the decay of the sources to render negligible the associated radiological risk [1].

One of the engineered barriers in such type of repository is Portland cement paste, used as a backfill between the steel pipe that encases the borehole and the surrounding geological medium, assumed to be, in this case, a crystalline granitic rock, at a few hundred meters below the earth surface.

The Portland 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 of chemical reaction with aggregates and substances of the environment [2]. As the long term behavior of cement hydrates is insufficiently known, in the present research, the durability of the cement paste is investigated aiming at establishing the service life of this engineered barrier.

Service life is defined as the period of time during which all functions established in the design are fulfilled within a given environment or, in other words, the period of time after the start up of the installation, during which all properties exceed the minimum acceptable value [3].

It is conceivable that cement paste will degrade as a consequence of the action of radiation, high temperature and pressure, and of the attack of aggressive chemical species dissolved in the repository neighbourhood groundwater. So, the long-term safety of the system depends on how the cement paste will perform under the environmental conditions prevailing at that depth.

Accelerated durability tests in laboratory can provide evidence of the service life under the expected conditions prevailing in a repository for sealed sources. In such tests, cement paste samples are exposed to the extreme values of the exposure range of each expected environmental condition, 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.

A series of multifactorial experiments was performed under laboratory conditions to investigate the degradation of the mechanical properties of the paste, after exposure of samples to elevated levels of those stressing forces.

2. METHODS

The accelerated laboratory tests were designed as a multifactorial design experiment, each factor at two levels. A minimum of five specimens of paste were exposed to the specified conditions at each level of each factor. One hundred forty four samples, in 24 groups, were used in a complete design run.

Cylindrical samples of cement paste with 2.5cm diameter x 5cm height were used. The selected cement was Portland Type V of Brazilian standards [4], which corresponds to Type III high-early-strength (HES) cement of ASTM standards [5]. Freshly produced cement bags from a local retailer were purchased and stored in a temperature and moisture controlled room in the laboratory.

Cement pastes were prepared with water/cement (W/C) ratio of 0.35, following the procedures of the Brazilian cement-work standards [6] and kept to set under moisture and temperature controlled environment, approximately 20ºC, for one week, before being exposed to the stressing factors. Test samples were kept in sealed plastic moulds during the setting period to avoid loss of water.

The exposure levels of each of the stressing factors were determined by the methodology recommended by ASTM [7]. The set of properties that were selected to show that all defined functions of the material are properly covered were: a) loss of mechanical strength, b) shrinkage/expansion, c) variation in hydraulic permeability/porosity, and d) depth of penetration profiles of aggressive chemical species.

Loss of mechanical resistance to axial compression of cylindrical samples, expansion and contraction, and increase/decrease of sample mass were measured after exposure of the samples to high temperatures, immersion in distilled water or salt solutions, and exposure to an ionizing radiation field. The results of the chemical changes in the cement paste are presented by Ferreira [8].

2.1. Irradiation

To accelerate the effect of radiation on the material, the integrated dose delivered by most active sources of the most relevant sources of the inventory, were calculated and established as the test radiation dose. The relevant sources in this respect are ^{137}Cs, ^{226}Ra, and ^{241}Am because of long half-lives, high activity in the inventory, and gamma emission characteristics. Samples of hardened cement paste were irradiated in a ^{60}Co irradiation facility to accumulate the integrated dose delivered by the most active and long-lived sources. The dose rate was the maximum delivered by the irradiator as to minimize irradiation time. Other dose rates and irradiation times will be used in future test runs because they can influence the intensity of effects of radiation in accelerated tests. So, the effects of different activities and half-lives are evaluated as regard to total doses and to dose rates. The multipurpose compact irradiator with 3.4 TBq of ^{60}Co was used to irradiate the samples. This facility delivers a dose rate of 4 kGy/h, and samples were irradiated by 100 hours to accumulate a dose of 400 kGy. The lower level of exposure was ‘no exposure’.

2.2. Temperature

The cement paste filling the annulus between the steel casing of the borehole and the adjacent rocks will be exposed to higher temperatures as deeper the emplacement zone. It is assumed that the temperature can negatively affect the performance of Portland cement due to the loss of pore water and due to the accelerating effect on deleterious chemical reactions.

The rate of increase in temperature per unit depth in the Earth is called geothermal gradient. It varies with location but is typically 25–30 degrees Celsius per kilometer [9]. Assuming a mean surface temperature in the repository site not higher than 35°C, the temperature at the bottom of the borehole, 400 m deep, will stay below 50°C.

The thermal treatment of the cement paste samples consisted in exposing the hydrated specimens to the selected temperature in controlled temperature ovens, during different periods of time, and then examining them to find changes that can be interpreted as degradation in their properties.

As a first upper limit in the accelerated tests, the higher temperature was set at 60°C and the lower limit was set at the room temperature, 20°C.

2.3. Aggressive Chemicals

Corrosion of the cement paste by the chemical species dissolved in the pore water of granite were simulated by immersion of the hardened cement samples in water solutions with the typical concentration that is expected to occur in a deep geological repository.

The composition of the water solution that simulates the exposure of cement paste to the potentially corrosive groundwater is a variable more complex than the two preceding. It depends strongly on site characteristics, as mineralogy and chemistry of the host rock, and it is not clear, at this moment, whether higher or lower concentrations of aggressive chemicals could result in worse effects of the combined factors on cement.

According to the literature [10], during a long exposure time, the cement paste in contact with granitoid rocks degrades as a consequence of chemical reactions with the ions dissolved in pore water. To evaluate the effect of this factor on cement paste, specimens were immersed in solutions with varying concentrations of the compounds that are expected to be present in representative repository's environment and then examined in respect to changes in their properties. A sufficiently general composition of granites pore water was used to simulate the repository environment (Table 1).

As a first choice, the solution composition was that one with the highest salt concentration found in the literature on granitic groundwater. As more is learned about the effects of individual chemical compounds and their combined effects on the cement chemistry, that composition will be changed.

Table 1. Summary data on composition of granitic groundwater. (g.L^{-1}) [10]

Ionic species	Lower value	Upper value	mean	median
Ca^{2+}	0.0011	1.89	0.27	0.0068
Na^{+}	0.001	2.1	0.37	0.02
K^{+}	0.000156	0.0251	0.01	0.002
Mg^{2+}	0.0000192	0.0734	0.01	0.003
Cl^{-}	0.002	6.34	0.99	0.02
F^{-}	0.0001	0.00627	0.0013	0.0003
HCO_3^{-}	0.01	0.309	0.10	0.04
SO_4^{2-}	0.0009	0.56	0.11	0.01
Si^{4+}	0.00297	0.039	0.01	0.009
Fe^{2+}	0.000056	0.0016	0.0005	0.0002
NO_3^{-}	0.0008	0.0015	0.0011	0.001

The effects of the factor ‘corrosive groundwater’, expressed as ‘immersion conditions’, were tested in three levels: no immersion at all, immersion in distilled water, immersion in a solution with the composition defined by the row “upper value” of Table 1.

3. RESULTS

3.1. Compressive Strength

The medians, averages and standard deviations of the cement sample mechanical resistances, as influenced by each factor are presented in Table 2.

Table 2. Mechanical resistance of the cement samples in each cohort, in MPa.

Factor	Level	Median	Mean ± s. d.
Immersion time (days)	0	19	21 ± 10
	20	20	23 ± 10
	60	21	23 ± 9
Immersion temperature (ºC)	20	21	21 ± 10
	60	19	21 ± 9
Irradiation dose (kGy)	0	24	25 ± 11
	400	10	20 ± 7
Immersion solution	Distilled water	22	25 ± 10
	Saline solution	20	22 ± 9

Figure 1a shows the effect of immersion time and temperature on the mechanical resistance of cement paste samples, as measured by axial compressive strength. Figure 1b shows the effect of irradiation and immersion solution on that property. Data are presented by relative frequency of each class interval of rupture pressure. The large observed variation in resistance of samples subjected to the stressing factors at the lower levels shadows the effects at the higher levels. This means that it was not possible to discriminate what is effect of the stressing factors from what is the ‘natural’ variation in the resistance.

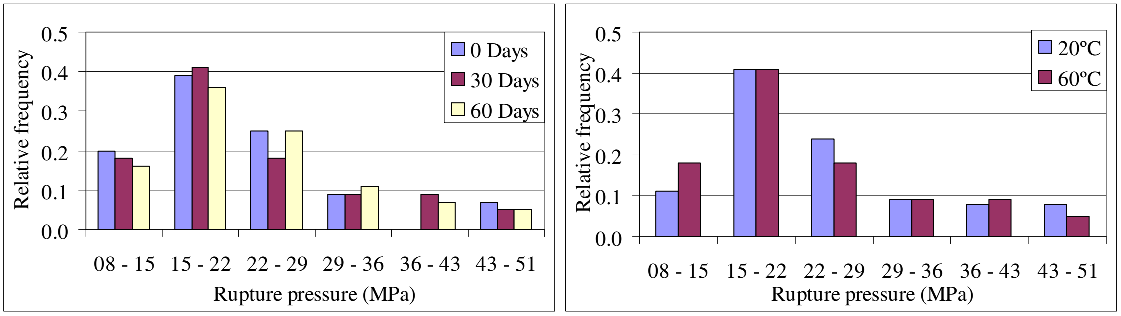

Figure 1a. Effect of immersion time and temperature on mechanical strength of cement samples.

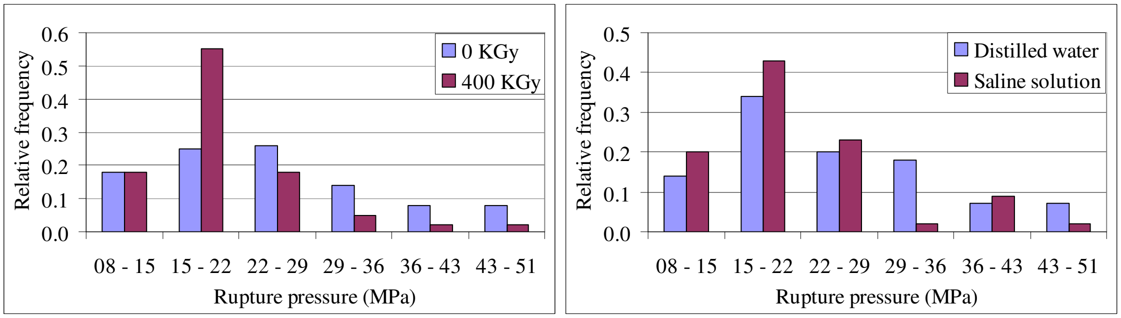

Figure 1b. Effect of irradiation and immersion on mechanical strength.

In the graphs of Figure 1b, it is possible to notice a change in the shape of the distribution of results, indicating a more intense effect of those factors on cement properties, than that observed as a result of exposure to the effects depicted on Figure 1a. Irradiation and immersion in saline solution lowered the mechanical resistance of samples to an extent that could be detected by this test. As it was concluded by Ferreira [11] only after this issue (the large variability) is resolved it will be possible to detect the expected effects at the levels of the stressing force used in this research.

3.2. Variation of Sample Volume and Mass

The influence of each factor on cement sample volume is depicted in Figure 2. Each bar on the graphs represents high, low, and median values. Notice the missing bars on upper right graph of Figure 2, relative to the measurements after irradiation of samples, because cohort '3' samples was irradiated at level '0 kGy'.

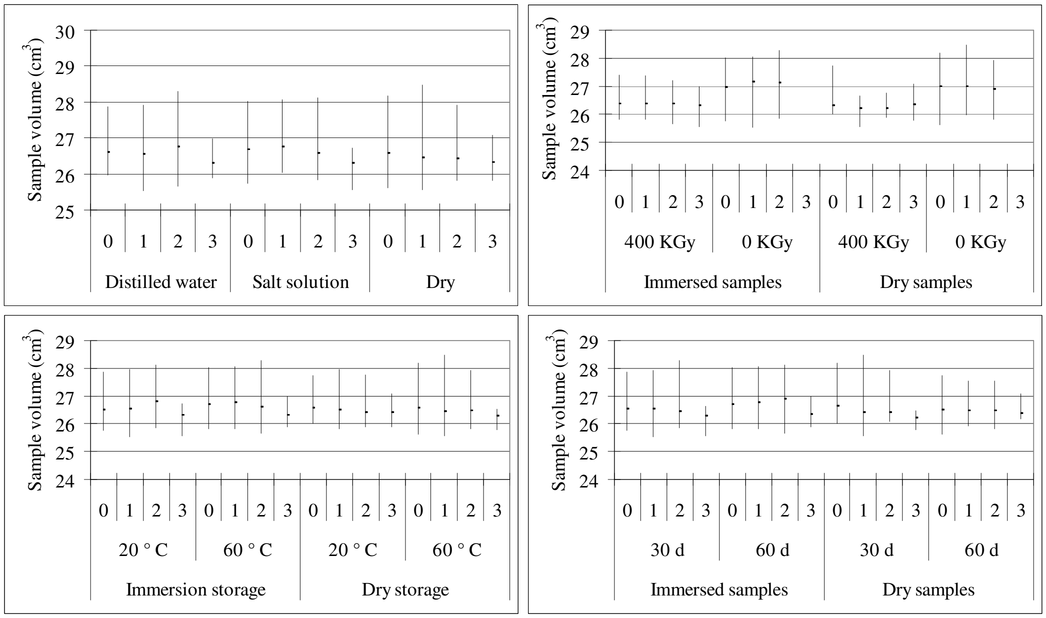

Figure 2. Changes in volume induced by each factor. Code for x axis numbers: 0) at the onset of tests; 1) after immersion; 2) before irradiation; 3) after irradiation.

All these results clearly indicate that no trend can be detected between sample treatment cohorts, except sample volume after irradiation, which are systematically lower than the others. However, this cannot be attributed to irradiation because corresponding samples stood several days in the uncontrolled temperature and relative humidity of the atmosphere in the irradiation facility. This is an aspect of the test program that must be further improved.

Figure 3 shows the frequencies of each class interval of mass percent variation as a function of each factor affecting the properties of the cement samples that were kept under immersion. Percent mass variation was calculated with measurement at the onset of tests, just after curing, and after all test exposures.

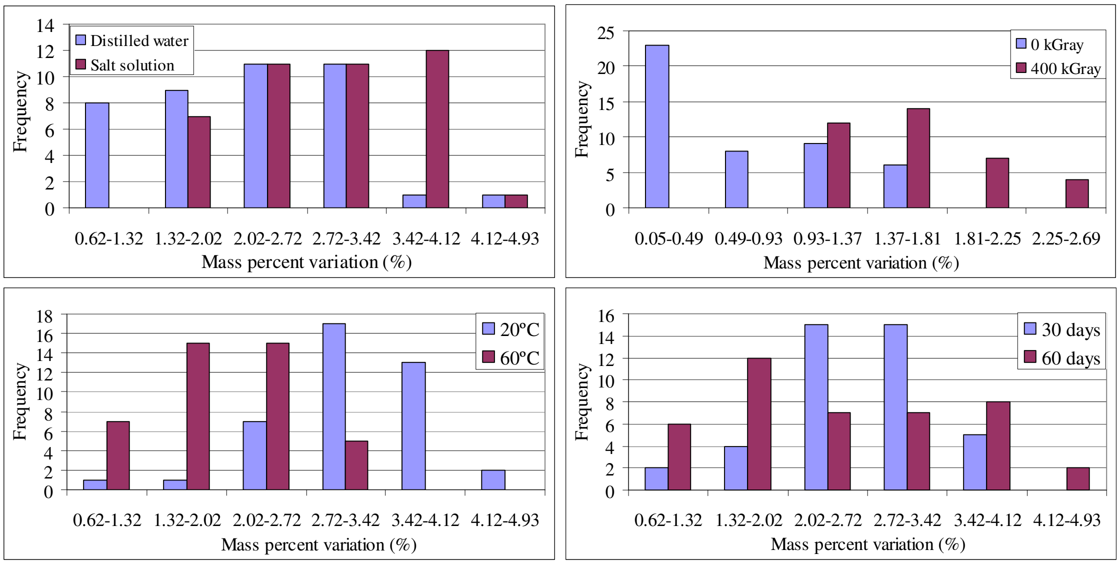

Figure 3. Mass variation as a function of each disclosed factor.

Similarly to what was observed for volume variations, the large difference of mass variation distributions in the two sample groups of the upper right graph, cannot be assigned to the irradiation rather to the increased evaporation of the free cement pore water during the time samples stood in the irradiation facility.

The marked differences observed in the groups depicted on the other three graphs were, as expected, due to the exposure factors. Three phenomena were observed at the sample–water interface: absorption of water into cement pores; precipitation of chemical compounds resulting from the reactions between cement minerals and ions in the solution; leaching of hydrated cement compounds. All the three tested factors – salts concentrations, temperature and time of exposure – influence the processes above and their rates. However, experimental plans must be improved to detect to what extent each process influence observed results. This is a key factor on the evaluation of the long-term behavior of cement paste under repository conditions.

Cement samples that were kept in dry storage were analyzed separately. Figure 4 shows the frequency of each class interval of mass variation, for samples kept in dry storage, as a function of radiation dose and storage temperature. The results of irradiation tests in these samples (left graph in Figure 4) emphasize the interpretation that, at this level, irradiation seems not relevant and that the variations are consequence of the storage temperature.

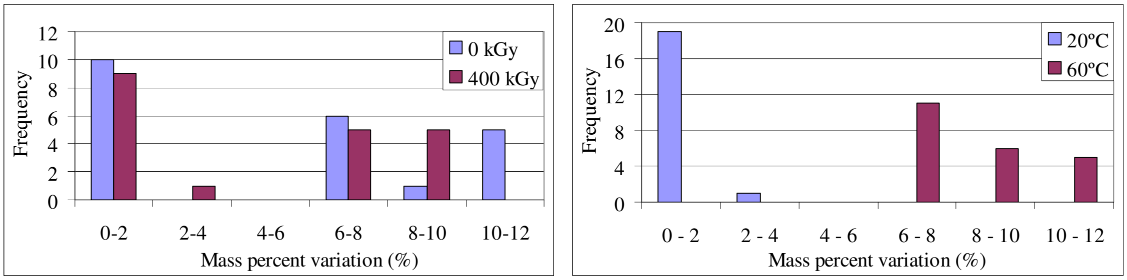

Figure 4. Percent variation of the mass of cement samples kept under dry store.

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. By ‘natural’ variation we mean the observed variability in cement samples, which is discussed by Ferreira [11]. Changes in volume and mass are clearly visible in most treatments but experimental conditions must be improved as to differentiate effects of each concurring factors. Further work is expected to elucidate how the investigated forces act upon the aging of cement paste, as to affect its service life under the repository conditions.

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